Synthesis and Characterization of Polyhedron-like Ag/AgCl Photocatalyst

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ABSTRACT

Polyhedron-like Ag/AgCl photocatalyst was synthesized through ion-exchange reaction between $AgNO_3$ and $ZrCl_4$ in the presence of vinyl acetate monomer acting as controlling agent. The obtained Ag/AgCl particles showed polyhedron shape with an average size of about 1-2 µm. The UV-visible study presented that polyhedron-like Ag/AgCl had visible light absorption at 470 nm and 600 nm due to the surface Plasmon resonance (SPR) of metallic Ag nanoparticles. The atomic ratio of Ag:Cl elements from EDX spectrum was higher than 1:1 suggesting the presence of metallic Ag coexisting with AgCl. The photocatalytic properties of the obtained product were investigated by evaluating on photodegradation of a model pollutant rhodamine B (Rh B), indicating that the polyhedron-like Ag/AgCl crystals exhibited a much higher photocatalytic activity than simple AgCl and commercial AgCl. The excellent photocatalytic activities could be attributed to the morphology and the surface Plasmon resonance of Ag/AgCl.

Keywords: Polyhedron morphology, Ag/AgCl, Metallic Ag nanoparticle, Photocatalyst

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Introduction

Dye pollutants from the textile industry are one of the main sources of environmental contamination and their release in the ecosystem is a dramatic source of eutrophication, esthetic and teratogenic pollution. Most dyes are resistant to biodegradation and direct photolysis, leading to secondary pollution [1-3]. However, there is the potential to utilize dye, specifically Rh B dye to synthesize plasmonic photocatalysts.

There has been an increased interest and research in plasmonic photocatalysts to replace semiconductor photocatalysts. Among the various semiconductor photocatalysts, TiO_2 is the most extensively employed photocatalyst, owing to its high photocatalytic activity, good chemical stability, non-toxicity, and low cost. However, TiO_2 absorbs only ultraviolet light, which accounts for only 4% of the total sunlight. Since about 48% of sunlight is visible light, it is strongly important to develop the photocatalysts which are active and effective under visible light. Recently, the application in photocatalysis with plasmonic photocatalysts (Ag/AgCl) having stronger absorption and activity under visible light has attracted scientists' attention all over the world and becomes a hotspot in the field of photocatalysis [4].

Besides, the morphology of AgCl has significant influence on its photocatalytic activity, so it is important to develop facile methods to synthesize size and shape controlled AgCl materials. The facile synthesis method is employed to synthesize variable micro and nano AgCl structures, including AgCl nanocubes [5], cube-like Ag@AgCl [6], and even near-spherical AgCl crystal [7]. For polyhedral crystals, the shape are often enclosed by a mix of {111} and {100} facets. For an fcc system, the crystal structure of commonly observed polyhedrons can be divided into two categories: single crystalline structures (e.g., cubes, octahedrons, and tetrahedrons) and twinned structures (e.g., decahedrons and icosahedrons) [8]. The AgCl nanocrystals that have been synthesized in high yields typically have a single crystal structure. For an fcc single crystal, the surface energies associated with the low-index crystallographic planes are in the order of $\gamma(111) < \gamma(100) < \gamma(110)$ [9]. From the viewpoint of Wulff construction, the energetically favored shape would be a truncated octahedron with the optimal truncation fulfilling the condition of $\gamma(100)/\gamma(111) = d(100)/d(111)$, where d represents the distance from the facet to the center of the particle and this parameter reflects the ratio of growth rates along <100> and <111> directions [10].

In this work, we report a new morphology of polyhedron-like Ag/AgCl with enhanced visible-light photocatalytic activity, which was prepared by a modified precipitation method. We characterized the polyhedron Ag/AgCl and evaluated its photocatalytic activity by degrading a typical dye, rhodamine B (RhB) under UV and visible light irradiation.

Objectives of the study

1. To study the effect of VAM on the controlled morphology.
2. To compare the degradation efficiency of Rh B dye with degussa P25

Materials and method

The main chemicals used were: Zirconium chloride ($ZrCl_4$ anh., AR, Merck), silver nitrate ($AgNO_3$, AR, Merck), glacial acetic acid (CH_3COOH, AR, BDH), vinyl acetate monomer (VAM, AR, Merck), and rhodamine B dye (Fluka, $C_{28}H_{31}ClN_2O_3$,

MW 479.02 g/mol). All the chemicals were used directly without further purification. Deionized (DI) water was used in all experiments.

