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Department of Industrial Pharmacy

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on the topic **Photoelectrochemical Catalysis of Waste Water in  
Pharmaceutical Industry**

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KYIV NATIONAL UNIVERSITY OF TECHNOLOGIES AND DESIGN

Institute, faculty Chemical and Biopharmaceutical Technologies

Department Industrial Pharmacy

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FOR THE MASTER'S THESIS**

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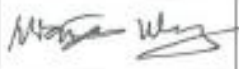
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**3. Initial data to work** scientific and scientific-practical sources, patents, articles, legislative, normative and normative-legal acts and documents, overview types of wastewater in Pharmaceutical Industry and methods of their treatment, analysis of pharmaceutical wastewater treatment technologies, design new materials and development technology of photoelectrochemical catalysis of pharmaceutical wastewater in China and all around the world

**4. Content of the thesis (list of questions to be developed)** Overview of pharmaceutical wastewater in China and all around the world, illustrate the pollutant in pharmaceutical wastewater, introduce the new materials and the idea of designing new photoelectrochemical catalysis materials, describe the techniques and equipments used in the experiments, describe the electrochemical, spectroscopic and microscopic analysis of the new hybrid films, discuss the results and conclusions

## 5. Consultants of the master's thesis sections

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## EXECUTION SCHEDULE

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3	Section 2 Research Methods, Chemicals and Materials	12.10 – 25.10.2021	Wei Dong
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The master's thesis is devoted to the study of photoelectrochemical treatment of the wastewater from pharmaceutical industrials. The aim is achieved through the new redox hybrid materials with viologen and AuNPs and CdS, respectively. The technical task is focused on the preparation of viologen-based hybrid films and improving their electrochemical and photocatalytic properties. Based on the electrochemical, spectroscopic and microscopic analysis, the materials have shown good redox properties, good stability and good photoelectrochemical performance.

The excellent redox properties and good photoelectrochemical performance of the hybrid films have improved their photocatalytic properties in wastewater treatment, and their easy preparation and good stabilities will also extend their application as the new wastewater treatment materials in the future.

*Key words: wastewater treatment, redox materials, photoelectrochemistry, photocatalysis, hybrid film*

## ABBREVIATIONS

ALD	Atomic layer deposition
AOPs	Advanced Oxidation Processes
AuNPs	Gold Nanoparticles
BOD	Biochemical Oxygen Demand
CA	Chronoamperometry
CE	Counter electrode
COD	Chemical Oxygen Demand
CV	Cyclic Voltammetry
CVD	Chemical vapor deposition
EF	Electrochemical Fenton
FTIR	Fourier transform infrared spectroscopy
GC	Glassy carbon
g-C <sub>3</sub> N <sub>4</sub>	Carbon nitride
H <sup>+</sup>	Proton
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
ITO	Indium tin oxide
KCl	Potassium chloride
LBL	Layer-by-layer
LSV	Linear sweep voltammetry
MB	Methylene Blue
MV <sup>2+</sup>	Methyl Viologen
OTE	Optically transparent electrode

PCE	Perchloroethylene
RE	Reference electrode
SEM	Scanning Electron Microscopy
TCE	Trichloroethylene
TEM	Transmission Electron Microscopy
UV-vis	Ultraviolet-Visible spectroscopy
WE	Working electrode

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## **Introduction**

With the increasing demand for pharmaceutical products, the wastewaters produced by the pharmaceutical industry have caused serious pressure to the society and the environment. The components of pharmaceutical wastewater are usually very complex and harmful to the environment, if it is discharged indiscriminately, it will seriously affect the ecological safety. In previous scientific surveys: the antibiotic content in most rivers in the world exceeds the standard, threatening the lives of tens of millions of people in 30 years, therefore, strengthening the treatment of pharmaceutical wastewater is an imperious demand, especially in China. According to the Chinese Environmental Statistics Annual Report in 2015, the industry wastewater discharge in 2015 was 19.95 billion tons, of which pharmaceutical industrial wastewater was 532.58 million tons, accounting for about 2.67% of the national industrial wastewater volume. Beyond that, the wastewater from the pharmaceutical industry not only contains a large number of heavy metals and harmful chemical substances, but also contains non-degradable pollutants, plus various acids, alkalis, tannins, and anthraquinones, so the impact will also restrict the sustainable development of the pharmaceutical industry. Based on these reasons, the treatment of pharmaceutical wastewater is an urgent challenge.

**The relevance of the topic.** In the previous years, different methods of wastewater treatment have been innovated, such as chemical oxidation process, biochemical process, photocatalytic oxidation technology, Fenton reaction, electrocatalytic oxidation, photochemical method and so on. Each method has its unique merits and disadvantages, furthermore, the combination of different

technologies has attracted more and more scientists' attention in recent years.

**The purpose of the study.** In this work, photoelectrochemical methods were utilized to study the degradation of wastewater from pharmaceutical industries. In order to achieve this aim, a series of viologen based hybrid films were synthesized and characterized, on the other side, the methylene blue solution was also utilized as the model object to instead the wastewater from the pharmaceutical industry.

**The research objectives of the study.** The viologens are the name of series of organic molecules contains the 1'1 disubstituted 4'4-bipyridine structures, which were first named by Michaelis in 1932 due to their unique color change. After that, the viologens have been widely utilized in various applications, the viologens have attracted more and more attention due to their stable and adjustable redox properties.

The research work is focus on the photoelectrochemical application of viologen based hybrid films, in the previous months, we have designed two different kinds of hybrid films (viologen materials with AuNPs and CdS, respectively).

**The object of MTh.** The methylene blue was utilized as the model object of the wastewater, and the photoelectrochemical catalysis was carried under the irradiation of UV light,.

**The subject of MTh study.** The aim of this work is to extend the application of viologen materials into new fields. The viologens have been widely used as the funtional materials and their good redox properties have huge potential in the photoelectrochemical applications. By combining together with the Gold Nanoparticles (AuNPs) and Cadmium Sulfide (CdS), the hybrid films will be studied and applied in wastewater treatment as new functional materials.

**Research methods.** The resulted hybrid films were characterized by electrochemical, photoelectrochemical, spectroscopic and microscopic methods, and both of them have shown good photoelectrochemical reduction properties to methylene blue.

**Practical value.** This work has the huge practical value in the pharmaceutical waste water treatment, since by combining the good redox properties of viologens, the photoelectrochemical catalysis efficiency can be increased and the recovery of the catalyst will also be improved. Beyond that, the viologen based hybrid films have also obtained the merits such like easy preparation and low cost, so they have great promising wastewater applications in future.

**Elements of scientific novelty.** The two hybrid films can be prepared with easy procedures, and both of them obtained good redox and photoelectrochemical properties. The preliminary work indicated that the viologen based hybrid films can degradate the methyle blue effectively which mean they can work as good photoelectrochemical catalysts in the treatment of waste water from pharmaceutical industries.

## Section 1 Overview types of waste water in Pharmaceutical Industry and methods of their treatment

### 1.1 Overview of pharmaceutical wastewater in China

Water is essential to life, and nowadays nearly 1 ninth of the people in the world lack access to it. According to a report by the World Economic Forum, the water crisis is the 5<sup>th</sup> global risk in terms of impact to society [1]. The global demands for water with good quality, whether for drinking, sanitation, irrigation, or industrial use. The water demand is increasing continuously, however, on the other side, the amount of wastewater is increasing all the time. In recent years, the treatment and reuse of wastewater have been overwhelmingly concerned by all scientists all over the world. In Figure 1.1 below, the population connected to the wastewater collecting system has been shown [2]. It can be observed that even some countries have been worked very well in wastewater treatment, quite many of the countries are still need to improve the wastewater reuse level, especially in Asian and African countries.

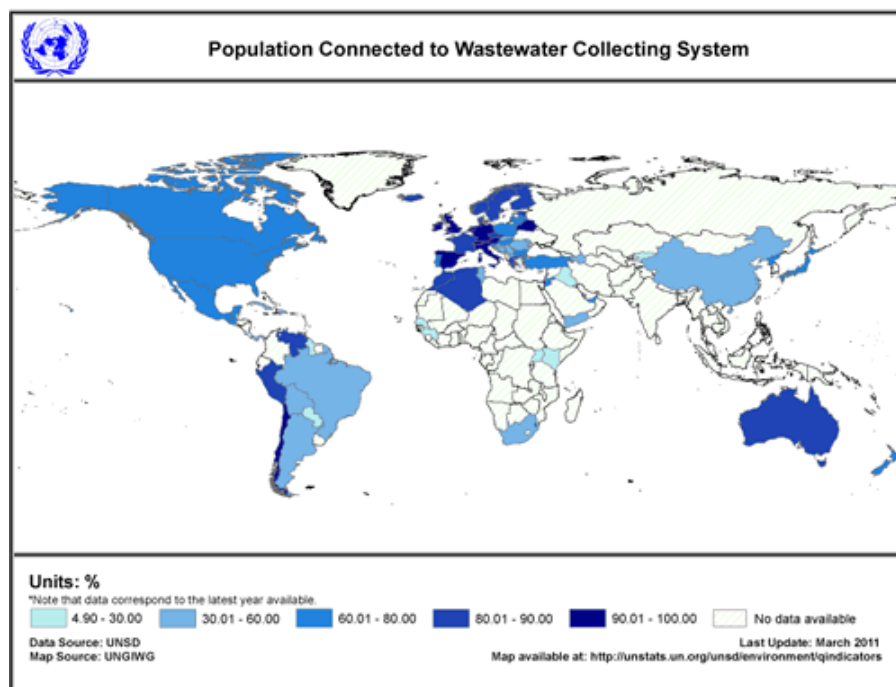


Fig. 1.1 Global population connected to the wastewater collecting system.

In order to save the global water crisis, wastewater treatment is an important path to improve the water quality and supply a good source of water. Wastewater is usually from water pollution, which is the contamination of water bodies, and it is usually caused by human activities. The water pollution would cause the inadequately treated wastewater into natural waters and it will lead to degradation of aquatic ecosystems. Furthermore, the wastewater can increase the water-borne diseases for people during drinking, bathing, washing or irrigation. Therefore, how to treat and reuse wastewater is a critical task for humans all over the world.

The industrial wastewater which is produced by industries as an undesirable by-product is an important source of sewage. For most industrial processes, such as petroleum refineries, chemical plants, agricultural productions and pharmaceutical industries have their own specialized facilities to treat their wastewaters. After treatment, the treated industrial wastewater can be reused or released to a sanitary sewer or surface water in the environment [3]. In all of the wastewaters, the one from the pharmaceutical industry is an important part, based on the *Chinese Annual Report of Environmental Statistics in 2015*, In 2015, China's industrial wastewater discharge was 19.95 billion tons, of which pharmaceutical wastewater discharge was 532.587 million tons, accounting for about 2.67% of the national industrial wastewater volume. The output value of the pharmaceutical industry only accounts for 1.7% of the national total GDP, but the discharge of pharmaceutical wastewater accounts for 2% of the national sewage discharge [4]. In Figure 1.2. below, it can be observed that in the past 20 years, the discharge amount of the wastewater was keeping increasing, especially the industrial wastewater [5]. In all kinds of industrial waster, the

pharmaceutical industrial waster has taken an important part. Beyond that, the pharmaceutical industrial wastewater components are also complex, not only containing a large number of heavy metals and harmful chemicals, but also containing non-degradable pollutants, and a variety of acids, bases, tannins and anthraquinones components [6-9]. If the treatment is not up to standard, it will not only bring a lot of negative impact on the environment, but also restrict the sustainable development of the pharmaceutical industry. Therefore, the treatment of pharmaceutical wastewater is critical to all pharmaceutical industries.

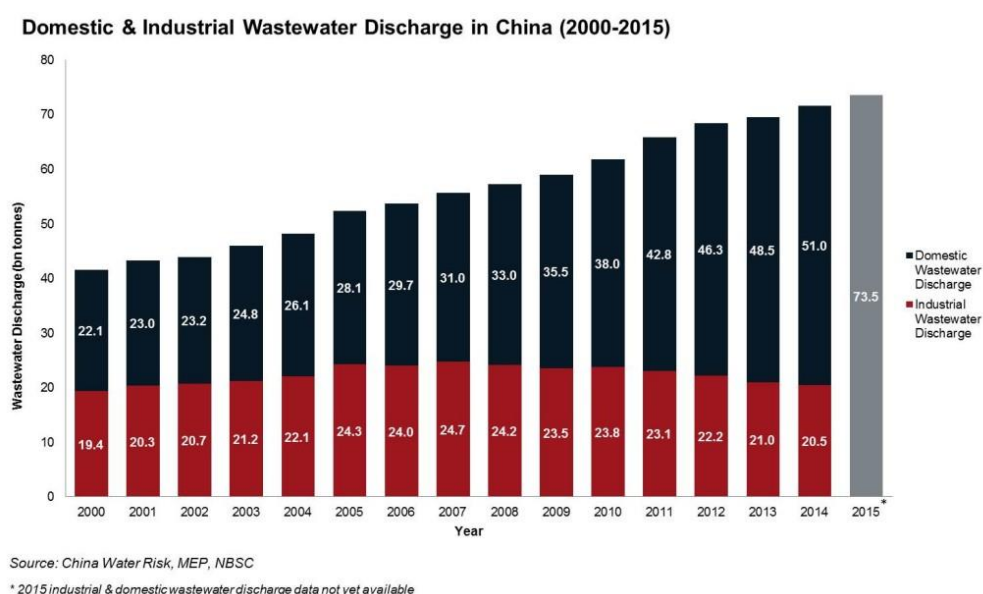


Fig. 1.2 The domestic and industrial wastewater discharge in China .

## 1.2 Types of wastewater in the pharmaceutical industry

With the development of the economy, the pharmaceutical industry has also experienced rapid development. For example, at present in China, it has been able to produce nearly 10,000 kinds of bulk pharmaceutical chemicals, with an annual output of more than 2 million tons [10]. The pharmaceutical industry mainly consists of biopharmaceuticals, chemical pharmaceuticals and Chinese traditional herbal

medicines. The production of various biopharmaceuticals uses microorganisms to ferment, filter, and refine organic raw materials to produce various drugs, raw materials and some pharmaceutical intermediates. Chemical pharmacy uses chemical reaction technology to make medicines from organic and raw materials. The production of Chinese herbal medicine is the processing and extraction of Chinese herbal medicines or Chinese patent medicines, and the pre-treatment and extraction of the main raw materials of the production process.

The development of production in the pharmaceutical industry has brought about waste discharge, and the pollution in the pharmaceutical industry mainly comes from the production of raw materials. Due to the increase in production technology and the synthesis of raw materials, the conversion rate of products is low and the amount of wastewater is high. The wastewater from the pharmaceutical industry is one of the more difficult to treat high-concentration organic wastewater, which varies greatly due to different pharmaceutical products and different production processes. In addition, pharmaceutical factories usually adopt intermittent production, and the types of products vary greatly, resulting in large changes in the quality, volume of wastewater and the types of pollutants [11].

