



## Synthesis of Pp-16@Ag/AgCl of high performance photocatalyst particles for decomposition of Rhodamine B and fast green dyes



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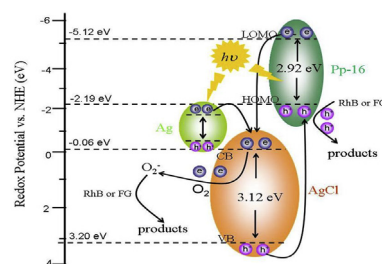
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### HIGHLIGHTS

- Novel polymer Ag/AgCl hybrid has been synthesized by in-situ polymerization.
- The energy gap of both Ag/AgCl and Pp-16 is diminished due to the bi-lateral interaction.
- Pp-16@Ag/AgCl exhibit significant enhancement in photocatalytic degradation of RhB and FG.
- Negative charge density on the dyes is responsible for declining degradation with rising pH.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

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### ABSTRACT

Poly (N-hexadecyl pyridinium acetylenic alcohols bromide)/silver/silver chloride (Pp-16@Ag/AgCl) composite as a novel photocatalyst is fabricated by in situ polymerization of N-hexadecyl pyridinium acetylenic alcohols bromide (p-16) on the surface of Ag/AgCl. The prepared composite photocatalysts were characterized by multiple techniques. The results indicated that Pp-16 layer was formed on the surface of Ag/AgCl, which promoted photoinduced electron–hole pairs separation and endowed the composite catalyst with high photocatalysis capacity. The photocatalysis evaluation tests manifested that 99% of Rhodamine B (RhB) and Fast green (FG) were effectively degraded in minutes by Pp-16@Ag/AgCl, while 51% of RhB and 69% of FG Ag/AgCl were decomposed by Ag/AgCl. The activity of Pp-16@Ag/AgCl was almost kept in four cycles of reutilization. Apart from the dosage of Pp-16@Ag/AgCl and irradiation time, pH value of the solution also affected the decomposition efficiency due to the different charge density on the two dyes. The probe of photocatalysis mechanism elaborated that photogenerated hole and superoxide radical were the main active species in the degradation of RhB and FG by Pp-16@Ag/AgCl, and Pp-16 could promote the generation of  $\cdot\text{O}_2^-$ . Therefore, Pp-16@Ag/AgCl demonstrates high catalysis activity under ultraviolet light irradiation.

## 1. Introduction

With the rapid development of Chinese economy, the energy and

environmental problems have been increasingly serious in recent years. Dyes, such as Rhodamine B (RhB) and Fast green (FG), are among the most organic pollutants [1,2]. So developing highly efficient and stable

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photocatalytic materials have received much attention as a promising solution to solve the energy crisis and environmental pollution [3–8]. Compared with traditional biochemical and physical purification method, photocatalytic degradation technology has many advantages, for example, green energy (sunlight or artificial light source) is used, simple and easy operating equipment is engaged in the process, pollutants are deeply oxidized, no secondary pollution is emitted, and a wide range of pollutants are removed. Therefore, it is considered to be the most economical and environmental benign technology. Reda M. Abdelhameed prepared  $\text{Ag}_3\text{PO}_4/\text{NH}_2\text{-MIL-125}$  composite which had highly efficient degradation activity for Methylene blue (MB) and Rhodamine B (RhB).  $\text{Ag}_3\text{PO}_4/\text{NH}_2\text{-MIL-125}$  catalyst showed higher MB and RhB degradation activity (about 100% and 74%) than P25 (about 30% and 25%),  $\text{NH}_2\text{-MIL-125}$  (about 55% and 50%) and  $\text{Ag}_3\text{PO}_4$  (about 80% and 74%) [9].

Among many photocatalysis agents, AgCl has attracted great interest because of its extremely high photocatalytic efficiency for decomposition of organic dyes. It is well-known that AgCl is a photosensitive material with a direct band gap of 5.15 eV and an indirect band gap of 3.25 eV [10], accordingly, AgCl locates its intrinsic light response within the UV region. In addition, AgCl, which is highly photosensitive, can additionally form the plasma Ag/AgCl under irradiation. Thus, Ag/AgCl exhibits stable and efficient photocatalytic properties due to the special surface plasmon resonance effect [11]. However, Ag/AgCl catalyst has some disadvantages, such as easy agglomeration, poor adsorption capacity for pollutants and so on. So much effort has been made to utmostly get rid of these drawbacks by doping with metal or nonmetal ions, sensitizing with organic dyes, functional carbonaceous materials and conducting polymers [12–16].

Conducting polymers possess special electrical, optical, magnetic and electrochemical properties. At present, many reports have shown that photocatalyst surfaces modified with conducting polymers demonstrate greatly enhanced photocatalytic activity for the degradation of organic compounds [17]. Li et al. successfully synthesized a magnetically separable  $\text{Fe}_3\text{O}_4/\text{PANI}/\text{TiO}_2$  photocatalyst by in situ chemical oxidative polymerization method, and this magnetic separable photocatalyst presented fast charge migration for photodegradation of EDTA under visible-light irradiation [18]. Ma et al. constructed a high-efficiency  $\text{MoO}_3/\text{polyimide}$  hybrid photocatalyst by one step thermal polymerization method. The degradation rate of Methyl Orange (MO) by the composite was 80% under visible light in 10 h [19]. Abdalla Abdal-hay et al. prepared polymer/ $\text{TiO}_2$  nanofiber composites membrane for photodegradation of MB and the degradation efficacy reached 88% in 100 min (sun light source) [20]. Assuredly, these composite photocatalysts improved by polymer have exhibited superior light response and enhanced photoactivity.