Synthesis of Ag/AgCl polyhedra: 0.2 g of $AgNO_3$ was dissolved in 40 mL of diluted CH_3COOH solution (conc. $CH_3COOH:H_2O$ = 1:1) and refluxed at 100°C for 2 h under vigorous stirring. A chloride solution of 5 g of solid anhydrous $ZrCl_4$ was prepared in 15 mL of DI water under magnetic stirring at room temperature. To this solution, 5 mL of VAM was added and transferred to a 250 mL three-necked flask for refluxing for 60 min at 60 °C. Then, 40 mL of $AgNO_3$ solution was slowly added to this solution held at 60 °C. When the product began to appear it dispersed in the hot solution. The precipitate was cooled down to room temperature and then washed multiple times with ethanol and DI water to remove VAM. At the end of the reaction, the product was collected and dried at 40 °C. In this way, the grey powder of polyhedron-like Ag/AgCl was obtained.

The morphology of the as-synthesized products was investigated by SEM (SEM, Quanta 400, FEI). The elemental composition was analyzed using an energy dispersive spectrometer (EDS) equipped with the SEM microscope system. Phase identification was performed on a Philips PW 3710 powder X-ray diffractometer (PHILIPS X'Pert MPD, The Netherlands), Cu K_α (Ni filtered) radiation λ=1.5406 Å. The diffractograms were recorded in the 2θ range of 5-90°. UV-visible diffuse reflectance spectra were recorded on a Shimadzu UV-3600 UV-vis spectrophotometer using $BaSO_4$ as a reference.

Rhodamine B (Rh B) was chosen as the target organic compound in this study to probe the photocatalytic performance of various prepared photocatalysts under UV and visible light irradiation. The batch experiments were conducted with 0.1 g of respective photocatalyst suspended in 100 mL of Rh B aqueous solution (2.5×10^{-5} M). The solution was pre-stirred vigorously in the dark for 30 min to establish adsorption-desorption equilibrium before irradiation. The zero time readings were then taken and the solution was irradiated. An aliquot (4 mL) was taken at time intervals and centrifuged (4500 rpm for 5 min) to separate the catalyst from the solution prior to the absorbance measurements. The degradation percentage of Rh B was followed by measuring absorbance at 554 nm using a UV-visible spectrophotometer (UV 2600, Shimadzu, Japan).

Results and discussion

In a typical synthesis, the grey powder of polyhedron-like AgCl was synthesized via the ion-exchange reaction of $AgNO_3$ and $ZrCl_4$ as precursors with a temperature of 60 ºC and may be simply expressed as follows:

$$ZrCl_{4\,(aq)} + 4H_2O_{\,(l)} \rightarrow Zr(OH)_{4\,(s)} + 4HCl_{\,(aq)} \qquad (1)$$

$$AgNO_{3\,(aq)} + HCl_{\,(aq)} \rightarrow AgCl_{\,(s)} + HNO_{3\,(aq)} \qquad (2)$$

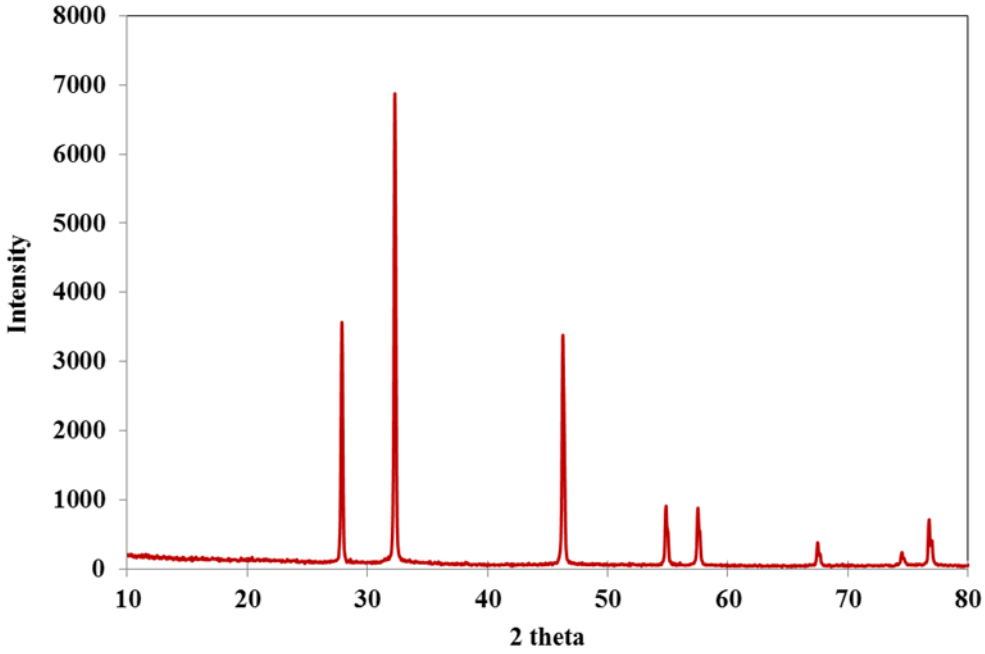

Figure 1 XRD patterns of polyhedron-like Ag/AgCl.