Biopharmaceutical wastewater mainly contains mycelium, residual nutrients, metabolites and organic solvents, currently the biopharmaceutical process is mainly used to produce antibiotics. Wastewater mainly comes from fermentation filtrate, extracted raffinate, distillation kettle residual liquid, adsorption waste liquid and catheter waste liquid, etc. The concentration of organic matter in wastewater is very high, the Chemical Oxygen Demand (COD) can reach 5000 ~ 20,000 mg/L,

Biochemical Oxygen Demand (BOD) can reach 2000~10000mg/L [12]. The main production process of chemical pharmacy is the chemical reaction, and the complex raw materials and multiple reaction steps result in a low product conversion rate and serious raw material loss. This type of wastewater contains a wide range of toxic and hazardous chemical substances, such as steroids, nitro compounds, aniline compounds, piperazines and fluorine, mercury, chromium copper and organic solvents ethanol, benzene, chloroform, petroleum ether, etc. Because the raw materials of the synthetic pharmaceutical industry are relatively complex, and the types of products of a pharmaceutical company are often not one type, the situation of pollutants in the wastewater of synthetic pharmaceutical companies is more complicated [13].

### **1.3 Hazards of wastewater in the pharmaceutical industry**

Due to differences in pharmaceutical products, production methods and raw materials used in the pharmaceutical industry, the quality of production wastewater varies quite much. However, in general, pharmaceutical wastewater has the characteristics of the high content of organic pollutants, large amounts of toxic substances, large amounts of organic solvents, large amounts of difficult-to-biodegradable substances, and high salt content. It is a kind of industrial wastewater with great harm [14]. In general, pharmaceutical wastewater may cause the following problems if it flows into the environment directly without treatment or the treatment processing is not up to the standard.



### 1) Consumption of dissolved oxygen in the water

When organic matter undergoes biological oxidation and decomposition in water, it will consume dissolved oxygen in the water. If the content of organic pollutants is too high and the rate of oxygen consumption by biological oxidation and decomposition exceeds the rate of reoxygenation of the water body, the water body will become anoxic or deoxygenated, causing the death of aerobic aquatic organisms in the water area [15-16].

### 2) Destroy the ecological balance of water bodies

Pharmaceuticals and their synthetic intermediates often have certain bactericidal or antibacterial effects, thereby affecting the metabolism of bacteria, algae and other microorganisms in the water body, and ultimately destroying the balance of the entire aquatic ecosystem [17].

### 3) Pollution hazards of pharmaceutical metabolites to the environment

At present, there is not much research on this aspect in the world, but they have been aware of it. In pharmaceutical wastewater, the relationship between the pollutants and the formation of nitrosamines must be particularly vigilant. For this reason, preventing and reducing the entry of organic pollutants with secondary amine structure into water bodies is of great significance for reducing the formation of nitrosamine carcinogens in the environment [18-19].

## **1.4 Pharmaceutical wastewater treatment technologies**

In order to dispose of the wastewater, the pharmaceutical industries employ a lot of wastewater treatment methods and techniques. The wastewater generated from

the pharmaceutical industries varies quite much, both in composition and quantity, so many alternative treatment processes are available to deal with the wide array of wastewater. In general, the common techniques which are utilized in wastewater treatments include absorption methods, coagulating sedimentation, reverse osmosis and membrane separation technology, Fenton reactions, photocatalysis, electrochemical reduction, hybrid treatment and so on [3,6-7,20].

#### **1.4.1 Adsorption method**

The adsorption method is one of the more important methods in the treatment of wastewater in the pharmaceutical industry, especially in the treatment of synthetic and semi-synthetic antibiotic wastewater. By using regenerated activated carbon which has been utilized in the production, the nitrobenzene derivatives in the wastewater can be effectively adsorbed, and the removal rate can achieve over 90%, and the COD can also be reduced up to 30% [21]. Beyond that, the adsorption method can also be used as the advanced treatment of high-concentration pharmaceutical wastewater after biological treatment. The three-stage of the adsorption process is: slag→charcoal/slag→activated carbon/slag is used for the advanced treatment of pharmaceutical wastewater. When the influent COD is 1084 mg/L, the third-stage COD can be reduced to 279 mg/L after adsorption [22].

The absorption materials such as active carbon and adsorbent resins take the advantage of high efficiency and easy preparation, so they have got quite much applications in the previous years in wastewater treatment [23]. However, due to their high price and potential blockage risk during the treatment process, the adsorption

method is mostly used for the advanced treatment to remove the chromaticity and suspended solids in the wastewater to achieve the discharge of wastewater up to the standard.

#### **1.4.2 Coagulating sedimentation**

Coagulation and sedimentation can not only remove suspended solids in wastewater but also reduce the chromaticity, COD and biological inhibitory substances [24-25]. It is one of the common treatment methods in t semi-synthetic antibiotic wastewater. For example, the compound flocculation method is used to treat the wastewater of the pharmaceutical industry, and the result shows that it contains  $\text{Ca}^{2+}$  composite flocculant that can greatly reduce the antibacterial ability of antibiotics remaining in wastewater, and the drug potency can be removed by 90%. After flocculation, the wastewater is close to ordinary organic wastewater, which is convenient for subsequent biological treatment. The organic/inorganic composite modified lignin flocculant is used to treat antibiotic pharmaceutical wastewater. When the pH of the wastewater is 6.0 and the amount of flocculant is 120 mg/L, the removal rates of COD and chroma in the wastewater can reach 61.2% and 91.6%, which is conducive to subsequent biochemical treatment. However, the coagulation treatment is easy to cause secondary pollution and it also has limited effect on the treatment of high-concentration wastewater [26].

#### **1.4.3 Reverse osmosis and membrane**

Reverse osmosis and membrane separation technology used in wastewater

treatment can not only produce environmental benefits but also recover part of the effective components in wastewater to produce economic effects [27]. Therefore, nanofiltration membrane separation methods are increasingly used in the treatment of pharmaceutical industry wastewater. In the treatment of cefazolin acid wastewater, field tests show that the recovery rate of cefazolin acid can reach 90.3% to 93.7%, and the entire investment can be recovered within 2 years.

By pre-coating filter aid on the surface of the microporous tube for microfiltration, and then performing reverse osmosis concentration, chlortetracycline is recovered from the wastewater [28]. The retention rate of chlortetracycline can reach 98%, and the formed filter cake is incinerated. Wastewater and waste residue are discharged outside, which not only recycles products, but also protects the environment. However, due to the relatively high price of the membrane and the easy clogging during the treatment process, the application of reverse osmosis and membrane separation technology is limited [29].

#### **1.4.4 Advanced Oxidation Processes**

With the rapid development of industry, the number of chemically synthesized organics entering the water resources has increased sharply, especially the rapid development of the pharmaceutical and fine chemical industries. The discharge of some high-concentration, non-degradable, toxic and harmful organic wastewater has caused serious pollution of water resources, which has threatened the survival and development of mankind. A lot of research has been conducted at home and abroad for refractory persistent organic pollutants. Advanced Oxidation Processes (AOPs)

have come to the fore in the past two decades with their huge potential and unique advantages [30-32]. Advanced oxidation technology refers to the generation of hydroxyl radicals ( $\cdot\text{OH}$ ) in the water treatment process, which oxidizes the macromolecular organic matter in the water body into biodegradable small molecules, and even directly degrades into a class of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and inorganic salts. The general term for the process, in a nutshell, all processes capable of generating hydroxyl radicals can be classified into the category of advanced oxidation technology [12, 14, 16, 31].

Advanced oxidation technology has the following characteristics when degrading wastewater:

1) A large number of  $\cdot\text{OH}$  radicals are generated. Advanced oxidation technology can produce highly oxidizing  $\cdot\text{OH}$  through technical means such as catalysis, light radiation or ultrasonic, and oxidize and decompose pollutants in water.

2) Wide application range and thorough oxidation of organic matter. The high oxidation potential allows  $\cdot\text{OH}$  to oxidize and decompose most organic matter into small molecules almost indiscriminately, and even mineralize into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and inorganic salts.

3) The response speed is fast  $\cdot\text{OH}$  is very active, and the reaction rate constant with most organics is  $10^6 \sim 10^9 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$ , which is close to the limit of rate control ( $10^{10} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$ ).

4) The reaction conditions are mild and easy to manage. Most advanced oxidation processes can be carried out under temperature and normal pressure, the reaction is easy to control, the advanced oxidation is a physical and chemical process,

the process is easy to be managed by the equipment, and the operation process can be simplified.

5) It can be used alone or in combination with other processing technologies. In particular, it can be used as a pretreatment for biological treatment, which can improve the biodegradability of difficult-to-biodegradable organics, which is conducive to the further degradation of biological methods.

According to the different production methods and reaction processes of OH, advanced oxidation technologies can be divided into chemical oxidation, wet oxidation, supercritical water oxidation, electrochemical oxidation, photocatalytic oxidation, ultrasonic oxidation, microwave oxidation, etc.

#### **1.4.4.1 Chemical oxidation catalytic oxidation technology**

##### **Fenton oxidation technology**

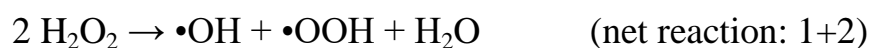
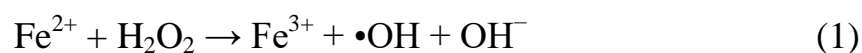
Fenton's reaction was firstly developed by Henry. J. Fenton as an analytical reagent in 1894, it was found that acidic aqueous solution can effectively oxidize tartaric acid under the condition of coexistence of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup>,<sup>33-34</sup> as shown in formula (1) below



Fenton's reaction is carried out through the Fenton's reagent, which is usually consisted of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) with ferrous iron. The Fenton's reagent can work as a catalyst to oxidize contaminants or wastewaters and it can be used to

destroy organic compounds such as trichloroethylene (TCE) and tetrachloroethylene (perchloroethylene, PCE).

In Fenton's reaction, the  $\text{Fe}^{2+}$  is firstly oxidized by  $\text{H}_2\text{O}_2$  to  $\text{Fe}^{3+}$  and then forming a hydroxyl radical ( $\bullet\text{OH}$ ) and a hydroxide ion ( $\text{OH}^-$ ) in the process. After that, the  $\text{Fe}^{3+}$  is then reduced back to  $\text{Fe}^{2+}$  by another molecule of  $\text{H}_2\text{O}_2$ , forming a  $\bullet\text{OH}$  and a proton ( $\text{H}^+$ ). The net effect is a disproportionation of  $\text{H}_2\text{O}_2$  to create two different oxygen-radical species, with water ( $\text{H}^+ + \text{OH}^-$ ) as a byproduct, as the formulas show below.



The  $\bullet\text{OH}$  generated by this process then engages in secondary reactions, and it is a powerful, non-selective oxidant.<sup>35</sup> Oxidation of an organic compound by Fenton's reagent is rapid and exothermic and results in the oxidation of contaminants to primarily carbon dioxide and water.

In the Fenton reaction,  $\text{Fe}_2\text{SO}_4$  is typically used as the iron catalyst, however, the exact mechanisms of the redox cycle are different depending on the different types of reactions. Fenton's reagent is widely used in the field of environmental science for wastewater purification and soil remediation. Various hazardous wastewater was reported to be effectively degraded through Fenton's reagent. However, the drawbacks of Fenton's reaction are that the extra  $\text{Fe}^{2+}$  ions will be added in order to achieve high efficiency, which will cause new pollution. On the

other side, during the reaction, the  $\text{H}_2\text{O}_2$  should be continuously added, so the cost of the materials is usually high. Due to these reasons, the research of new kinds of Fenton reagents should be continuously studied in the future.

#### **1.4.4.2 Photocatalysis**

"Photocatalysis" means the organic combination of photochemistry and catalyst. Therefore, light and catalyst are necessary conditions for initiating and promoting photocatalytic redox reactions. The reason why semiconductor materials can be used as photocatalysts is determined by their own photoelectric properties. The energy band of a semiconductor is discontinuous, and there is a forbidden band between the valence band and the conduction band. It is excited, jumps over the forbidden band and enters the conduction band, produces corresponding holes in the valence band, forming an electron-hole pair. Photo-generated holes have a strong ability to obtain electrons and have strong oxidizing properties. They can take away the electrons in the organic matter or solvent on the semiconductor surface, so that substances that do not absorb incident light are actively oxidized. Photocatalytic material refers to a type of material that can initiate or induce the oxidation-reduction reaction of other substances under the action of light, mainly semiconductor photocatalytic materials. At present, there are many reports on photocatalytic materials, including  $\text{TiO}_2$ , non- $\text{TiO}_2$  metal oxide,  $\text{Ag@AgX}$ ,  $\text{CdS}$ , bismuthate, cobaltate, phosphate, and graphite phase carbon nitride ( $\text{g-C}_3\text{N}_4$ ), etc. Photocatalytic materials have different advantages and disadvantages, such as high degree of light response, easy preparation process, good light stability, and low economic cost.



The basic principles of photocatalytic degradation of organic pollutants can generally be divided into the following processes:

- 1) The semiconductor's electrons absorb light energy greater than its band gap, and the electron band transition occurs;
- 2) The electrons are excited to migrate to the conduction band, and the valence band generates holes to form electron-hole pairs;
- 3) The electron-hole pairs that migrate to the semiconductor surface undergo oxidation-reduction reactions respectively;
- 4) The recombination of electrons and holes occurs simultaneously with the migration of charged carriers;
- 5) The organic matter adsorbed on the semiconductor surface is oxidized by valence band holes, and at the same time, the electrons that have not recombined quickly react with the  $O_2$  on the semiconductor surface to form peroxy ions  $\cdot O_2^-$ ;
- 6) Over Oxygen ions  $\cdot O_2^-$  form  $H_2O_2$  in the aqueous solution, produce hydroxyl radical  $\cdot OH$  which plays a decisive role in photocatalytic oxidation, and then react with organic pollutants and mineralize them,<sup>36-37</sup> as shown in Figure 1.3 below.

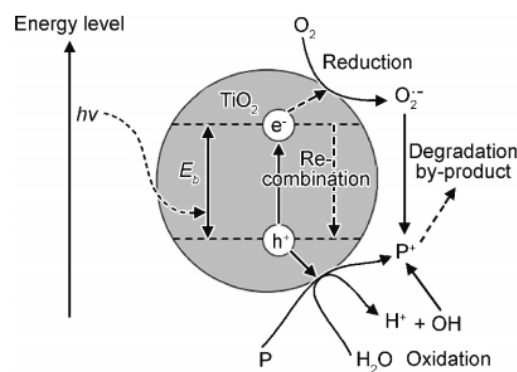


Fig. 1.3 The mechanism of photoelectric cavitation

The reaction process is as follows:



It can be seen from this that the photocatalyst is mainly used for the oxidation-reduction reaction of photogenerated carriers. The main factors affecting the photocatalytic activity are:

- 1) the range of photoresponse;
- 2) the efficiency of generating photogenerated carriers, which is the quantum yield;
- 3) The recombination rate of photogenerated electron-hole pairs, which is the lifetime of photogenerated carriers;
- 4) The need to overcome photocorrosion – stability [38-39].

The photocatalytic oxidation method has the characteristics of mild reaction conditions, low operating cost, high efficiency, no secondary pollution and easy to be combined with other advanced oxidation technologies. However, there are also disadvantages such as the high cost of the catalyst, low light utilization efficiency, possible production of more toxic intermediate products, and difficulty in catalyst recovery. Therefore, in-depth research is needed to facilitate its application in actual wastewater treatment.