In this work, a novel photocatalyst, Pp-16@Ag/AgCl was successfully synthesized by in situ chemical polymerization and its photoactivity was checked through the photodegradation of RhB (one of the most applied dyes) and FG (food, drug and cosmetic additive, and suspected cancer agent). Comparing with pure AgCl and Ag/AgCl, we have ascertained that Pp-16@Ag/AgCl exhibits enhanced photocatalytic activity in the decomposition of RhB and FG.

## 2. Experimental

### 2.1. Materials

4-(bromomethyl) pyridine hydrochloride, propargyl alcohol, 1-bromohexadecane,  $\text{AgNO}_3$ , NaCl and sodium dodecylsulphate were purchased from Aike reagent (Chengdu, China). Tetrahydrofuran (THF), methanol and dichloromethane were supplied by Chengdu Kelong Reagents Factory (Chengdu, China) and distilled before use. Bis (triphenylphosphine) palladium (II) dichloride was purchased from Zhengzhou Alfa Chemical Co., Ltd (Zhengzhou, China).

### 2.2. Preparation of Pp-16@Ag/AgCl

#### 2.2.1. Preparation of Ag/AgCl

Ag/AgCl was prepared according to the references by a method assisted by surfactant with a slight modification [21–23]. In a typical procedure, 1.7 g  $\text{AgNO}_3$  was dissolved into 500 mL of deionized water, and  $\text{NH}_3\cdot\text{H}_2\text{O}$  was added to  $\text{AgNO}_3$  solution drop by drop to form silver ammonia solution. Subsequently, a mixture of 600 mg NaCl and 10 mg sodium dodecylsulphate was dissolved into 100 mL of deionized water, then, the mixture was slowly dropped into the silver ammonia solution. After standing for 2 h, the sample was washed several times with distilled water. Ultimately, the sample was dried under vacuum at 45 °C.

#### 2.2.2. Preparation of p-16

According to our previous work [24], the monomer (p-16) was synthesized. The concrete steps are as follows: first, 12.6 g  $\text{NaHCO}_3$  and 16.4 g 4-(bromomethyl) pyridine hydrochloride were added to a flask, and reacted in THF (solvent) for 6 h at 70 °C. Second, 4.8 g NaH was put to a three necked flask with THF as solvent and 5.7 mL of propargyl alcohol dropped bit by bit. 4 h later, the solution prepared in the first step was added to the three necked flask and further refluxed for 48 h. Thirdly, the product of the second step was reacted with the 1-bromohexadecane for 24 h under 80 °C. After filtration, the sediment was collected. Ultimately, N-cetyl pyridine acetylenic alcohols bromide was obtained by silica gel column chromatography ( $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH} = 25:1$ ) and characterized by NMR.

#### 2.2.3. Preparation of Pp-16@Ag/AgCl

10 mg N-alkyl pyridine acetylenic alcohols bromide, 300 mg Ag/AgCl and 1 mg Pd-C catalyst were added to a 50 mL flask, mixed with chloroform and methanol ( $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH} = 3:1$ ) and refluxed for 72 h at 60 °C in a nitrogen atmosphere. Then, the precipitate was formed by removing the solvents, washed several times with deionized water to get rid of the catalyst and dried in vacuo for 12 h at 45 °C. Finally, the compound material was obtained and marked as Pp-16@Ag/AgCl (1:30). A series of Pp-16@Ag/AgCl (x) (x = 1:30, 1:40, 1:50) were prepared by the similar method.

#### 2.2.4. Preparation of Pp-16-eluent

Pp-16@Ag/AgCl was immersed in  $\text{CH}_3\text{OH}$ . The filtrate is obtained by filtration and  $\text{CH}_3\text{OH}$  is removed by rotary evaporation. Then, the obtained solid was dissolved with dichloromethane  $\text{CH}_2\text{Cl}_2$  and washed with distilled water. The organic liquid is collected by separation and dried. Finally, the product was dissolved with THF, the precipitate was formed by adding petroleum ether to the THF solution and dried at 60 °C for 24 h and the target product was labeled as Pp-16-eluent.

#### 2.2.5. Preparation of Pp-16

As described in subsection 2.2.3, all of raw chemical reagent (except 300 mg Ag/AgCl) and solvents are mixed and refluxed for 72 h at 60 °C in a nitrogen atmosphere. At the end of the reaction, the solvent was removed. Then, do as that described in subsection 2.2.4. The obtained product was labeled as Pp-16. The result of Gel Permeation Chromatography (GPC) analysis in Fig. S1 showed that the number mean molecular weight ( $M_n$ ) of Pp-16 is 6364, weight average molecular weight ( $M_w$ ) is 8350, polydispersity index of Pp-16 is 1.31, and the polymerization degree of polymer is 14. GPC result confirms the polymerization of P-16.

#### 2.2.6. Characterization of Pp-16@Ag/AgCl

FTIR spectra of the samples in KBr pellet were recorded on a Nicolet-6700 spectrophotometer. XRD analysis was performed on a SmartLab X-ray diffractometer with Cu K $\alpha$  radiation. The morphologies of the samples were characterized using a JJSM-6510LV scanning electron microscope (SEM). UV–vis diffuse reflectance spectra were obtained on Shimadzu UV-3600 spectrometer by using  $\text{BaSO}_4$  as a

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