Fig. 1 showed the typical XRD pattern for the product. The pattern of 2θ peaks clearly shows the diffraction peaks located at 27.82°, 32.24°, 46.25°, 54.82°, 57.45°, 67.42°, 74.44°, 76.72° and 85.67°, corresponding to the crystal planes of the face center cubic crystal of AgCl (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), (4 2 0) [4,11]. The diffraction peaks can be indexed to a cubic phase of AgCl (JCPDS no. 31-1238). However, the peaks that are assigned to Ag are hardly detectable in this XRD pattern due to the low content of Ag, beyond the detection limit of XRD analysis.

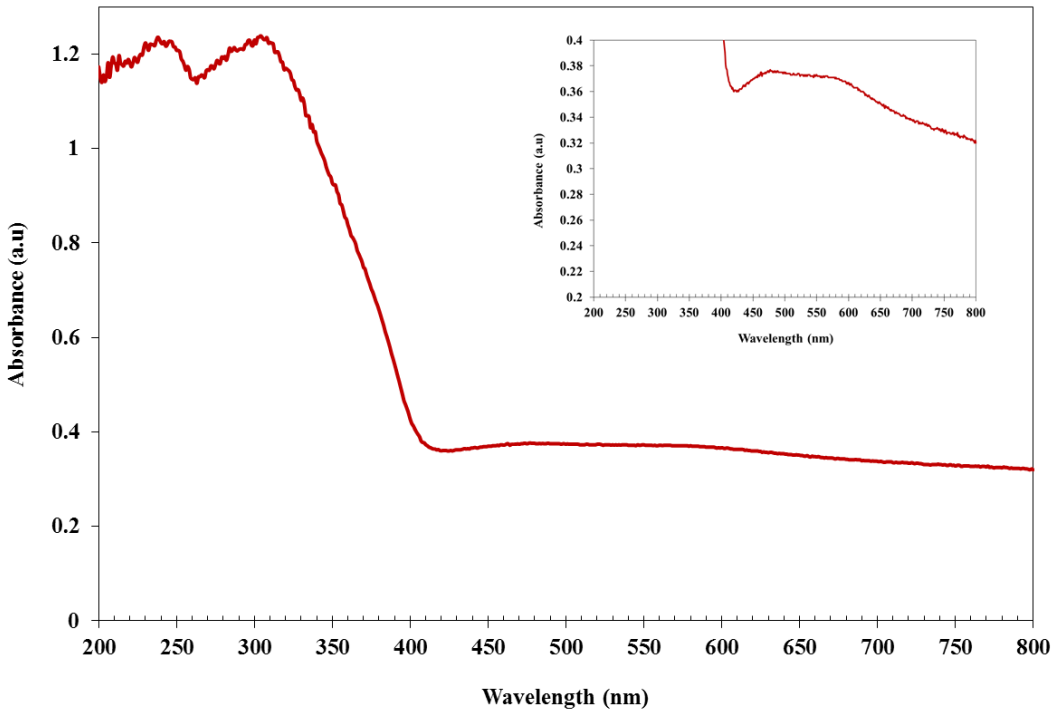

Figure 2 UV-Vis diffuse reflectance spectrum of the obtained Ag/AgCl different product.

UV-visible diffuse reflectance spectroscopy (DRS) was employed to characterize the optical properties of the obtained product. The polyhedron-like Ag/AgCl exhibited strong absorption both in the ultraviolet and visible-light regions (Fig. 2). The strong absorption between 200-350 nm is characteristic of AgCl, where two peaks at 241 and 282 nm can be ascribed to the direct and indirect band gaps, respectively [12]. Notably, the absorbance in the range of 450–650 nm appeared, which could be attributed to the characteristic absorption of the SPR of Ag nanoparticles (inset figure). The Ag/AgCl polyhedron is grey in color whichsuggests the existence of Ag nanoparticles, consistent with the EDX result. It is expected that the distinct absorption in the visible-light region will promote the light-harvesting of the Ag/AgCl polyhedron as an effective visible-light photocatalyst. The estimated band gap of indirect band gap energies of the polyhedron-like Ag/AgCl energy was 2.81 eV; this value agreed with the reported band gap energy for AgCl [13]. The investigated AgCl crystals showed a narrower band gap than that of the conventional AgCl crystals at 3.25 eV [14].