#### **1.4.4.3 Electrocatalytic degradation**

The basic principle of electrochemical degradation of organic matter is to make these organic pollutants undergo redox transformation on the electrode. The direct electrocatalytic conversion of organic matter is carried out in two categories. The first

is electrochemical conversion, that is, the conversion of toxic substances into non-toxic substances, or the conversion of non-biocompatible organic substances into biocompatible substances such as aromatic ring-opening oxidation to fatty acids for further biological treatment. The second is the electrochemistry process, the substances are oxidized into small molecules.

Electrochemical oxidation technology is a technology based on electron transfer to generate OH radicals to oxidize organic matter. Electrochemical oxidation technology can be divided into two methods from the source of  $\bullet\text{OH}$  radicals: anodic oxidation (AO) and electrochemical Fenton (EF) [40]. Electrochemical oxidation technology has received rapid attention due to environmental safety and compatibility. It has the advantages of rapid degradation, thorough oxidation, versatility, low cost, and high degree of automation. It is widely used in industrial toxic organic wastewater treatment [41].

According to the principle of electrochemical catalysis, electrocatalytic oxidation of organic wastewater can be divided into direct oxidation and indirect oxidation. Direct oxidation is the oxidation and removal of organic matter on the electrode surface through electrochemical reactions. At present, the degradation mechanism of direct oxidation of organic wastewater is generally recognized by Johnson et al. The research results are shown in Figure 1.4.

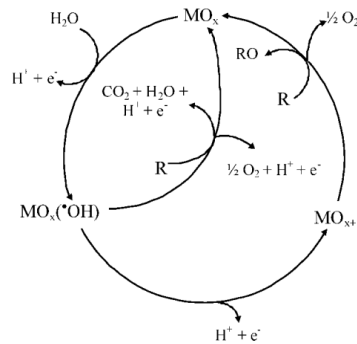
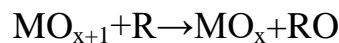
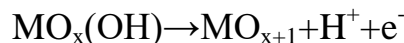


Fig. 1.4 Mechanism of direct oxidation of organic compounds

Direct oxidation means that organic pollutants are directly oxidized and removed by an electrochemical reaction on the electrode surface. The degradation mechanism of oxidation reaction can be expressed as:



In the reaction mechanism,  $\text{MO}_x(\text{OH})$  and  $\text{MO}_{x+1}$  are called "active oxygen", organic matter can be completely oxidized by  $\text{MO}_x(\text{OH})$  to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and the high-valence state of  $\text{MO}_{x+1}$  is selectively oxidized to oxygen-containing compounds. This depends on different electrode materials.

Indirect oxidation refers to the use of redox substances produced by electrochemical processes as reactants or catalysts to convert pollutants into less toxic substances. The indirect oxidation reaction plays the role of anode direct oxidation to a certain extent, and at the same time utilizes other active oxidants induced, greatly improving the degradation efficiency of organic matter. According to the strong

oxidizing substances produced, there are mainly indirect oxidation processes such as  $\text{OCl}^-$ ,  $\text{O}_3$ , and  $\text{H}_2\text{O}_2$ .

The electrochemical oxidation reaction conditions are mild, simple and easy to operate, and little or no secondary pollution occurs. As a new type of environmental pollutant reduction technology, electrochemical catalysis technology has attracted the attention of researchers from all over the world. Some research institutions at home and abroad have successively carried out a lot of creative research work and achieved many results. But in general, this technology still has the following shortcomings:

1. Catalytic electrode materials have a significant impact on the degradation effect, but their development lacks theoretical guidance. If an electrode with good catalytic performance, high stability and reasonable cost can be developed, it will surely drive the environmental electrochemical technology to treat organic pollutants. Revolutionary development.

2. In the electrochemical treatment of organic pollutants, the optimization and selection of electrochemical reactors have not attracted enough attention. There is a lack of systematic research on the structure, power supply mode, etc.

3. In terms of the degradation mechanism, the research on the reaction mechanism lacks direct identification of the possible active species, the reaction pathway is still at the stage of speculation, and there is no relationship to the general degradation process of a certain type of special pollutant. In terms of kinetics, the research is relatively superficial, and the reaction kinetic model is much less than other advanced oxidation processes. And seldom take or other comprehensive indicators as the object, and these two will be more effective in actual wastewater

treatment.

4. The coupling of electrochemical technology and other technologies shows good application prospects. The current range of optimized combinations still needs to be expanded. For example, joint research with other processes that belong to the same advanced oxidation process is not very in-depth. Through the investigation and study of the treatment effect and the mechanism of co-operation, several effective electrochemical composite advanced oxidation technologies will eventually be formed, which will surely have broader application prospects.

Through the analysis of various technologies mentioned above for the treatment of organic pollutants, it is found that the current research in the field of photocatalysis and electrocatalysis is more concentrated and more effective in application prospects, but photoelectric catalytic degradation was limited by the low efficiency. In order to solve this problem, an organic functional material named viologen was utilized to improve the performance of photoelectrochemical catalysis properties. Based on the previous research, we have utilized a hybrid technology to degrade the organic pollutants, which is the photoelectrochemical catalysis method, and the Methylene Blue (MB) was utilized as the simulant reactant to instead the wastewater. In this work, two different kinds of viologen polymers were utilized together with CdS and AuNPs form the hybrid film and to improve the degradation efficiency of organic pollutants.

## **1.5 Viologens**

The viologens are the name of a series of organic molecules containing the 1'1

disubstituted 4'4'-bipyridine structures, which were first named by Michaelis in 1932 due to their unique color change [42-43]. After that, the viologens have been widely utilized in various applications, such as electrochromic devices [44-45], biosensors [46-47], biofuel cells [48-49], redox flow batteries [50-52], and so on [53-55]. As shown in Figure 1.5 below, the viologen can undergo two redox processes and exhibit three different states: the dication, radical cation and neutral. Generally, the viologens exist in the dication state, which is the most stable state and usually colorless. The dication state viologen can be reduced into the radical cation state by accepting one electron. In this state the viologens are usually extensively colored due to the radical electron can transfer freely inner the bipyridine units, and the colors can be adjusted by changing the substituted groups, which enables the application of viologen as the electrochromic materials [56-57].

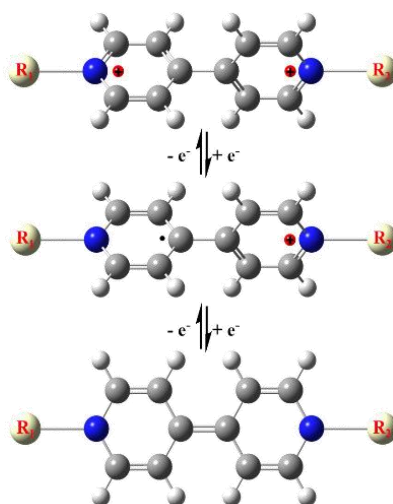


Fig. 1.5. Three states of viologen during redox processes, from top to bottom: dication, radical cation and neutral

The radical cation state viologen can be further reduced into a natural state, however, the reversibility of this process is depending on substituted groups. The research on the application of neutral state viologen is pretty less, and the main

applications are focus on utilizing the strong reductive properties to dope other functional materials, such as Carbon Nanotubes [58-59].

The unique properties of viologens have gotten increased attention in the preparation of hybrid materials, and a lot of functional materials, such as enzymes [60-61], CdS [62-63], Zeolite [64-65], Carbon materials [66-68], and Gold Nanoparticles (AuNPs) [46, 69-73]. In all of these functional materials, the CdS and AuNPs have attracted much attention due to their unique photochemical and catalytic properties [74-76]. Moreover, the CdS and AuNPs have also occupied the unique merits as good stability, easy preparation and controllable sizes.

In the previous years, our group has synthesized a series of polyviologen films with different structures[77-79], and some of them occupied the different porous structures, which can be utilized as the host to disperse and immobilize the CdS and AuNPs. Beyond that, the unique redox property of viologen has attracted a lot of attention in preparing hybrid materials.

Tianquan Lian's research team reported in 2012 that a colloidal quasi-type II CdSe/CdS nanorod was used as a light absorber and a charge separator, and mercaptopropionic acid was used as a sacrificial electron donor to perform photodetection on methyl viologen ( $MV^{2+}$ ) based drive recovery system (shown in Figure 6 below). In the presence of platinum nanoparticles, the system can effectively convert sunlight into hydrogen, providing a universal method based on redox mediators for the conversion of solar energy to fuel. The comparison of the charge separation, recombination and hole filling rate of these complexes shows that this point-and-rod structure enables the ultra-fast electron transfer of methyl viologen, the



fast hole removal of the sacrificial electron donor, and the slow charge recombination. The photoreduction of  $MV^{2+}$  has a high quantum yield. Their findings indicate that by controlling the composition, size and shape of quantum confined nano heterostructures, the wave functions of electrons and holes can be tailored to produce efficient light collection and charge separation materials [80].

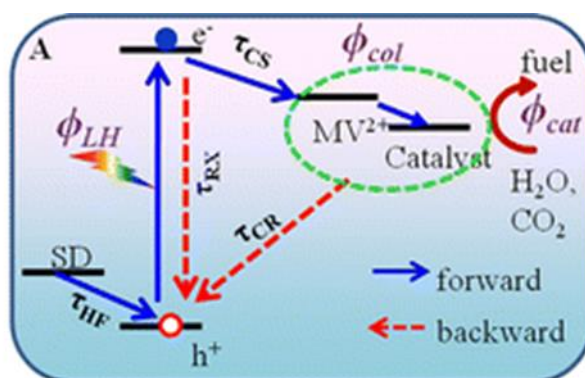


Fig. 1.6 Schematic depiction of relevant processes in a solar-to-fuel conversion system containing sacrificial electron donor (SD), sensitizer, redox mediator (methyl viologen,  $MV^{2+}$ ), and catalyst.

### Conclusions to section 1.

Based on the unique redox properties of the viologens, and the good photochemical properties of CdS and AuNPs, the viologen based hybrid films will be prepared and utilized for the photoelectrochemical wastewater degradation. In order to achieve this aim, the following tasks still need to be solved in the experiment part:

- a. Prepare a stable hybrid film;
- b. Test the electrochemical performance of the viologen materials;
- c. Find the best ratio of the hybrid films;
- d. Test the photoelectrochemical performance of the hybrid films;
- e. Photoelectrochemical degradation test of hybrid films;
- f. Photoelectrochemical catalysis ratio of MB.

## **Section 2 Research Methods and Chemicals and Materials**

In order to prepare and characterize the viologen hybrid materials and their photocatalysis applications, the electrochemical, spectroscopic and microscopic techniques were utilized in this work as main characterization techniques. In this chapter, cyclic voltammetry (CV), chronoamperometry (CA), modulated light test, Ultraviolet-Visible (UV-vis) spectroscopy, FTIR, Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM) techniques will be discussed.

### **2.1 The electrochemical techniques**

In this work, most of the electrochemical experiments were carried out in a typical three-electrodes cell which working principle is shown schematically in Figure 2.1. The cell contains a working electrode (WE), a reference electrode (RE), a counter electrode (CE) and it is filled with electrolyte solution with or without the reactants. Usually the WE materials are inert, having good conductivity and good thermodynamic stability are used, such as glassy carbon, Au, Pt and ITO. The REs should be kept in a stable potential ranges during the measurement, and in all the experiments here performed, the commercial Ag/AgCl electrode or SHE electrode were utilized. The Pt-wires or Glassy sticks were utilized as CE due to their good stability. As electrolytes, aqueous or, organic solvents and ionic liquids can all be used together with the preparation and characterization of viologen based hybrid films. In this work, all the experiments were carried out with the aqueous solution.

In a three-electrode cell the current is passed between the WE and a CE, so the current value can be obtained. The potential during the experiments is monitored

between the WE and RE. The device used to measure the potential difference between the WE and the RE has high input impedance, so only a negligible current is drawn through the RE. During the experiment, the potential is applied between the WE and CE and measured vs. the RE, and the current is detected between the WE and CE. By controlling all these parameters such as time ( $t$ ), charge ( $Q$ ) and scan rate ( $v$ ) varies of electrochemical properties can be measured.

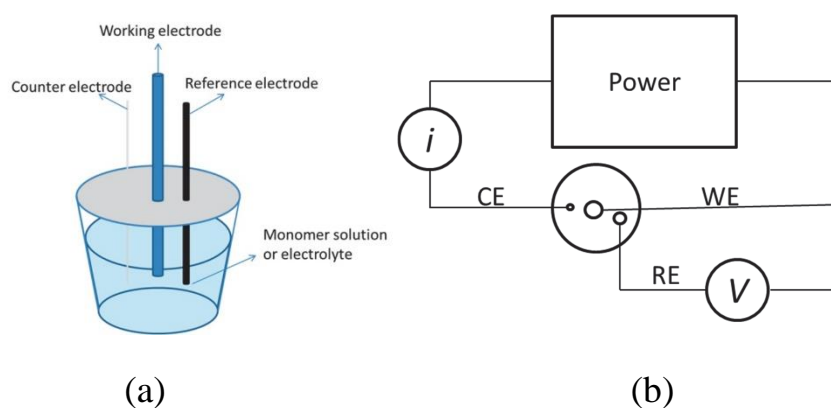


Fig. 2.1. (a) The three-electrode electrochemical cell, and (b) the measuring scheme.

### 2.1.1 Cyclic Voltammetry

Of all the electrochemical techniques, Cyclic Voltammetry (CV) is one of the most versatile and utilized electrochemical techniques. CV is usually the first method which are applied for detection of redox potentials, determining kinetics of the electron transfer and the diffusion properties. CV has been applied in varies conditions for the electrochemical synthesis and analysis. In the electrochemical synthesis, it is easy to carry out the CV to detect the oxidation or reduction potential of different reactants. Furthermore, after the electrosynthesis, CV is usually carried out in a monomer free electrolyte solution for further characterization i.e. to study the redox reactions for the formed material. By changing the scan direction; the reversibilities of the materials can

be measured; and by repeating the CV continuously, the stabilities of the materials can be characterized.

The working principle of CV is shown in Figure 2.2 below. At a certain starting potential ( $E_{\text{initial}}$ ) a continuously higher potential is applied at a certain scan rate  $v$  between the electrodes until a certain potential value ( $E_{\text{final}}$ ) is reached. The potential scan can be applied in either positive or negative direction, which will lead to an oxidation or a reduction reactions, respectively. If the experiment ends at  $E_{\text{final}}$  the technique is named linear sweep voltammetry (LSV). After achieving the highest (lowest) end potential, the potential will be reversed back to its initial value, and one CV cycle is completed. During the CV sweep, the current resulting from the reaction is measured, and the  $I$  vs.  $E$  plot is named a cyclic voltammogram, which is a time-dependent function. In Figure 2.2 (b), a theoretical reversible redox process in a CV is shown. It is assuming that only one reductant is present in the solution. The scan is applied from 0 V (vs. Ag/AgCl) and is increased until the characteristic potential for the oxidation process of the studied material is achieved; an anodic current peak is formed. The peak current ( $I_{\text{pa}}$ ) can be obtained when the peak value ( $E_{\text{pa}}$ ) is achieved, after that the current will drop down with increasing potential. The reason is due to that the reaction is limited by the diffusion, which means the reductant surrounding the working electrode surface is consumed, and the diffusion of the same is not fast enough to maintain the reaction. The depletion causes the current decrease even if the potential is continuously increasing. The sweep is reversed when the final potential is reached, and at the same potential, the oxidants which are formed during the forward half-cycle are reversible reduced. The cathodic current peak is formed correspondingly. With

repeating cycles, the material will be synthesized.

