Dealloying-driven synthesis and characterization of AgCl/Ag/TiO₂ nanocomposites with enhanced photocatalytic properties

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Abstract. The combination of dealloying with acid treatment was used to fabricate mesoporous anatase TiO₂ with high specific surface area of 233 m²/g. Using anatase TiO₂ as a matrix, a photoreduction strategy was developed to synthesize AgCl/Ag/TiO₂ nanocomposites with different Ti/Ag molar ratios. The morphology and properties of AgCl/Ag/TiO₂ nanocomposites were investigated by X-ray diffraction, field emission scanning electron microscopy and transmission electron microscopy. The AgCl/Ag/TiO₂ nanocomposites showed an enhanced photocatalytic activity for the degradation of methyl orange solution under visible light irradiation. The optimum Ti/Ag molar ratio in the AgCl/Ag/TiO₂ nanocomposites was shown to be 6:1, which was attributed to its high specific surface area of 207 m²/g and the surface plasmon resonance effect.

Keywords: AgCl/Ag/TiO₂ nanocomposites, anatase TiO₂, dealloying, specific surface area, photocatalysis.

1. Introduction

For the sustainable development of human society, the solution of both environmental pollution and energy shortage is an urgent task. To solve these problems, semiconductor photocatalysis has emerged as one of the most promising technologies because it represents an easy way to utilize the energy of either natural sunlight or artificial indoor illumination. To date, TiO₂ semiconductors have proved to be one of the best photocatalysts for the purification of water, air and other environment pollutants [1]. And it was widely employed for photocatalytic applications because of its cheapness, non-toxicity, and stability.

Ever since Fujishima and Honda reported that TiO₂ irradiated with ultraviolet radiation could split water [2], discovery of TiO₂ as an effective photocatalyst was recognized as the landmark event that stimulate the investigation of photonic energy conversion by photocatalytic methods. Unfortunately, TiO₂ is not ideal for all purposes due to its wide band-gap of 3.2eV and the recombination of the photogenerated electron-hole pairs. Therefore, the improvement of the photocatalytic activity of TiO₂ is an important issue to be addressed in the photocatalytic field.
In recent years, considerable efforts were made to fabricate semiconductor-noble metal heterojunctions to align the Fermi energy levels for improving the photocatalytic activity [3]. Among all noble metals, silver is of particular interest because of its much lower cost as compared with Au, Pd and Pt etc. Recent studies have shown that nanostructure Ag enhanced the photocatalytic activity of TiO$_2$ [4-6]. In addition, the rapid development of plasmonic Ag@AgCl photocatalysts has offered a new platform to improve the photocatalytic activity of TiO$_2$ [7-9]. For example, Yu et al. [10] prepared TiO$_2$/AgCl/Ag with excellent photocatalytic activity for the degradation of methyl orange (MO). Moreover, Li et al. [11] introduced the Ag/AgCl@helical chiral TiO$_2$ nanofibers with enhanced photocatalytic activity for the degradation of 17-β-ethinylestradiol.

Thus, exploration of the nanosized Ag and AgCl to modify nanocrystalline TiO$_2$ is of great interest. As is known to all, the higher the crystallinity and the higher surface area of components, the better is the photocatalytic performance of the catalysts [12]. Therefore, it is essential to investigate the AgCl/Ag/TiO$_2$ nanomaterials with high crystallinity and specific surface area.

There are many reports on photocatalytic properties of AgCl/Ag/TiO$_2$ nanocomposites under UV-light irradiation. In our work, we have reported the novel AgCl/Ag/TiO$_2$ nanocomposites with high specific surface area and enhanced photocatalytic activity under visible light irradiation. We have found the optimum Ti/Ag molar ratio which could improve the photocatalytic properties of TiO$_2$ more effectively under visible light. The anatase TiO$_2$ was firstly prepared by chemical dealloying of Al-Ti precursor and subsequent acid treatment. Dealloying (i.e., selectively removing one or more active elements from alloys) was proven to be effective in producing three-dimensional (3D) nanoporous materials [13-17]. In order to improve the photocatalytic activity of anatase TiO$_2$, the AgCl/Ag/TiO$_2$ nanocomposites with different Ti/Ag molar ratios were prepared by a photoreduction process. The photocatalytic activity of the anatase TiO$_2$ and AgCl/Ag/TiO$_2$ nanocomposites was evaluated by the degradation of MO solution under visible light irradiation, in order to understand the influence of the noble metal.