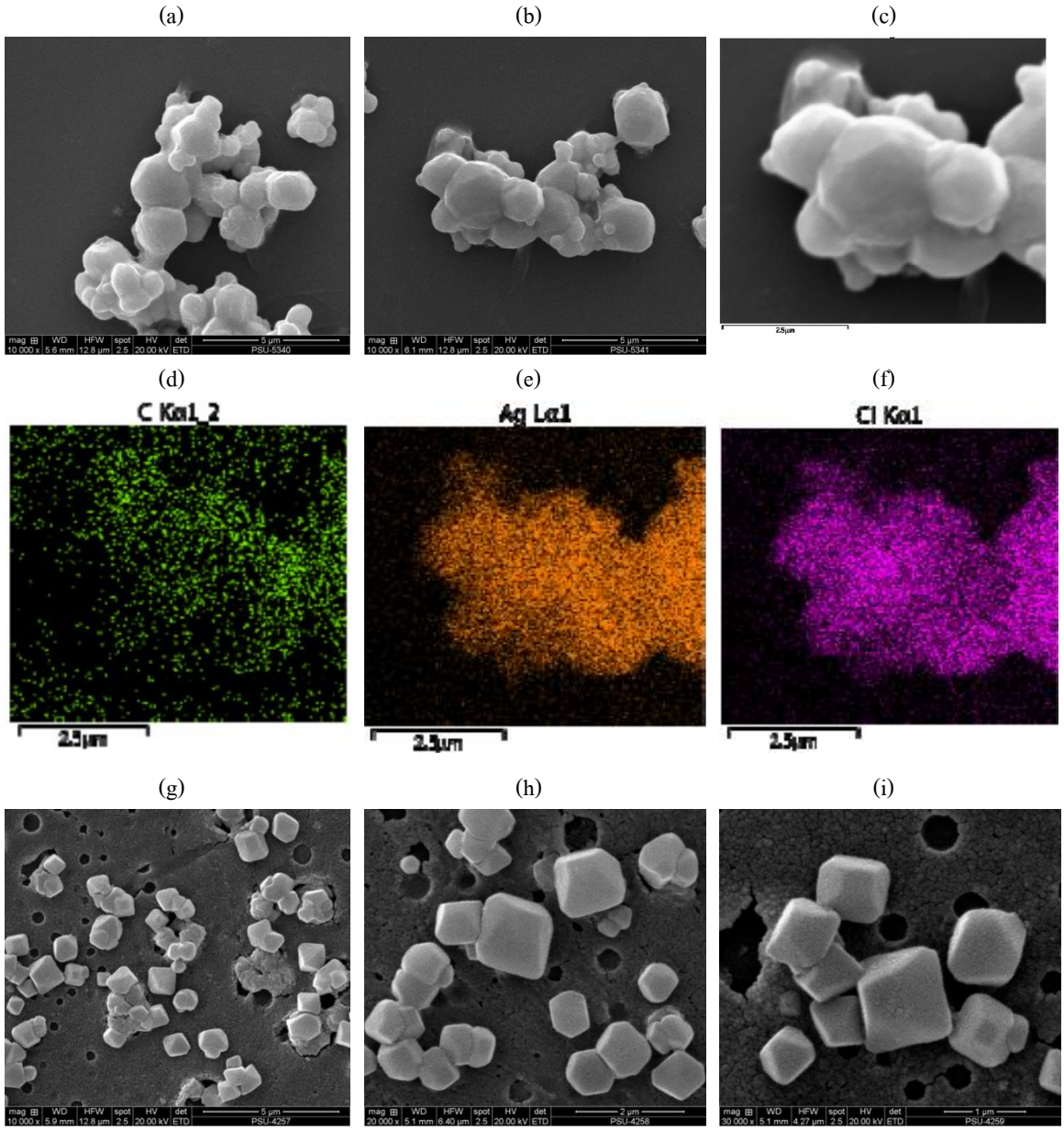

Figure 3 (a)–(c) SEM images of polyhedron-like Ag/AgCl with different magnification, (d)–(f) mapping analysis of polyhedron-like Ag/AgCl (g)-(i) SEM images of commercial AgCl with different magnification.