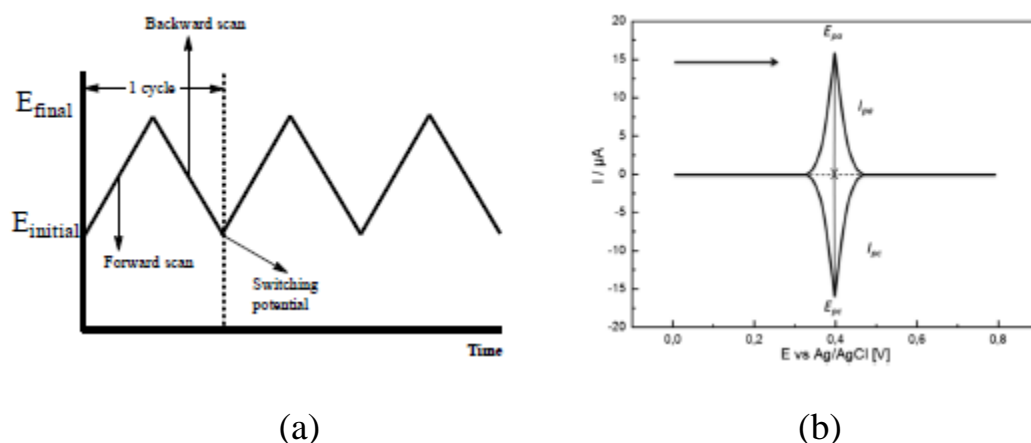


Fig. 2.2: (a) Potential-time signals in cyclic voltammetric experiment, and (b) idealized cyclic voltammogram showing the redox process of a hypothetical redox couple.

### 2.1.2 Chronoamperometry

Another common electrochemical technique is chronoamperometry (CA), which has also been utilized in this work as polymerization and characterization technique. In Figure 2.3, the typical CA process is shown. Similar as the CV, the CA is also a time dependent function.

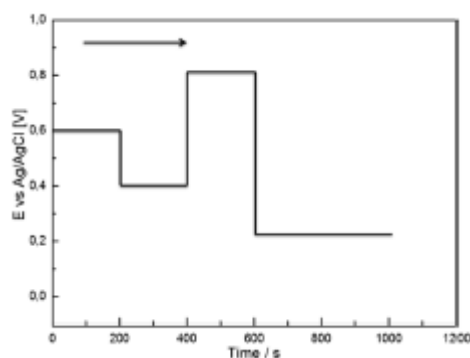


Fig. 2.3. A chronoamperometry measurement with four different potential levels

In a CA measurement, one or more potential levels can be applied on the WE. In contrast to CV, the changes in potential are not continuous but can be applied directly from one value to another. Additionally, the time at each potential can be set at any

particular values for different measurements. Comparing to the CV, the advantage of CA in electrochemical synthesis is that it is easier to control the amount of charge (Q) used during the electropolymerization, and indirectly the thickness of the resulted adsorbed films, especially in the synthesis of conducting polymers.

The CA is also widely utilized in electrochemical analysis, especially in in situ measurements when combined with other techniques. This technique is more efficient, especially for redox polymers, where one wants to analyze the difference in material properties at precise potentials. Additionally, as the redox reaction occurring at the electrode surface is usually diffusion controlled, CA can be used for determining the diffusion coefficient of the redox material according to the Cottrell equation (2-1).

$$i(t) = nFACD^{1/2}/(\pi t)^{1/2} \quad (2-1)$$

Where:  $i$  is current (A);  $n$  is number of electrons;  $F$  is Faraday constant ( $C \cdot mol^{-1}$ );  $A$  is the surface area ( $cm^2$ );  $C$  is the concentration (unit);  $D$  is the diffusion coefficient ( $cm^2s^{-1}$ ) and  $t$  is time (s).

### 2.1.3 Modulight

The Modulight is a programmable light source that has been specifically designed to investigate photo-electrical devices and the relatively photoelectrochemical properties, such as solar cells, photo-hydrolysis devices and so on. The add-on module will operate in combination with the IviumStat, which means the light intensity and the electrochemical parameters can be easily controlled and measured within the same equipment and software. In this work, the photocatalytic properties of the viologen based hybrid materials were all measured by the modulight

together with the electrochemical potentiostat.

In general, the Modulight contains 7 LEDs with wavelengths ranging from 365-740 nm, respectively. In this work, the UV LED was utilized to test the photoelectrochemical properties and photocatalytic performances of the viologen based hybrid films. During operation an LED can be programmatically selected. The sinewave generator of the potentiostat can then be used to modulate the light intensity of the LED with a frequency of 10 $\mu$ Hz to 2MHz. By switching the intensities and frequencies of the UV light, the viologen based hybrid films with best photoelectrochemical performance can be obtained.

## **2.2 Spectroscopic techniques**

Spectroscopic techniques are widely utilized in the characterization of materials. The measurements study the interaction between matter and electromagnetic radiation which can be determined through absorption, transmission and reflection. Depending on the energy level of the electromagnetic spectrum, shown in Figure 2.4, the samples can be measured focusing on different purposes. For example, at high energy, the X-rays can be used to detect the elements of the sample, and at lower energy, the structure of the sample can be analyzed by Infrared spectroscopy. In order to measure and analyze the materials, a series of different instrumentation have been design based on the different electromagnetic ranges.

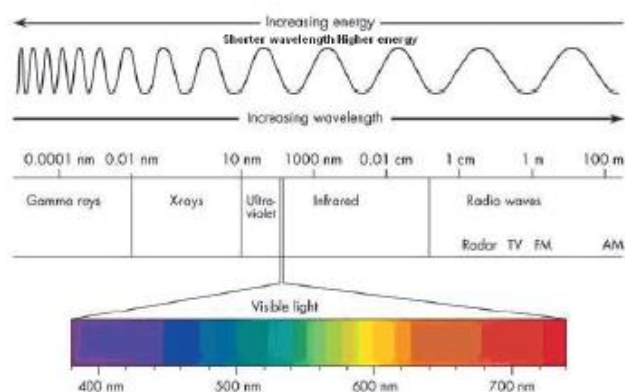


Fig. 2.4. Electromagnetic spectrum showing its wavelength and energy range.

### 2.2.1 In situ UV-vis spectroscopy

The combination of electrochemical and spectroscopic methods has been applied from last century in order to investigate the properties of the materials during an electrochemical process. With the combination, the electrochemical properties, especially the redox property can be successfully measured. Different electrochemical methods and various spectroscopic instrumentation have been combined together for many different applications. In situ UV-vis spectroscopy is one of the most utilized methods in the characterization of various organic monomers and polymers. In the previous part, the redox properties of the viologens have been described from several aspects. The common methods for characterizing the redox processes are CV and UV-vis spectroscopy. As the absorptions of viologens in their different redox forms are characteristic, in situ UV-vis spectroscopy is very useful to determine redox states and redox induced changes in viologens and polyviologens.

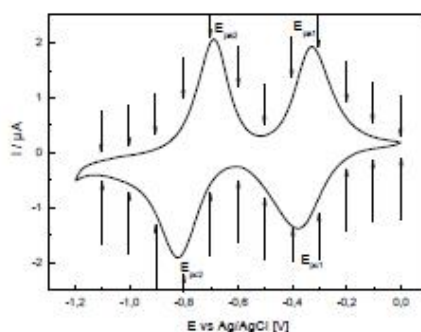
The optically transparent electrode (OTE) is the most central part in the in situ UV-vis measurement setup. Their Transmission is the critical parameter in order not to limit the light passing through to the electrode surface. However, while the absorptions of the materials are controlled by the electrochemical measurement, the conductivity of



the OTE is also very important. Usually the OTEs consist of glass, quartz or metal micromesh. In order to increase their conductivity (for glass and quartz based OTEs), a metal (Au, Pt) or semiconductor (indium tin oxide/tin oxide) layer of a certain thickness is deposited on the substrates. In Figure 2.5 (a), the electrochemical cell which was used for the in situ UV-vis spectroscopic measurement is shown. The ITO glass is placed in the cell as working electrode, so that the electromagnetic beam can pass. A Pt wire works as a counter electrode and a commercial Ag/AgCl electrode is used as reference electrode. They are placed on the sides of the ITO glass so that the UV-vis beam will have a clear passage. In this work, the polyviologen films were firstly synthesized by electrochemical methods (CV or at constant potential) in an electrolyte solution containing the monomer. After film formation the WE was rinsed with electrolyte and placed in a cuvette filled with monomer free electrolyte solution. By comparing the UV-vis absorption before and after the electrochemical polymerization, new absorbance bands due to the formed material can be obtained. These together with CV data can furthermore be used for calculation of the band gaps of the different polyviologens.



(a)



(b)

Fig. 2.5. (a) Electrochemical cell used for in situ UV-vis measurements (b) the applied potentials during the in situ measurements shown by arrows.

After electropolymerization, the formed polyviologen film was characterized by UV-vis during staircase increasing constant potential. As shown in Figure 3.5b, the potential is increased by 0.1 V for every staircase applied on the electrode for a certain time (from several seconds to several minutes) between 0 and -1.1 V. After this the scan is reversed and the material studied on the backward scan. In the UV-vis experiments, the UV-vis absorptions of the polyviologens films were recorded when a stable current value was achieved. By analysis of the absorption variations at different applied potential, the redox properties of the viologen materials can be analyzed. Furthermore, by comparison of the shifts in absorbance, changes in the structure of varies viologen material can be studied. Additionally, the new bands which are formed during potential application indicate the different specific redox forms of the viologen units.

### **2.2.2 FTIR spectroscopy**

Fourier transform infrared spectroscopy (FTIR) was used in this work to verify the structure of the electrochemically synthesized polyviologen films. As shown above in Fig 2.3a, the energy of the IR source is weaker than that used in the UV-vis. In the IR range the molecular vibrations which are caused by interaction between the sample and the IR light source can be studied and provide information of the structure of the materials, which is particularly useful in the characterization for different organic materials. There are three types of vibrations: bending, stretching and rotating, and each of them contain different sub types. Based on the frequencies, the IR spectrum is usually divided into three regions: near-infrared region (from 13000 to 4000  $\text{cm}^{-1}$ ), mid-infrared region (from 4000 to 400  $\text{cm}^{-1}$ ) and far-infrared region (from 400 to 100

$\text{cm}^{-1}$ ). The intensities of the bands in the near infrared region are much weaker than those in the mid-infrared region, and the far-infrared regions are usually utilized for the characterization of the compounds which contain heavy metals, the molecular torsions and the crystal lattice vibrations. Due to these reasons, the application of IR spectroscopy is mainly focused on the mid-infrared region. A mid-infrared spectrum with the different vibration-regions is outlined in Figure 2.6 below.

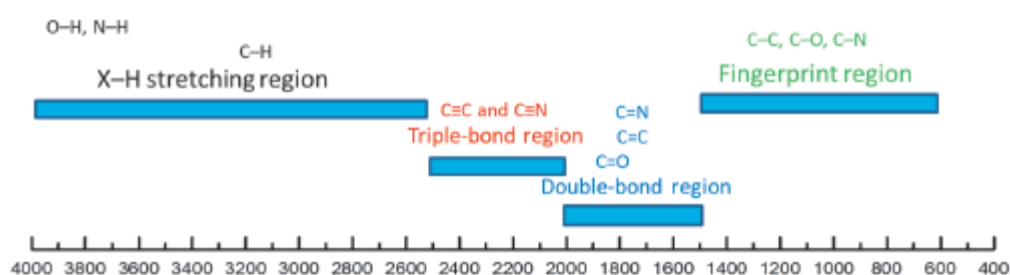


Fig. 2.6. The mid-infrared spectrum

The mid-infrared spectrum can be divided into four regions: 1), the X-H stretching region ( $4000\text{-}2500\text{ cm}^{-1}$ ); 2), the triple-bond region ( $2500\text{-}2000\text{ cm}^{-1}$ ); 3), the double bond region ( $2000\text{-}1500\text{ cm}^{-1}$ ); and 4), the fingerprint region ( $1500\text{-}600\text{ cm}^{-1}$ ). It should be pointed out that the vibrations of each bonds are not constant, which means they can be affected by several parameters, such as skeleton, neighboring molecule or atoms, the conjugated structure and so on. The complexity of the  $1500$  to  $600\text{ cm}^{-1}$  region makes it difficult to assign all the absorption bands, and because of the unique patterns found here, it is often called the fingerprint region.

In this work, FTIR was utilized in the characterization of both the monomers and the resulting viologen materials. By comparing the absorption value in the triple-bond regions, the electrochemical synthesis of the viologen materials can be followed, due to decreasing absorption of  $\text{C}\equiv\text{N}$  bonds and increasing intensity of  $\text{C}=\text{N}$ . Furthermore, the

different absorption bands and the shift of the band indicate changes in the structures of the polymers.

### **2.3 Microscopic techniques**

In order to characterize the morphology and coverage of the viologen films, microscopic (imaging) techniques were introduced for the characterizations. In this work, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were applied to measure the surface morphology of the films.

#### **2.3.1 Scanning Electron Microscopy**

The Scanning Electron Microscope (SEM) is a type of electron microscope that produces images of the sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. The electron beam is scanned in a raster scan pattern, and the position of the beam is combined with the intensity of the detected signal to produce an image. In the most common SEM mode, secondary electrons emitted by atoms excited by the electron beam are detected using a secondary electron detector. The number of secondary electrons that can be detected, and thus the signal intensity on specimen topography.

Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown above. A wide range of magnifications is possible, from about 10 times (about

equivalent to that of a powerful hand-lens) to more than 500,000 times. Due to the high resolution of SEM, it was utilized to analysis the surface morphology of the viologen based hybrid films in this work.

### **2.3.2 Transmission Electron Microscopy**

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image. The specimen is most often an ultrathin section less than 100 nm thick or a suspension on a grid. An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen. The image is then magnified and focused onto an imaging device, such as a fluorescent screen, a layer of photographic film, or a sensor such as a scintillator attached to a charge-coupled device.

Transmission electron microscopes are capable of imaging at a significantly higher resolution than light microscopes, owing to the smaller de Broglie wavelength of electrons. This enables the instrument to capture fine detail—even as small as a single column of atoms, which is thousands of times smaller than a resolvable object seen in a light microscope. Transmission electron microscopy is a major analytical method in the physical, chemical and biological sciences. As the same as SEM, the TEM was also utilized to analysis the morphology of the CdS nanoparticles and viologen based hybrid films.

In this work, the potassium chloride (KCl) was utilized as the electrolytes in all experiments. The KCl (Sigma-Aldrich) was prepared as electrolytes of 0.1 mol/L. All solutions used in the experiments were prepared from deionized water and purged prior

to use with  $N_2$ . The  $HAuCl_4$  was bought from Tunan heavy metal company and it was diluted into solutions with different concentrations. The viologen materials, both the monomer precursors and the polymers, were synthesized as the methods in previously published papers.