2. Experimental

Al$_{95}$Ti$_5$ (nominal composition, wt.%) alloy was prepared from pure Al (purity, 99.99 wt.%) and Ti (purity, 99.9 wt.%) in a quartz crucible under argon atmosphere using a high-frequency induction furnace. Using a single roller melt spinning instrument, the pre-alloyed ingot was remelted by high-frequency induction heating and then melt-spun onto a copper roller with a diameter of 0.35 m at a speed of 1000 revolutions per minute (rpm) in a controlled argon atmosphere.

The as-spun Al$_{95}$Ti$_5$ ribbons were dealloyed in a 4 M NaOH aqueous solution under free corrosion conditions. After dealloying for 2 h at ambient temperature, titanate nanomaterials were obtained (Ti+NaOH→Na-titanate). Then the as-dealloyed samples were washed thoroughly with deionized water for several times, in order to remove the residual chemical substances. After drying in air, the as-dealloyed samples were immersed in a 0.1 M HCl aqueous solution in a water bath at 70℃ for 2 h (Na-titanate + HCl → TiO$_2$ + NaCl) and then washed thoroughly with deionized water. Finally, the anatase TiO$_2$ was acquired.

AgCl/Ag/TiO$_2$ nanocomposites with different Ti/Ag molar ratios of 12:1, 6:1 and 3:1 were prepared by the photoreduction method. A typical fabrication process of AgCl/Ag/TiO$_2$ with the molar ratio of 12:1 was described as follows: 20 mg as-obtained anatase TiO$_2$ was dispersed in a 10 mL ethanol solution, and 3.5 mg of AgNO$_3$ was added to the suspension. The mixture was stirred magnetically for 30 min. Then, the above mixture suspension was illuminated with UV radiation with the use of a 250 W high-voltage mercury lamp for 10 min. After illumination, the obtained AgCl/Ag/TiO$_2$ products were thoroughly washed with distilled water and dried at ambient temperature.

All products were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM) with selected area electron diffraction (SAED), and high-resolution transmission electron microscopy (HRTEM). In addition, N$_2$ adsorption-desorption experiments of the samples were carried...
out at -196 °C by a Gold APP V-Sorb X800 surface area and porosity analyzer. Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area. The pore size distribution was measured from the desorption branch of isotherm using the corrected form of Kelvin equation by the Barrett-Joyner-Halenda (BJH) method.

The photocatalytic activity of the samples was evaluated by the degradation of MO aqueous solution at ambient temperature [18-21], because MO is a kind of chemically stable and persistent pollutant dye. The photocatalytic experiments were carried out by adding 10 mg TiO₂ or AgCl/Ag/TiO₂ photocatalysts into 25 mL MO solution (10 mg/L). A 300 W xenon lamp with a 420 nm cut-filter was used as the visible light source. The suspension was stirred in the dark for 20 min to obtain the saturated adsorption of MO before illumination. The concentration of the MO solution was measured by monitoring the absorbance at 464 nm (the maximum absorbance wavelength of MO) on a UV-Vis spectrophotometer as a function of irradiation time. The photodegradation efficiency, given as a percentage, refers to the difference in the concentration of MO solution before irradiation (C₀) and after light irradiation for M (M= 20, 40 and 60 min) (Cₘ) divided by C₀ (i.e., 100[C₀-Cₘ]/C₀).

3. Results and Discussion

Figure 1 shows XRD patterns of sodium titanate (Na-titanate) and anatase TiO₂ of the Al₉₅Ti₅ ribbons after dealloying process in NaOH solution. It indicates that the titanium atoms in the Al₉₅Ti₅ alloy were completely transformed to Na-titanate in figure 1(a) [22-24]. Figure 1(b) presents the XRD pattern of the anatase TiO₂, which was prepared by acid treatment of the Na-titanate samples in the 0.1 M HCl solution. During the course of acid treatment, the phase transformation (from Na-titanate to anatase TiO₂) has occurred on the basis of the typical Bragg reflections of the as-treated samples, according to the standard PDF file (# 21-1272).