Fig. 3a-3c depict typical SEM images of the Ag/AgCl product that was formed in the presence of VAM. Clearly, a large number of uniform polyhedron existed in the product, and they have an average side length of 1-2 μm with more than 12 facets on their surfaces. Meanwhile, the shape of commercial AgCl was the uniform octahedron as shown in Fig. 3g-3i. The composition of the product was further studied by mapping analysis. Fig. 3d-3f show the population of color point of Ag element is distinctly higher than the color point of Cl element which could be interpreted that the atomic ratio of Ag:Cl elements is higher than 1:1. In addition, the survey EDX spectrum for the typical product indicated the existence of Cl and Ag. Atomic ratio of the samples was 35:7 implied that surplus Ag^+ ions were reduced to form Ag nanoparticles. AgCl:Ag nanoparticles that correspond to those shown in their absorption band of DRS spectrum, suggesting the presence of metallic Ag coexisting with AgCl.

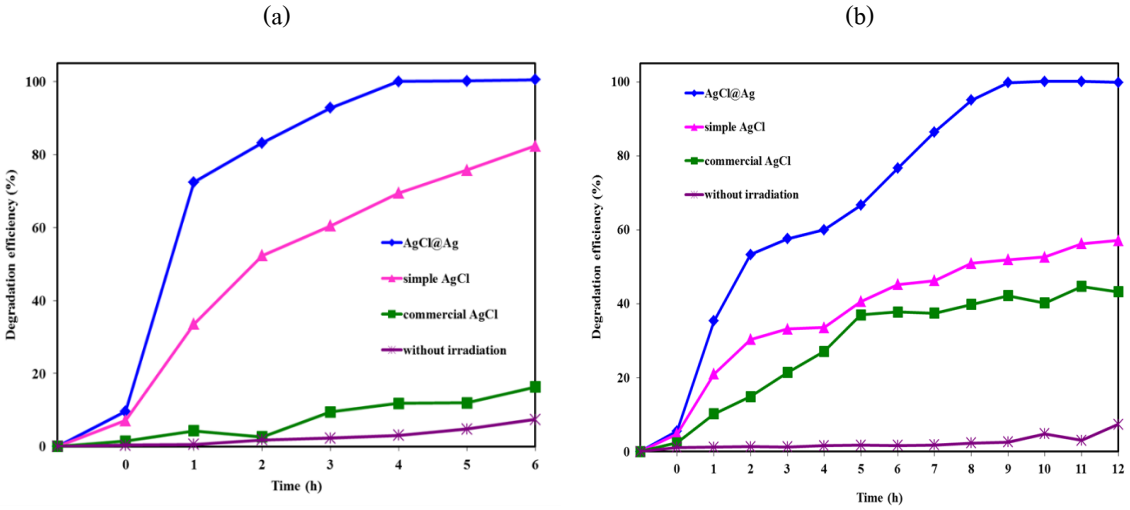

Figure 4 photodegradation efficiency of Rhodamine B dye with different AgCl catalysts under UV (a) and visible light irradiation (b).

The photocatalytic activity of polyhedron-like Ag/AgCl powder was investigated with rhodamine B dye which is cationic dye. The maximum absorption at 554 nm was used to follow the degradation caused by the Ag/AgCl catalyst. For comparison, the photodegradation by two other catalysts: simple AgCl and commercial AgCl were also carried out under the same conditions with both UV and visible light irradiations as shown in Fig. 4a and b respectively. From Fig. 4a and b, it can be seen that the photodegradation time to reduce the colored solution to colorless was 4 and 9h. The polyhedron-like Ag/AgCl samples, clearly, possessed a higher photocatalytic activity than that of both the simple and commercial AgCl powders in the order: polyhedron-like Ag/AgCl > simple AgCl > commercial AgCl. The superior photodegradation property of the polyhedron-like Ag/AgCl particles relative to the simple and commercial Ag/AgCl powders might be attributed to its larger reactive area that originated from the highly active facets having a large number of atomic steps, edges, and kinks [15].

Conclusion

The polyhedron-like Ag/AgCl composite have been successfully synthesized by the reaction between $AgNO_3$ and $ZrCl_4$ as precursors in acetic acid solution at 60 °C with VAM controlling agent. The as-prepared polyhedron-like Ag/AgCl displayed

the highest photocatalytic over the degradation of Rh B dye, which was greatly improved in comparison with simple AgCl as well as commercial AgCl. The enhanced photocatalytic performance is attributed to the more active site, leading to low recombination rates of the photoinduced electron-hole pairs. The efficient composite photocatalyst could be widely used for the environmental purification of organic pollutants in aqueous solution.

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