## 2.4 The electrochemical measurement part

The cyclic voltammetry experiments were done in a three-electrode one-compartment cell connected to an Ivium Technologies potentiostat (IviumStat.h). The viologen films were synthesized electrochemically on a glassy carbon (GC) electrode with 3 mm  $\varnothing$  and ITO glasses with 0.6\*1 cm, respectively. The GC electrode was polished with diamond paste (1/4 to 1 mm) and rinsed with deionized water before use. Ag/AgCl electrode was utilized as reference electrode obtained from CHI (2 mm  $\varnothing$ ). A coiled Pt wire (1 mm  $\varnothing$ ) and a carbon stick (3 mm  $\varnothing$ ) were used as counter electrodes. The electrochemical polymerization was carried out in aqueous solution according to the procedure reported for polyviologens. Polymerization of FCP and  $HAuCl_4$  were carried out in the concentrations of 5 mM FCP monomers and certain concentrations of  $HAuCl_4$  in 0.1 M KCl solution, and the hybrid films were synthesized either by CVs from 0 to -1.2 V during 20 or 30 consecutive cycles using 50 mV/s as scan rate or alternatively potentiostatically at -0.8 V for a specific time. All solutions were purged with nitrogen and experiments were performed under nitrogen. Prior to the measurement of the redox response in monomer free electrolyte solution the film was rinsed with deionized water and 0.1 M KCl solution to remove traces of monomer.

## 2.5 The spectroscopic equipments

In the UV–vis experiments indium tin oxide (ITO) glass was used as a working electrode (8–12 ohms, Delta Technologies Limited). The ITO glass was cleaned with ultrasonication in acetone, ethanol and deionized water solutions for 15 minutes each. The measurements were made in a 1 cm path length quartz cuvette using a Pt-wire as counter-electrode and Ag/AgCl as reference electrode. The in situ UV–vis spectra were recorded between 300 and 1100 nm on a Hewlett Packard 8453 and Agilent Technology Cary 60 UV–vis spectrophotometer. The viologen based hybrid films were deposited onto ITO-glass electrodes by potential cycling between 0 to -1.2 V using 50 mV/s as scan rate and 40/20 cycles. The UV–vis spectra from the redox response of the viologen films were measured in the potential range of 0 to -1.1 V at every 100 mV. The background spectrum was measured using a blank ITO glass in electrolyte solution.

Fourier transform infrared (FTIR) spectra were measured by using a dry-air-purged VERTEX 70 FTIR spectrometer (Bruker) equipped with a MCT-A detector. The monomers were measured on diamond ATR accessory part and the viologen films were measured from the ITO glass directly. For each spectrum, 32 scans at a resolution of  $4\text{ cm}^{-1}$  were co-added. The viologen base hybrid films were synthesized on ITO glass as described above in previous UV-vis part.

## 2.6 The microscopic equipments

Scanning electron microscope (SEM) images were recorded on a JEOL JSM-7600F microscope at 5 kV. Transmission electron microscopy (TEM)

observations were performed using a JEOL JEM-1400 TEM microscope working at 100 kV and a JEM-2100 TEM microscope working at 200 kV. All samples subjected to TEM measurements were dispersed in ethanol ultrasonically and then dropped on carbon grids.

### **Conclusions to section 2.**

In this work, all the electrochemical experiments were carried out in a three-electrode cells, and the 0.1 M KCl solutions were used as the electrolytes in most of the experiments. The good and repeatable electrochemical measurement is important for both the preparation and characterization of the hybrid films. The spectroscopic and microscopic techniques were mainly used for analyzing the redox properties and surface structures of the hybrid films. In order to synthesize the hybrid films and utilize them in wastewater treatment applications, the experiment procedures will be followed as synthesis, characterization and applications. So in the following parts, the experiments will be carried out in the following orders:

- a. Electrochemical synthesis of hybrid films;
- b. Electrochemical test of the redox properties of the hybrid films;
- c. Spectroscopic test of the redox properties of the hybrid films;
- d. Photoelectrochemical test of hybrid films with modulight;
- e. Microscopic analysis of the hybrid films for their surface structures;

Photoelectrochemical catalysis of the MB with electrochemical and spectroscopic.



### Section 3. Prepare a stable hybrid film and test the electrochemical performance of the viologen materials

In this work, two different viologen based hybrid films, FCP/AuNPs and PHV/CdS, were prepared by electrochemical synthesis and layer-by-layer methods, respectively. Both the FCP/AuNPs and PHV/CdS films were varied with different ratio in order to find the best proportion of the materials to achieve the best electrochemical and photoelectrochemical performance.

#### 3.1 Electrochemical synthesis of FCP/AuNPs hybrid films

The polyviologen film (FCP) and FCP/AuNPs was electrochemically synthesized by the cyclic voltammetry methods with the reductive potentials from 0 to -1.2 V for certain cycles. The cyanopyridine based FCP monomers was used as the precursors and the mechanism of the electrochemical reduction from precursors to viologen units is shown below in Figure 3.1.

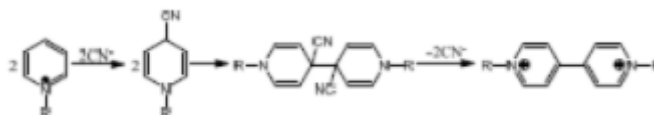


Fig. 3.1. Electrochemical synthesis of viologen with coupling of 1-substituted pyridine cations

Due to the branched structures of the precursors, the polyviologen films can be obtained with the porous structures, which have good potential to immobilized the AuNPs and to form the hybrid films. One more advantages is that the electrochemical synthesis is accomplished by applying the negative potential onto the working electrodes, and the AuNPs can also be formed by the electrochemical reduction of  $\text{HAuCl}_4$  solutions, so in this work, the FCP/AuNPs hybrid films were electrochemical

synthesized by the one-step electrochemical reduction processes.

At the beginning, the FCP polymers were electrochemically synthesized with CVs, for different numbers of cycles, such as 20, 30 and 40, respectively. After that all the redox responses of the FCP polymers were tested by the electrochemical methods, so the one with the best electrochemical performance was chosen, and the charge which was consumed in the CVs was calculated. In the next step, the CA method was used to electrochemical synthesis because it is much easier to control the charge during the synthesis process and then the polyviologens with similar thickness were obtained. As the same methods, the FCP/AuNPs hybrid films were also firstly synthesized by CV method and then CA methods, respectively. The images of the FCP/AuNPs hybrid films which were synthesized on ITO glasses can be seen in Figure 3.2 below.

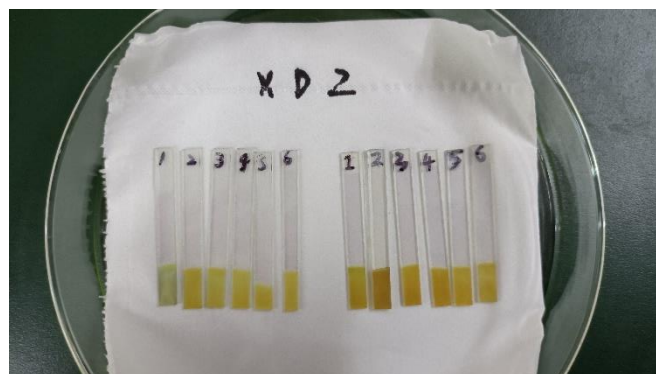


Fig. 3.2 Images of FCP/AuNPs hybrid films on ITO glasses

### 3.2 Layer-by-layer (LBL) preparation of PHV/CdS hybrid films

Layer-by-layer (LBL) assembly is an easy and powerful technique to prepare multilayer films and coatings with nanoscale thickness control of the overall films. Traditionally, the LBL method was utilized to prepare the polyelectrolyte multilayers with solubilized polymers, however, it can also be modified with different functional

materials and polymers, especially for the nanomaterials.

LBL is useful for creating conformal coatings because of the versatility of substrate options and nanoscale control over the layered composite film thickness due to the self-limiting nature of the adsorption. The gentle conditions of LBL assembly and choice of precursors (e.g., polyelectrolyte pairs and charged proteins) offer the ability to tune optical and physicochemical properties of various multifunctional films in a manner impossible through simple solution casting, vacuum-assisted filtration, or chemical vapor deposition (CVD). In addition, LBL assembly takes advantage of natural forces (e.g., electrostatic interactions, hydrogen bonding, metal-organic coordination, charge-transfer interactions, and molecular interactions) to form a multilayer, which requires much less investment in manufacturing infrastructure and energy than other thin-film deposition techniques such as atomic layer deposition (ALD) and electron beam evaporation.

Thus, LBL method was chosen to prepare the viologen based hybrid films, a soluble viologen polymers (PHV) and CdS nanoparticles were combined together. With LBL methods, the concentration of PHV or CdS in the hybrid film can be easily adjusted, which means by changing the LBL layers and the volume, the PHV/CdS films with different ratio can be obtained, so the electrochemical and photoelectrochemical performance of the hybrid film can be tested. In Figure 3.3 below, the PHV/CdS hybrid film prepared with LBL method with different ratio can be seen, and in this work, a series of PHV/CdS hybrid films were prepared and the best ratio was found after the electrochemical and spectroscopic analysis.

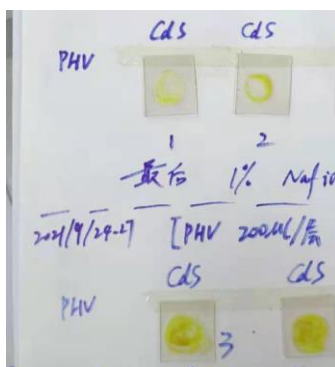


Fig. 3.3 Images of PHV/CdS hybrid films on ITO glasses

In this work, the experimental work which has been done in previous semesters and the preliminary results will be shown and discussed in the following parts. The work is mainly focus on the electrochemical and spectroscopic measurements.

### 3.3 Electrosynthesis of FCP polymers

As describe before, the viologen can be synthesized by the electrochemical reduction of cyanopyridine based precursors. It can be observed in Figure 3.4; the electrodeposition process was carried out by the cyclic voltammetry from 0 to -1.2 V with the scan rate as 50 mV/s. In this process, 20 cycles were applied, and the first cycle was inserted in the top-left of Fig. 3.4. It can be observed that the first reductive peak was formed at the the potential around -0.7 V, which indicated that the viologen units was successfully formed between the precursors. With continuing the CVs, the reductive was shifting a little bit to even negative side, which will be end at approx. -0.9 V, and it is cause due to the formation of the viologen polymer, which is named as FCP in the following parts. The shift of the potentials was supposed due to the weak conductivity of the viologen units, which means the higher potential was needed to be applied to maintain the electropolymerization, and it also indicated the FCP was continuously formed on top of the GC electrode.

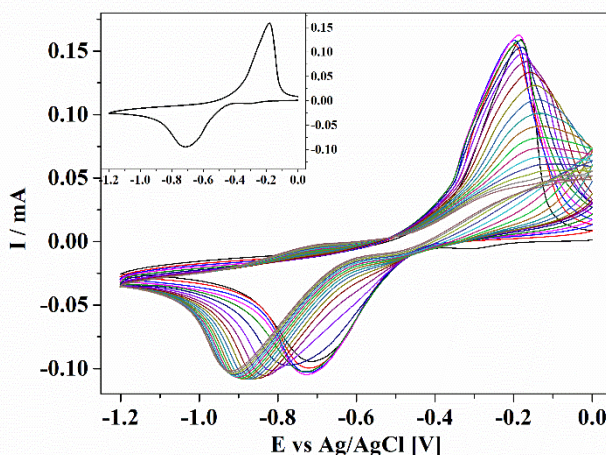


Fig. 3.4 CVs of the electrodeposition of the FCP on GC electrode in the potential range 0 to -1.2 V for 20 cycles, scan rate 50 mV/s. The first CV cycles was inserted in the top-left of the graph

After the electrochemical polymerization, the redox properties of the synthesized FCP polymers were also tested by the cyclic voltammetry method in the monomer free electrolyte. The potential range was also from 0 to -1.2V and the scan rates were switched from 5 to 200 mV/s, respectively. The redox responses of the FCP polymer under different scan rates were shown in Figure 3.5 below, it can be observed that two redox couples are clearly formed during the electrochemical process. The two reductive peaks were marked as  $I_{pa1}$  and  $I_{pa2}$  respectively, and the correspondingly formed oxidative peaks were marked as  $I_{pc1}$  and  $I_{pc2}$  respectively.

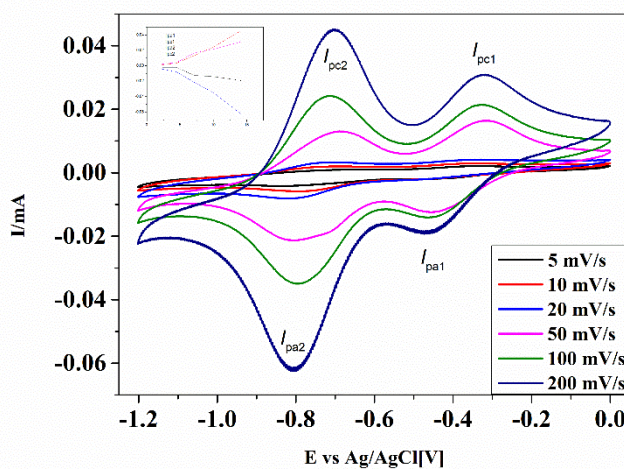


Fig. 3.5 CVs of the redox response of FCP polymers in 0.1 M KCl in the potential range 0 to -1.2 V at scan rates of 5, 10, 20, 50, 100 and 200 mV/s for PV. The inserted image shows the reduction/oxidation peak currents for the two redox pairs vs. the root of the scan rates.

The first reductive peak,  $I_{pa1}$  was formed at about -0.4V due to the reduction of viologen unites from the dication states to radical cation states. As described in previous part, the viologen units in radical cation states can be further reduced into the neutral states, and it can also be noticed from the Figure 3.5, when the higher negative potential was achieved, the second reductive peak  $I_{pa2}$  was formed. The second reductive peak was formed at approx. -0.8 V, so after that no more peak can be found. The good reversibility of the viologen materials is one of its key feature, so when the cyclic sweep was shifted from -1.2 V to 0 V, two oxidative peaks can be observed at -0.3 V and -0.7 V, which were marked as  $I_{pc1}$  and  $I_{pc2}$  respectively.

Theoretically, the peak potentials in each redox couple should be in the same value. However, due to the diffusion of the electrons inner the electrolytes, the potentials of the oxidative peaks are always formed with a little bit lower potential shift. The shift value in the FCP polymers were quite similar, both were -0.1 V for the two peak couples, so it indicated that the redox response of the FCP polymers were quite stable. Additionally, in the inserted image in Figure 3.5, the redox peak currents for the two redox pairs vs. the root of the scan rates was shown. It can be noticed that the curves were pretty linearly, so we can conclude that the FCP polymer obtained good electrochemical performance and good reversibility.