![Figure 1. XRD patterns of the (a) Na-titanate samples obtained by dealloying the Al₉₅Ti₅ precursor in the 4 M NaOH aqueous solution and (b) the anatase TiO₂ samples acquired via sacrificing the Na-titanate in the 0.1 M HCl aqueous solution at 70°C.](image)

The Na-titanate samples can be easily prepared by selective leaching of the Al component from Al-Ti alloy in the 4 M NaOH solution in our experiment. Figure 2(a) shows the typical FESEM image (left) and corresponding EDS spectrum (right) of the Na-titanate samples. The Na-titanate samples adopt a uniform 3D network structure and are composed of Na, Ti and O elements. Figure 2(b) presents the morphology and corresponding EDS spectrum of the anatase TiO₂ obtained by acid treatment of Na-titanate in the 0.1 M HCl solution. As can be seen clearly from the EDS spectrum, the anatase TiO₂ samples are mainly comprised of O and Ti elements. In addition, an amount of Cl elements could also be detected due to the strong adsorption of Cl⁻ ions during the acid treatment in the HCl solution.
The microstructure of the anatase TiO$_2$ was further characterized by TEM and HRTEM (Figure 3). Figure 3(a) presents the morphology of anatase TiO$_2$. The corresponding SAED pattern (Figure 3(b)) exhibits a diffuse ring pattern, implying the nature of nanocrystals. The polycrystalline reflection rings can be indexed as (101), (004), (200) and (211) planes of the anatase TiO$_2$(PDF#21-1272). It is clear that the anatase TiO$_2$ exhibits a mesoporous structure formed between intra-agglomerated uniform dinky nanoparticles at higher magnification (Figure 3(c)). The HRTEM (Figure 3(d)) image shows the lattice fringes of one anatase TiO$_2$ nanoparticle. The lattice fringe with a spacing of 0.35 nm can be assigned to the (101) lattice plane of anatase TiO$_2$.

Using the mesoporous anatase TiO$_2$ as the matrix, the AgCl/Ag/TiO$_2$ nanocomposites with different Ti/Ag molar ratios were prepared by the photoreduction process. Figure 4 presents the XRD patterns for the AgCl/Ag/TiO$_2$ nanocomposites with the Ti/Ag molar ratios of 12:1 (AgCl/Ag/TiO$_2$-1), 6:1 (AgCl/Ag/TiO$_2$-2) and 3:1 (AgCl/Ag/TiO$_2$-3). All XRD diffraction peaks can be identified to be anatase TiO$_2$, metallic Ag and AgCl, according to the standard PDF files (#21-1272, #65-2871 and #31-1238). It implies that the most of the Ag$^+$ successfully converted to metallic Ag during the photoreduction process. It should be noted that the AgCl phase was obtained in the tested samples, resulting from the substantial Cl$^-$ absorbed on the surface of anatase TiO$_2$ during the acid treatment of

Figure 2. FESEM images and the related EDS spectra of (a) Na-titanate and (b) anatase TiO$_2$. 
the as-dealloyed Na-titanate in the 0.1 M HCl solution. In addition, AgCl is an important photosensitive semiconductor material due to its self-sensitization process [25-27].

Figure 3. (a, c)TEM and (d) HRTEM images showing the microstructure of the anatase TiO$_2$. (b) Related SAED pattern corresponding to (c).

Figure 4. XRD patterns of (a) AgCl/Ag/TiO$_2$-1, (b) AgCl/Ag/TiO$_2$-2 and (c) AgCl/Ag/TiO$_2$-3.

Figure 5 shows the FESEM images (left) and related EDS spectra (right) of the different ratio AgCl/Ag/TiO$_2$ nanocomposites. It can be seen that a certain amount of Ag and AgCl nanoparticles are loaded onto the surface of the anatase TiO$_2$. Obviously, with the decrease of Ti/Ag molar ratio, the quantities of Ag and AgCl nanoparticles increase in the AgCl/Ag/TiO$_2$ nanomaterials. Moreover, the loading of AgCl/Ag nanoparticles has no obvious influence on the morphology of anatase TiO$_2$ matrix. The Ag and AgCl nanoparticles can be observed evidently on the surface of anatase TiO$_2$ for the
AgCl/Ag/TiO2-1 sample in the circled region (Figure 5(a)). Moreover, the EDS result clearly indicates the existence of Ag and Cl elements in the AgCl/Ag/TiO2-1 sample (right part of Figure 5(a)). In comparison, more Ag and AgCl nanoparticles can be found in the AgCl/Ag/TiO2-2 and AgCl/Ag/TiO2-3 samples, as shown in Figure 5(b and c). In addition, the Cl element is also detected from each related EDS spectrum. Furthermore, the AgCl particles with size of about 100 nm are discovered (marked by arrows), because of their decomposition under electron beam irradiation. Generally, the EDS results are in agreement with the XRD patterns (Figure 4) of the AgCl/Ag/TiO2 nanomaterials (AgCl/Ag/TiO2-1, AgCl/Ag/TiO2-2 and AgCl/Ag/TiO2-3).