The chronoamperometry (CA) methods is one of the most frequently utilized electrochemical techniques, especially in the electrochemical synthesis. In order to maintain the hybrid films with the same thickness, the CA method is utilized to because it is much easier to control the Charge (Q) comparing to the cyclic voltammetry method. We assumed that the thicknesses of the FCP polymers were the

same if the charges were consumed during the electrosynthesis processes.

After calculated the charge which has been consumed in the CVs, we decided to use 75 mC for the CA polymerization. The FCP polymer has been electrochemically synthesized with CA method at the potential for -0.8 V for approx. 1200s. After that, as the same above, the FCP polymer was tested in the monomer free electrolyte for its redox properties. It has been shown in Figure 3.6 below, the redox performance of the CA-formed FCP polymer has similar performance as the one synthesized by the CVs. The two redox couples were also shown in the similar potential range, and the inserted image also shows the reduction/oxidation peak currents for the two redox pairs vs. the root of the scan rates. It can be observed that the peak current is also increasing linearly corresponding to the root of the scan rates. Based on this, we can confirm that the FCP polymers can be successfully synthesized by the CA methods, and the redox properties and reversibility is still in good conditions.

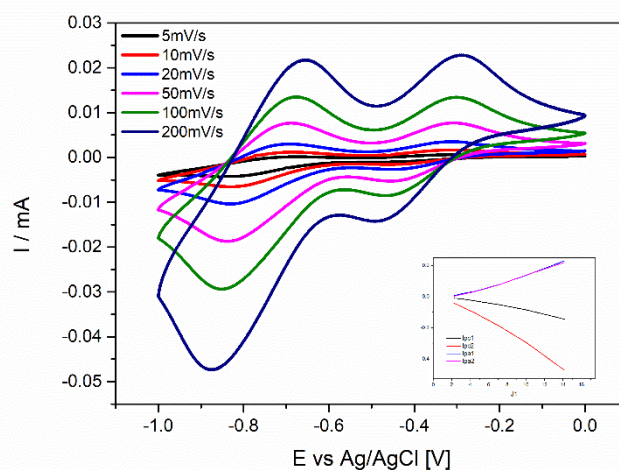


Fig. 3.6 CVs of the redox response of FCP polymers in 0.1 M KCl in the potential range 0 to -1.2 V at scan rates of 5, 10, 20, 50, 100 and 200 mV/s for PV. The inserted image shows the reduction/oxidation peak currents for the two redox pairs vs. the root of the scan rates.

### 3.4 Electrosynthesis of FCP polymers and FCP/AuNPs hybrid films

After the electrochemical synthesis and redox test of the FCP polymers, the FCP polymers can be reproduced with similar electrochemical performance, so the viologen based hybrid films were prepared by the electrochemical synthesis of FCP monomers together with  $\text{HAuCl}_4$  solutions. Since the FCP polymer can be synthesized by the reduction process, and the AuNPs can also be synthesized by the reduction of  $\text{HAuCl}_4$ , so the electrochemical reduction methods were used for preparing the FCP/AuNPs hybrid films. The FCP monomer solution was mixed together with  $\text{HAuCl}_4$  solution with different proportions, and after that, the electrochemical reduction methods, such like CVs and CA, were utilized to synthesize hybrid films by the one-step process.

The FCP/AuNPs hybrid film was firstly synthesized by the cyclic voltammetry methods on GC electrode in the potential range 0 to -1.2 V for 20 cycles, and the scan rate is 50 mV/s. As the same in Fig 3.7, the negative potential was applied on the GC electrode, and with continuing the potential to a certain range, the FCP monomers were synthesized together as the viologen units, and during this process, the  $\text{HAuCl}_4$  was also reduced into AuNPs. The first CV was inserted in the top-left of Fig. 3.7, and it can be seen that the reductive potential is shown at approx. -0.65 V, which is a little bit lower than the reductive peak in the electrochemical synthesis of FCP polymers. It was supposed that was caused by the absence of  $\text{HAuCl}_4$ , which was reduced in the lower negative potential, and formed the AuNPs. As the same as before, by continuously applying the CVs, the FCP polymers were formed, and during the same time, the formed AuNPs were immobilized inner the porous structure



which were formed by the FCP polymers. Thus, the FCP/AuNPs hybrid films were successfully synthesized.

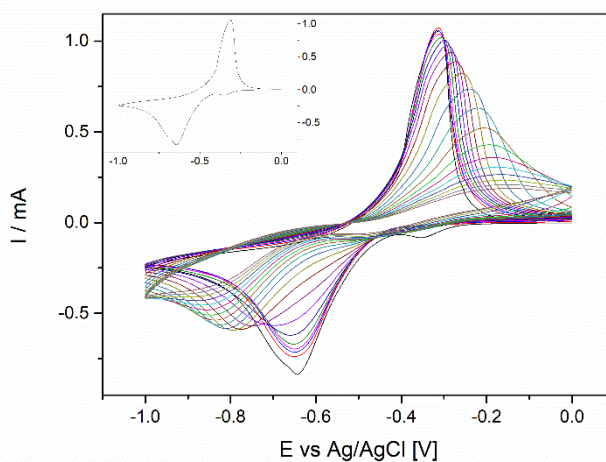


Fig. 3.7. CVs of the electrodeposition of the FCP and  $\text{HAuCl}_4$  on GC electrode in the potential range 0 to -1.2 V for 20 cycles, scan rate 50 mV/s. The first CV cycles was inserted in the top-left of the graph

In order to find out the FCP/AuNPs hybrid films with the best electrochemical and photochemical performance, a series of FCP/AuNPs hybrid films were prepared by adjusting the proportions of FCP monomers and the  $\text{HAuCl}_4$ . In this work, the FCP monomers were maintained with the same level and the concentrations of  $\text{HAuCl}_4$  were decreased scale down. After the electrochemical polymerization, the redox properties and reversibility of the FCP/AuNPs hybrid films were characterized by cyclic voltammetry again, which is shown in Figure 3.8 below.

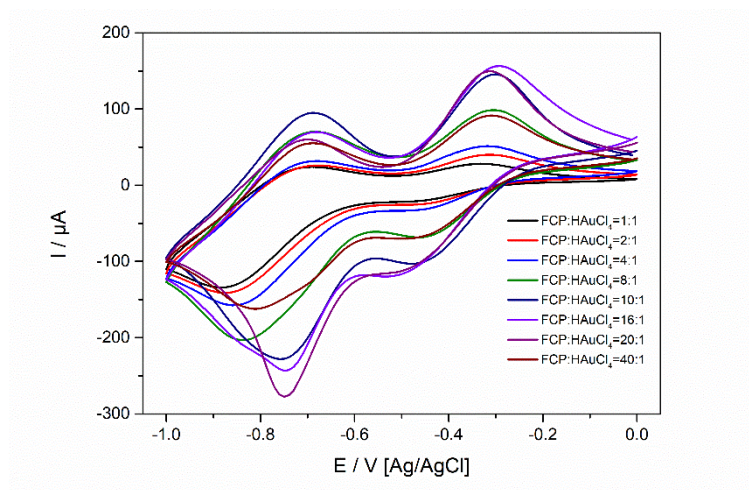


Fig. 3.8. CVs of the redox response of FCP/AuNPs hybrid polymers in 0.1 M KCl in the potential range 0 to -1.2 V at scan rates of 50mV/s. The proportions of initial FCP and HAuCl<sub>4</sub> solutions were from 1:1 till 40:1

Based on the CVs, firstly, we can notice that all of the hybrid films have good redox properties, even the peak currents have a big difference. Secondly, when the concentrations of HAuCl<sub>4</sub> were high, such like from 1:1 till 4:1, the redox peaks were not so significantly, especially for the first redox couple. Additionally, the potentials of the second reductive peaks have shifted to more negative range, comparing to the potentials from the other curves. It is supposed that when the concentrations of HAuCl<sub>4</sub> were high in the initial mixed solutions, it was much easier to formed the AuNPs with large particle sizes, so it was hard for the FCP polymers to immobilized the AuNPs, and the large AuNPs could also blocked the formation of viologen units between the cyanopyridine monomers.

With decreasing the concentrations of the HAuCl<sub>4</sub>, it can be observed that the peak currents of the FCP/AuNPs hybrid films were increased. For the same reason, when the concentrations of HAuCl<sub>4</sub> were low, the AuNPs can be formed with small sizes. Therefore, the good conductivities of the AuNPs can improved the electron transfer performance of the viologen units, so the peak currents were correspondingly

increased. It should also be mentioned that when the proportion achieved to 40:1, the peak current of the FCP/AuNPs hybrid films became lower, which is more or less the same as the pure FCP polymers. It can be explained that the concentration of  $\text{HAuCl}_4$  was too low to form enough AuNPs. Based on these values, we can conclude that by adjusting the concentrations of  $\text{HAuCl}_4$ , the sizes of the AuNPs can be adjusted and we can prepare the FCP/AuNPs hybrid films with different performances. By comparing the CVs, the FCP/AuNPs hybrid films with the initial monomer ratio as 16:1 has the best performance, so in the following experiments, this ratio was kept for preparing the hybrid films.

### **3.5 In situ UV-vis spectroscopy**

In Section 2, it has been described already that the in situ UV-vis spectroscopy is a powerful and effective techniques which are frequently utilized to analysis the molecular orbital and the spectroscopic properties of different organic materials. Furthermore, since viologens can exhibit in three different states, and usually the viologens are in the dication state, so it is pretty hard to measure their spectroscopic properties in radical cation state and neutral state. By combining the electrochemical and UV-vis spectroscopy together, the UV-vis absorbance of viologens in radical cation state and neutral state can be easily detected.

In this experiment, the FCP/AuNPs hybrid film were prepared as before with the proportions of initial FCP and  $\text{HAuCl}_4$  solutions as 16:1. Since the ITO glass could block the UV light and distract the UV-vis measurement, the Pt-Net was utilized as the working electrode for the electrochemical synthesis of FCP/AuNPs hybrid films. As

shown in Fig. 3.8, the first reductive peak was shown in approx. -0.45 V and the second one was shown in -0.75 V, so the negative potentials -0.5 V and -0.9 V were applied on the working Electrode, with which the viologens can be maintained in radical cation state and dication state, respectively. The 0 V was applied at the beginning in order to test the UV-vis absorbance of hybrid film when viologens were under dication state, and the in situ UV-vis measurement of the FCP/AuNPs with three different states is shown in Figure 3.9 below.

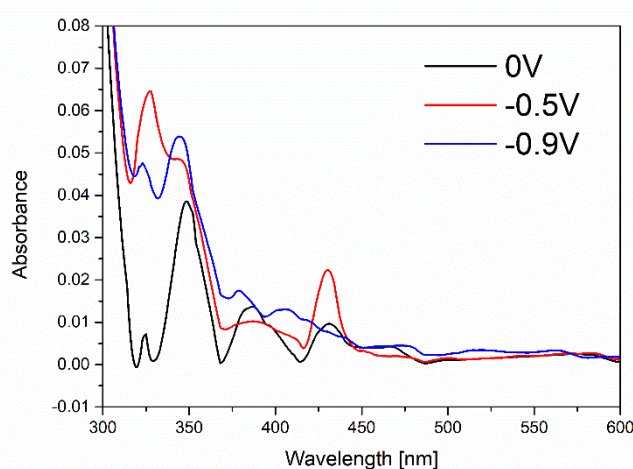


Fig. 3.9. The in situ UV–vis spectra of FCP/AuNPs hybrid film covered Pt-net electrode under potentiostatic conditions, spectra recorded at 0, -0.5 and -0.9 V (vs. Ag/AgCl electrode).

In the previous research, we have proved that the UV-vis absorbance of the viologen based polymers could change if the potentials which were applied on the working electrode changed. In Figure 3.9, the similar phenomenon can be observed. However, the Pt-net is a little bit rough, so the signals have been smoothed because the noise was pretty high. The UV–vis spectra showing the  $\pi$ – $\pi^*$  transition, the peaks at approx. 325 nm and 350 nm were caused due to the absorbance of the two pyridine rings, so when the negative potentials were applied on the working electrode, the absorbance values increased continuously. On the other side, the peak at approx. 425

nm was caused by the  $n-\pi^*$  transition, which was also caused by the two pyridine rings. However, the tendency of change is different as the one in previous peaks, even the hybrid film was maintained under the same potentials.

When the potential was increased from 0 V to -0.5 V, the absorbance value has increased significantly. However, when the potential was continuously increased to -0.9, the absorbance peak started to decrease. It is supposed that this phenomenon was caused by the change of the redox states of the viologens. So when the viologen was reduced from dication to radical cation state, the absorbance strongly increase. However, with continuously increased potential, the absorbance peak at 425 nm start to decrease, which is not the same as the peak at 350 nm. It supposes that it is caused due to the switch of the redox states, since when the viologen was further reduced into the neutral form, the radical disappear so the corresponding absorbance start to decrease. In general, the in situ UV-vis has also proved that the FCP/AuNPs hybrid film has good redox performance, which indicated that the hybrid film can work as good photoelectrochemical applications.

### 3.6 FTIR measurements

FTIR is one of the most frequently utilized techniques for the analysis of organic materials, and in this work, we have also utilized the FTIR to analysis the FCP monomers and the FCP/AuNPs hybrid polymers. In Figure 3.10 below, the FTIR spectra of the two materials are shown. Since the FCP monomers contains the cyanopyridine group, so we can observe that a sharp peak at  $2239\text{ cm}^{-1}$ , which is caused by the CN vibration of the aromatic nitriles. Strong Bands can also be

observed at  $1500\text{--}1400\text{ cm}^{-1}$ , which were assigned to C=C and C=N stretch vibration. The bands at  $1250\text{--}1200\text{ cm}^{-1}$  are from the in-plane deformations of the pyridine groups. In the spectrum of the monomer FCP a series of weak bands unique for the monomer can be seen at  $780\text{--}700\text{ cm}^{-1}$  from the 1,2,4,5-trisubstituted benzenes and at approx.  $1480\text{ cm}^{-1}$  from the  $\text{CH}_2$  group.

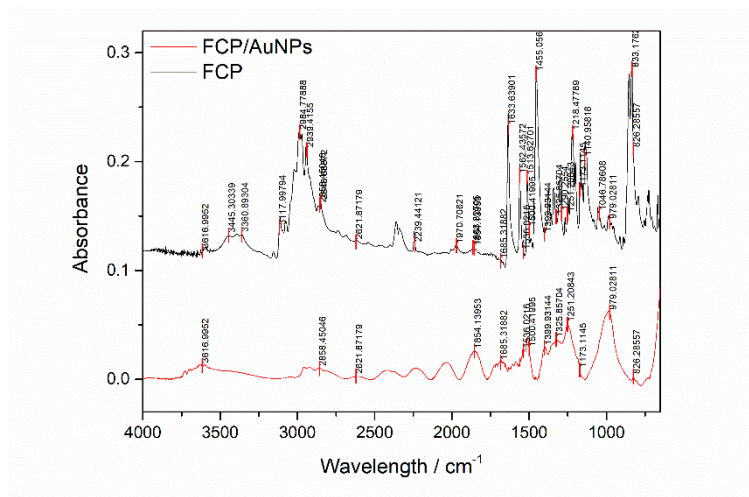


Fig. 3.10. FTIR spectra of the monomers FCP and the FCP/AuNPs hybrid film

As described above in the polymerization process the cyano groups were reductively coupled to the viologen unit forming polymers. The monomer and hybrid film have a similar spectrum, which indicates that the FCP is the major unit and works as the skeleton in the hybrid film. In the spectra there is a weak band at approx.  $2300\text{ cm}^{-1}$ , which indicates that most cyano groups were reductively coupled into viologens. In the hybrid film spectrum, the bands around  $1500\text{ cm}^{-1}$  and  $1000\text{ cm}^{-1}$  are assigned to phenyl structures in the FCP indicating successful incorporation of the FCP and AuNPs.