**Figure 5.** FESEM images and related EDS spectra of (a) AgCl/Ag/TiO2-1, (b) AgCl/Ag/TiO2-2 and (c) AgCl/Ag/TiO2-3.
Figure 6 depicts the microstructure of the AgCl/Ag/TiO$_2$-2 sample. The TEM image (Figure 6(a)) shows that a large quantity of Ag or AgCl nanoparticles is distributed in the TiO$_2$ matrix. Furthermore, it can be found by close observation that the Ag and AgCl nanoparticles with size of around 5-50 nm distribute on the surface of TiO$_2$ matrix (Figure 6(b)). Figure 6(c) shows the corresponding SAED pattern. Besides the diffraction rings of the anatase TiO$_2$, the strong spots originate from the nanocrystalline Ag and AgCl. As shown in HRTEM image (Figure 6(d)), the clear lattice fringe of 0.35 nm matches the (101) crystallographic plane of the anatase TiO$_2$. And the fringe spacing of 0.24 nm corresponds to the (111) plane of the Ag phase.

![Figure 6. (a, b)TEM and (d) HRTEM images showing the microstructure of AgCl/Ag/TiO$_2$-2 photocatalyst. (c) SAED pattern corresponding to (a).](image)

It is well known that the specific surface area is an important parameter for enhancing photocatalytic activity. The porous structures of the anatase TiO$_2$ and AgCl/Ag/TiO$_2$ samples have also been probed by N$_2$ adsorption/desorption experiments. Figure 7 presents the N$_2$ adsorption-desorption isotherms and BJH pore size distribution curves (insets) of the anatase TiO$_2$ and AgCl/Ag/TiO$_2$-2 samples. Based upon the Brunauer classification [28], Figure 7 displays type IV adsorption-desorption isotherms, which is typical characteristics of mesoporous materials. The loading of AgCl/Ag nanoparticles has a noticeable effect on the adsorption/desorption process of the anatase TiO$_2$. This result suggests the inter-connected mesoporosity and high pore connectivity in the framework for the anatase TiO$_2$ and AgCl/Ag/TiO$_2$ nanocomposites. According to the adsorption-desorption isotherms, the BET surface area of anatase TiO$_2$ and AgCl/Ag/TiO$_2$-2 samples was determined to be as high as 233 m$^2$/g and 207 m$^2$/g, respectively. The loading of Ag and AgCl nanoparticles slightly decreases the specific surface area of the AgCl/Ag/TiO$_2$ nanocomposites. The pore size distribution of the tested samples was determined using the BJH model (Figure 7(b) and (d)). The pore size analysis clearly demonstrates that both the anatase TiO$_2$ and AgCl/Ag/TiO$_2$ nanomaterials possess mesopores with pore sizes of 2–10 nm. The Ag and AgCl particles grew on the
surface of anatase TiO₂, without damaging the pore structure. In addition, the specific surface area of the anatase TiO₂ is much higher than that of TiO₂ nanoparticles reported in the literature, such as Aeroxide P25 (BET 50 m²/g, 21 nm in diameter, anatase 80% + rutile 20%, Degussa), Aeroxide P90 (BET 90-100 m²/g, 14 nm in diameter, anatase 90% + rutile 10%, Degussa) [29].

According to above results and analysis, herein we elaborate the formation mechanisms of the anatase TiO₂ and AgCl/Ag/TiO₂ nanocomposites. Based on related literature [30], the Na-titanate has a layered structure as schematically shown in Figure 8. However, during the reaction with the dilute HCl at 70 °C, the dehydrated titanate rearranges to form anatase lattice with changing the morphology [31]. In the mild condition, the anatase TiO₂ nanocrystals tend to form the nanoparticles, which would agglomerate to shape a mesoporous structure. In addition, the Cl⁻ ions can be easily absorbed on the surface of anatase TiO₂ because of the large specific surface area of the TiO₂ and the strong adsorption of Cl⁻ ions [32, 33]. The adsorbed Cl⁻ ions on the surface of anatase TiO₂ nanomaterials act as active sites for adsorption of Ag⁺ ions before photoreduction. The chemical reaction leads to AgCl nanoparticles forming on the surface of the anatase TiO₂. When irradiating with UV, the Ag⁺ ions are reduced to metallic Ag by the photo-generated electrons and the Ag nanoparticles nucleate on the surface of the anatase TiO₂. With the increase of Ag content, the surface area of the mesoporous anatase TiO₂ decreases in the AgCl/Ag/TiO₂ nanomaterials.

![Figure 7](image-url)

**Figure 7.** Nitrogen adsorption-desorption isotherms and BJH pore size distribution curves (insets) of the anatase TiO₂ (a),(b) and AgCl/Ag/TiO₂-2(c),(d).
**Figure 8.** Proposed mechanism to form AgCl/Ag/TiO₂ nanocomposites.

**Figure 9.** Absorption spectra of MO before and after photodegradation by P25 and AgCl/Ag/TiO₂ photocatalysts: (a) P25, (b) AgCl/Ag/TiO₂-1, (c) AgCl/Ag/TiO₂-2, (d) AgCl/Ag/TiO₂-3. (e) Comparison of photocatalytic activities of all the photocatalysts.
The photocatalytic activities of P25 and Ag/AgCl/TiO2 nanocomposites with different Ti/Ag molar ratios were tested for the photodegradation of MO solution under visible light irradiation. Figure 9(a-d) presents the MO absorbance spectra with different photocatalysts. Obviously, the degradation of MO is slight in the presence of P25, while it is greatly enhanced with the nanocomposites (AgCl/Ag/TiO2-1,2,3). The photocatalytic efficiencies of P25 and AgCl/Ag/TiO2 nanomaterials were calculated and the results are shown in Figure 9(e). From Figure 9(e) we found that the saturated adsorption capacity of AgCl/Ag/TiO2 nanomaterials before illumination is higher than P25, because of its high specific surface area. In addition, the photocatalytic activities of all AgCl/Ag/TiO2 samples are higher than that of P25. When visible light is irradiated to the Ag/AgCl/TiO2 photocatalysts, the Ag nanoparticles lead to a surface plasmon resonance effect. The excited electrons in the noble metal nanoparticles transfer to a conduction band of semiconductor, resulting in an interfacial separation of electrons and holes that causes photocatalysis [34-36]. Interestingly, the AgCl/Ag/TiO2-2 shows the best photocatalytic performance among all the four samples. Obviously, AgCl/Ag/TiO2-2 degrades the MO solution quickly, and the degradation ratio is almost 100% after visible light irradiation of 60 min. The optimal amount of Ag and AgCl nanoparticles can improve the photocatalytic activity of TiO2 photocatalysts. Although the degradation ratio of AgCl/Ag/TiO2-3 sample is also almost 100% after visible light irradiation of 60 min, with the increase of Ag content, the cost will be greatly increased.

4. Conclusions
The mesoporous anatase TiO2 with large specific surface area of 233 m²/g can be synthesized through chemical dealloying of the Al-Ti precursor and subsequent acid treatment of the as-dealloyed samples. The AgCl/Ag/TiO2 nanocomposites with different Ti/Ag molar ratios can be obtained by the photoreduction of AgNO3 using the mesoporous anatase TiO2 as the matrix. The Ti/Ag molar ratios have a significant influence on the photocatalytic activity of the AgCl/Ag/TiO2 nanocomposites towards the degradation of MO. And the AgCl/Ag/TiO2-2 nanocomposite with the Ti/Ag molar ratio of 6:1 displays the best photocatalytic performance. In addition, the enhanced photocatalytic activity of the AgCl/Ag/TiO2-2 catalyst could be rationalized by the surface plasmon resonance effect and its high specific surface area of 207 m²/g.

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