### 3.7 Photoelectrochemical measurements

In this work, we are planning to utilize the photocatalytic properties of

FCP/AuNPs hybrid film to treat the wastewater, so the photo-electrochemical performance of the hybrid film is an important parameter for the further application. The modulight system, which is the accessory of the Ivium potentiostat, was utilized to measure the electrochemical performance of the hybrid films when they were under the irradiation by the light with different wavelengths. At the beginning of experiments, in order to find the relationship between the light and the hybrid films, which means what is the hybrid films should have the electrochemical changes, neither potential or current, when the light irradiates onto the films. The modulight system contains 7 LEDs with wavelengths ranging from 365-740 nm, respectively, so at the beginning, all the lights were utilized to irradiate the different hybrid films alternatively, and the result can be seen in Figure 3.11 below.

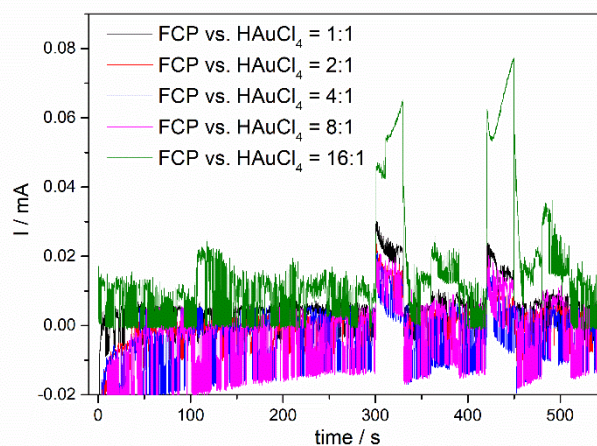


Fig. 3.11 Modulight measurement of the FCP/AuNPs hybrid film with different ratios, the wavelengths of the lights were switched from 740 to 365nm

Since the modulight system is carried by the irradiation of the lights with different wavelength, so when the wavelength is low, the energy which the hybrid films can obtained is not enough to excite electrons. Thus, at the beginning, there was no photocurrent response until the wavelength reached a certain level. When the blue light was applied onto the hybrid films, the photocurrent was generated, and after that,

a higher photocurrent value was obtained when the UV light was applied onto the hybrid films. The last light which was applied is the white light, which is a mix light contains the wavelength from 365-740 nm, so there was still photocurrent response. Based on these results, we could know that the FCP/AuNPs hybrid films have good photoelectrochemical properties to blue light and UV light, and since the materials have better performance when the UV light was utilized, so in the following modulight experiments, the UV light was chosen as the irradiation light.

After the selections of the irradiation light, the photoelectrochemical performance of the FCP/AuNPs hybrid films was tested by the irradiation of UV light, with a switch on/off mode. Firstly, the CA was applied onto the hybrid films so the materials were maintained in the initial state, and after that, the UV light was switched on and the photocurrent was generated, The UV light irradiation was switched off after 1 min and the hybrid films were reverse back to the initial state for another 1 min. This kind of test was repeated for 4 more times and finally the photoelectrochemical performance of the hybrid film under the UV light irradiation was recorded in Figure 3.12 below.

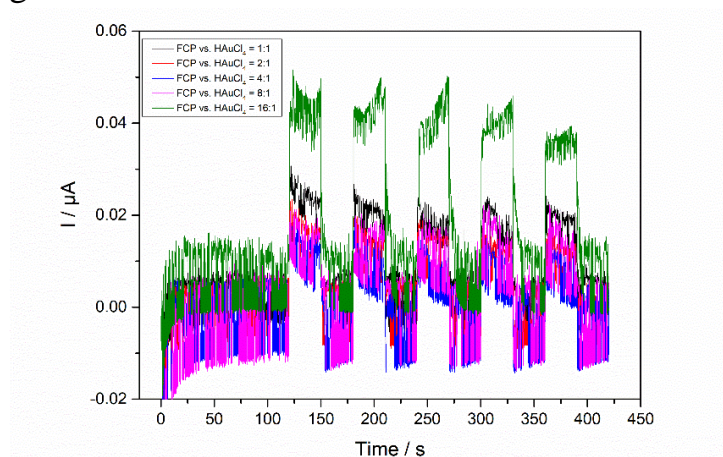


Fig. 3.12 Modulight measurement of the FCP/AuNPs hybrid film with different ratios, the UV light was utilized as the wavelength is 365nm



In this test, the photoelectrochemical performance of all the FCP/AuNPs hybrid films which were electrochemically synthesized from the different ratios of FCP and  $\text{HAuCl}_4$  solutions has been measured, and the peak photocurrent value from the different FCP/AuNPs hybrid films was calculated and recorded in Figure 3.13 below, it can be observed that all the hybrid films generated the photocurrents, which means the AuNPs have been successfully synthesized inner the hybrid films. Additionally, by adjusting the concentration ratios of the initial solutions, the FCP/AuNPs hybrid films have shown totally different photocurrent values, and the FCP/AuNPs hybrid films with the initial monomer ratio as 16:1 has the best performance, so it has proved again that this ratio is the best one to prepare the FCP/AuNPs have the best performance. Finally, we could conclude that the FCP/AuNPs have good photoelectrochemical performance to UV light irradiation and it has good photocatalytic potential in the further applications.

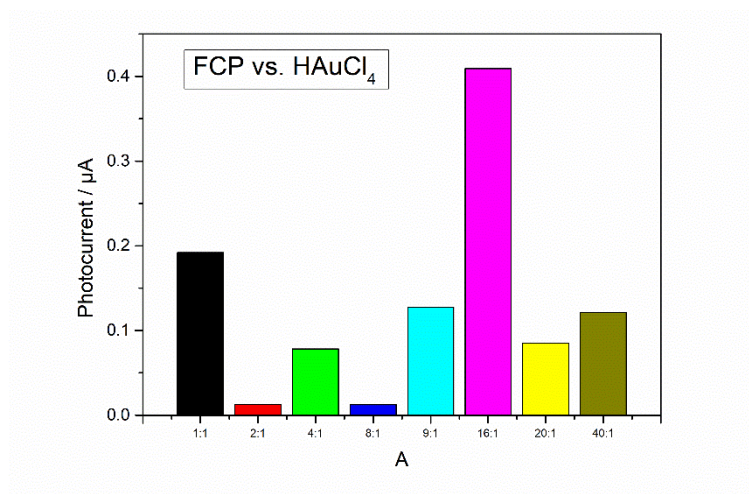


Fig. 3.13. The peak photocurrent value from the different ratios of FCP/AuNPs hybrid films.

### 3.8 SEM measurements

The Scanning Electron Microscope (SEM) is a powerful technique to analysis the surface structures of different materials. In order to morphologies of the hybrid films, the SEM was utilized in this work. Based on the previous experience, the cyanopyridine monomers can form the viologen polymers with porous structures, which can be a merit for the application for the viologen polymers. For the same reason, the FCP based hybrid films can also have the same porous structures, and in order to prove that, the SEM was used to characterize the surface structures.

In Figure 3.14 below, the surface structure of FCP/AuNPs hybrid film with the initial monomer ratio as 16:1 has been measured by SEM. From image Fig. 3.14a to 3.14d, the surface structure of FCP/AuNPs hybrid film can be observed. In the images, it can be observed that the hybrid film has also obtained the porous structures, which increase the surface area and enable the electrolytes and large particles to shuttle in and out in the future applications. Additionally, plenty of small nanoparticles can be observed in the left corner of Fig 3.14a, and the similar particles have also been noticed in Fig. 3.14b and 3.14c. The nanoparticles were the absence of AuNPs, so we can prove that the AuNPs was successfully formed inner the hybrid films. From Fig. 3.14c to 3.14d, the surface structures of FCP/AuNPs hybrid film were scaled up and zoomed in, and the porous structures can be clearly noticed. Furthermore, the porous sizes which we can observe from the images were pretty homogeneous, which is good for the future photocatalytic applications.

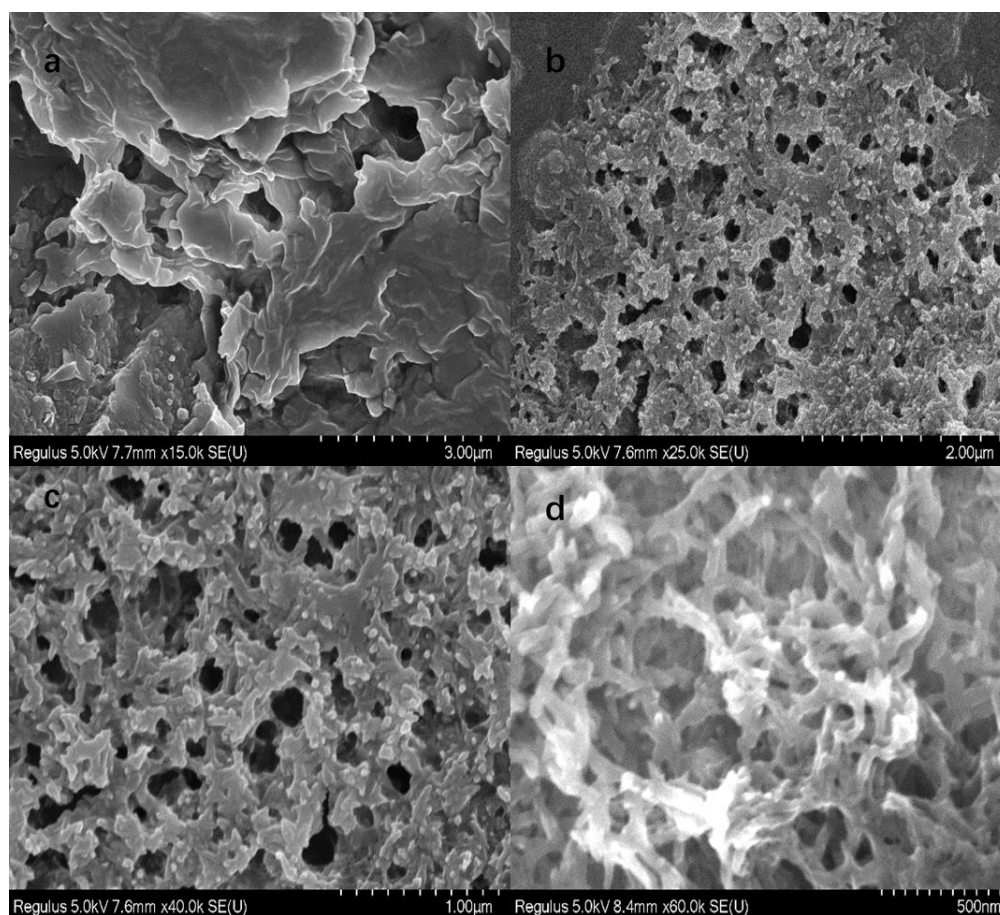


Fig. 3.14. The SEM images of FCP/AuNPs (16:1) hybrid film.

### 3.9 TEM measurements

The Transmission Electron Microscopy (TEM) is another technique which also been frequently utilized in the characterization of the surface structures of different materials. In this work, since the AuNPs were electrochemical synthesized in a one-step process, it is hard to analysis the size and distribution of the AuNPs in the hybrid films. In order to analysis the AuNPs, the TEM was utilized. After the polymerization of the FCP/AuNPs hybrid film on ITO glass, the film was immersed in the ethanol solution for about 15 mins and then peeled off from the ITO glass.

The TEM images of the FCP/AuNPs hybrid film was shown in Figure 3.15 below, so the distribution of the AuNPs can be observed in the TEM images. Firstly, it

can be seen that the AuNPs have been synthesized inner the hybrid film, and the size of the AuNPs were quite homogeneous. Secondly, the AuNPs inner the hybrid film was dispersed pretty well, and no aggregation was observed. Finally, we can conclude that the FCP/AuNPs hybrid film were successfully synthesized by the electrochemical methods.

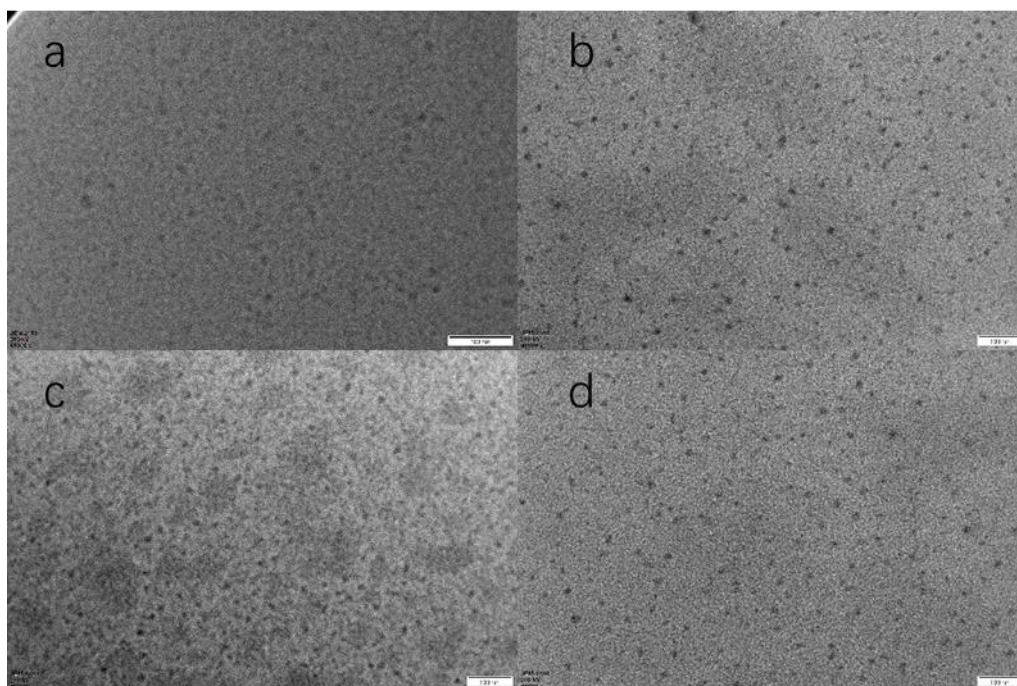


Fig. 3.15. The TEM images of FCP/AuNPs (16:1) hybrid film.

### 3.10 Photocatalytic of Methylene Blue with FCP/AuNPs hybrid film

The aim of this research work is to prepare the viologen based hybrid films and utilize them into the wastewater treatment applications. In this work, the Methylene Blue (MB) was utilized as the simulant materials, since MB is also one of the most common wastewater pollutants. After the synthesis of FCP/AuNPs (16:1) hybrid films, a certain amount of MB was added into the electrolyte, and then the UV light was utilized to irradiate the MB solutions for a certain time. The initial MB solution and the one after the photocatalytic reactions were analyzed by the UV-vis

spectroscopy, and the results were shown in Figure 3.16 below.

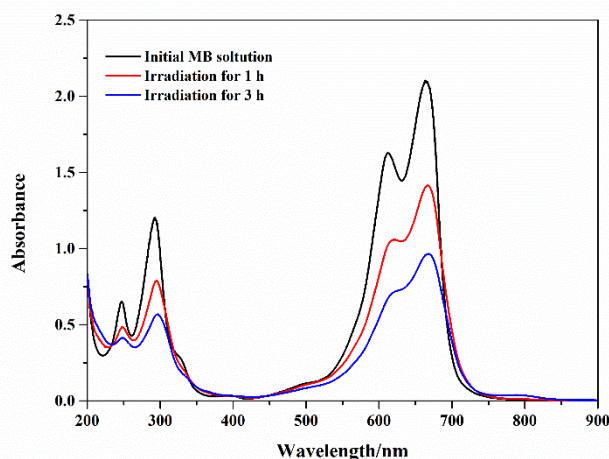


Fig. 3.16 The UV–vis spectra of MB solution after irradiation of FCP/AuNPs hybrid film

The UV-vis absorbance of MB was shown in Fig. 3.16 with black colors, 4 absorbance peaks can be observed, which are at 245, 292, 611 and 665 nm, respectively. After that the FCP/AuNPs hybrid films were put into the electrochemical cells and then the UV light was applied on. After 1-hour irradiation, it can be observed that all the absorbance peaks started to decrease, meaning that the MB has been photocatalytic reduced, with continued the irradiation for another 2 hours, the absorbance peaks were also continued reduced, which indicated the MB has been successfully catalyzed by the FCP/AuNPs hybrid films, and it also proved that this hybrid film have good application potential in the wastewater treatments in the future.

### 3.11 Electrochemical test of PHV/CdS hybrid films

Another viologen based hybrid film which we are interested to utilized in wastewater treatment is prepared by the PHV and CdS nanoparticles. PHV is a kind

of soluble viologen based polymers, so it is a very good candidate to be utilized as the LBL materials to prepare functional films. In this work, the CdS was chosen since it has suitable bandgap and its photocatalytic has been proved already in the previous research.

In order to prepare the PHV/CdS hybrid films, the PHV solutions and CdS suspension solutions were dropped onto the ITO glasses with alternatively layers. By adjusting the concentration of PHV and CdS, the performance of the PHV/CdS hybrid film can be verified. In the Figure 3.17 below, the redox response of PHV/CdS hybrid polymers was measured in 0.1 M KCl by cyclic voltammetry. The proportions of PHV and CdS were from 1:1 till 8:1, and it can be observed that all the CVs have good two redox couples, which indicated that the PHV have been successfully prepared inner the hybrid films. By comparing the redox peak values, the PHV: CdS=2:1 has the best redox performance, so in the following experiments, this ratio was utilized in the following experiments.

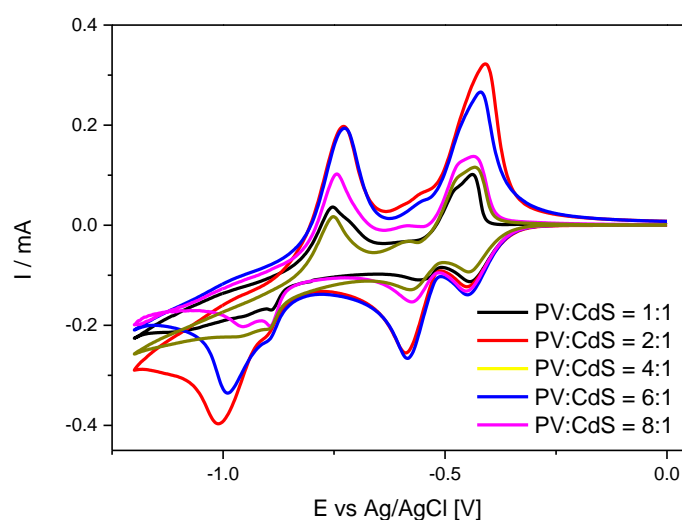


Fig. 3.17. CVs of the redox response of PHV/CdS hybrid polymers in 0.1 M KCl in the potential range 0 to -1.2 V at scan rates of 50mV/s. The proportions of PHV and CdS were from 1:1 till 8:1

After finding the best ratio for preparing the PHV/CdS hybrid film, the redox performance was also tested by CVs, as shown in Figure 3.18 below. It is similar as the previous experiments of FCP and FCP/AuNPs hybrid films, both the reductive peaks and oxidative peaks were increased correspondingly to the increase of the scan rates, which means the redox performance of the PHV/CdS hybrid film were maintained in a good condition. It enables the application of electron transfer between the CdS and PHV, which also gives the potential in the photocatalytic applications.

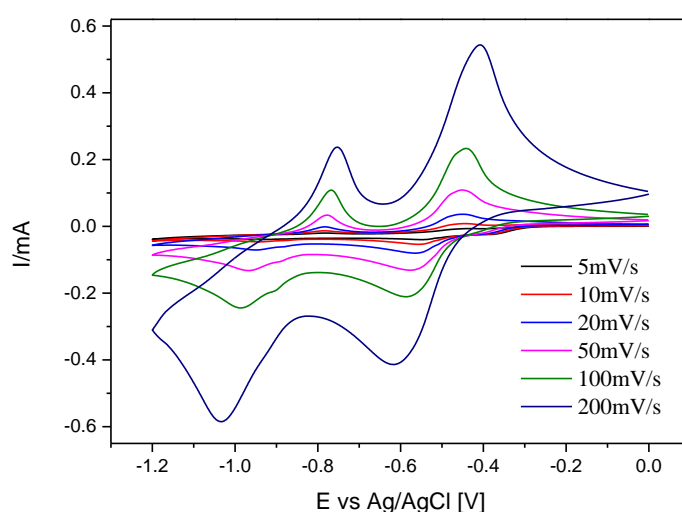


Fig. 3.18. CVs of the redox response of PHV/CdS hybrid film in 0.1 M KCl in the potential range 0 to -1.2 V at scan rates of 5, 10, 20, 50, 100 and 200 mV/s for PV.

### 3.12 SEM and TEM of PHV/CdS hybrid films

As the same as before, in order to analysis the surface structure of the PHV/CdS hybrid film, the SEM and TEM techniques were utilized. In the Figure 3.19 below, the morphology of the PHV/CdS hybrid film can be observed. Comparing to the previous FCP/AuNPs hybrid film, the CdS nanoparticles can be observed more clearly, especially on Fig 3.19d. On the other side, this hybrid film did not have so much porous structures, which means the surface area of PHV/CdS hybrid film may be lower than that of the FCP/AuNPs hybrid film. Additionally, the

size of CdS was also analyzed by the TEM techniques, and it can be seen in Figure 3.19e and 3.19f, the size of CdS is pretty homogeneous and the scale is about 20-30 nm, which is very suitable for the photocatalytic applications.

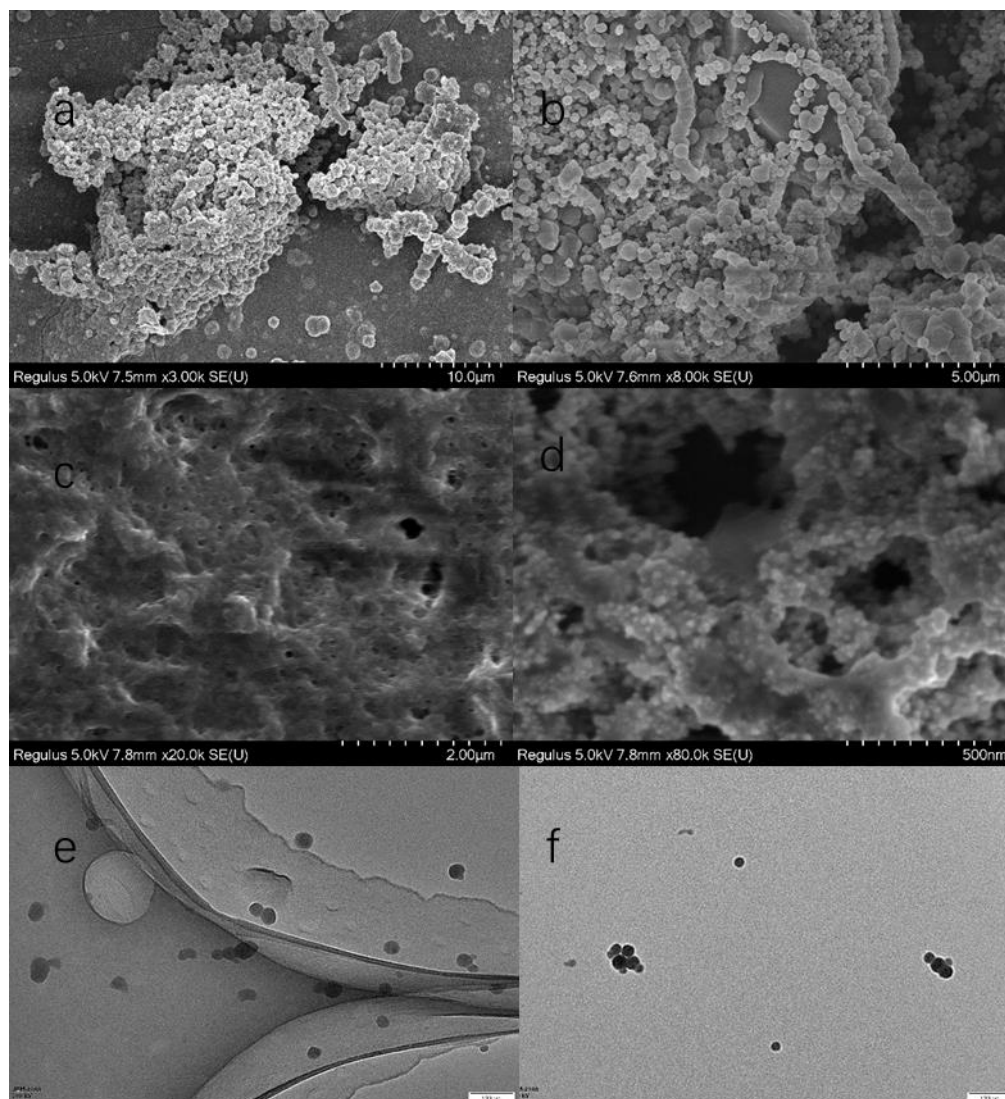


Fig. 3.19. The SEM (a-d) and TEM (e,f) images of PHV/CdS (2:1) hybrid film.

### 3.13 Photocatalytic of Methylene Blue with PHV/CdS hybrid film

As mentioned in the previous part, the CdS has been widely utilized in the wastewater treatment due to its good photochemical properties, so the photocatalytic properties of PHV/CdS hybrid film was tested by modulight together with MB as the simulant materials. As the same as described in part 5.08, the UV light was applied



onto the working electrode for a certain time (0.5 h and 2 h), and the UV-vis spectroscopy was utilized to analysis the concentration of MB before and after the light irradiations. The result is shown in Figure 3.20 below, and it can be observed that MB can also be reduced by the PHV/CdS hybrid film after the UV irradiation, and the absorbance peaks of MB were also reduced corresponding to the irradiation time. However, comparing to the previous experiments which were done with FCP/AuNPs hybrid film, the photocatalytic performance of PHV/CdS film was a little bit weak, so in the following experiment, the photoelectrochemical performance of PHV/CdS hybrid film will be analyzed and improved in order to improve their photocatalytic properties.

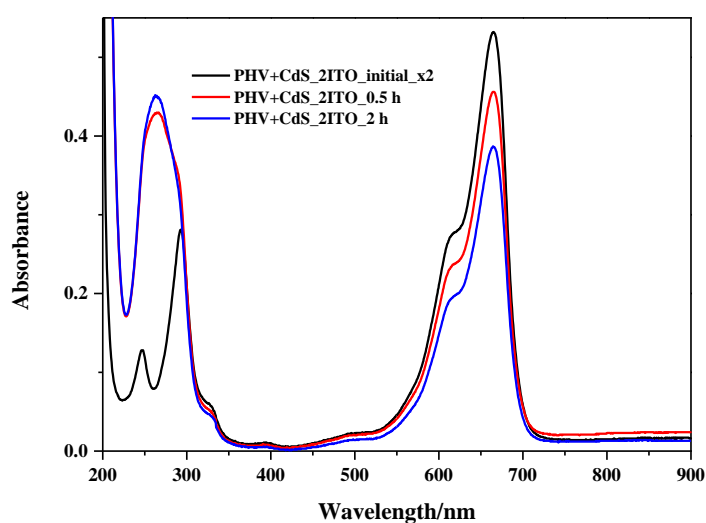


Fig. 3.20. The UV-vis spectra of MB solution after irradiation of FCP/AuNPs hybrid film

### Conclusions to section 3.

Since the  $\text{HAuCl}_4$  will be directly synthesized together with FCP, so the electrochemical synthesis will be carried out through the CV and CA methods. However, on the other side, since the CdS has been synthesized initially before the experiments, so by using the LBL methods it is easier to adjust and control the

concentration ratios of the PHV/CdS hybrid films.

In this part, the synthesis and characterization of the viologen based hybrid films were shown and discussed. The synthesis of the hybrid films was carried out through the electrochemical methods and LBL method, respectively. The adjustments of the hybrid films were achieved by changing the concentration of  $\text{HAuCl}_4$  or the concentration of CdS in the initial solutions. The following experiments have proved that these methods were effective to find the best parameters to prepare the hybrid films with improved photoelectrochemical performance. The photoelectrochemical measurements indicated that these viologen based hybrid films can degrade the MB effectively and their application can also be extended into large-scale applications in pharmaceutical industries.

## Conclusions

The aim of this thesis work is focus on the photoelectrochemical catalytic application of viologen based hybrid films in the treatment of wastewater from pharmaceutical industry. Based on the work we have done in the previous months; we can summarize the following conclusions:

a) The FCP/AuNPs hybrid film can be successfully synthesized with the one-step electrochemical synthesis process, and by adjusting the initial concentrations, the size of AuNPs inner the hybrid films can be controlled.

b) The LBL method can be utilized as an easy method for preparing the viologen based hybrid films, such as PHV/CdS hybrid film, and the performance of the hybrid films can be adjusted by changing the ratios of the LBL solutions.

c) All the hybrid films we have obtained in this work have maintained good redox properties, and they have also obtained good surface structures.

d) Both the FCP/AuNPs and PHV/CdS hybrid films have obtained good photoelectrochemical performance and good catalytic performance in the treatment of methylene blue.

e) The viologen based hybrid film have huge potential in the wastewater treatment application in the future.

In general, the unique properties of viologens, such as good redox property, good stability, easy preparation, and low cost, enable the viologens to be utilized together with other functional materials for the wastewater applications. In this work, we have done the experiments on the preparation and analysis of the hybrid films, and also the preliminarily test of their photoelectrochemical catalytic applications. All

the results proved that the viologen based hybrid film can work as the excellent new material in the future wastewater treatments, and we will continue on the research in the future.

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