Silver nanoparticles decorated anatase TiO₂ nanotubes for removal of pentachlorophenol from water

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GRAPHICAL ABSTRACT

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ABSTRACT

One-dimensional nanotubes are promising materials for environmental applications. In this study, anatase TiO₂ nanotubes (TNTs) were fabricated using an alkaline hydrothermal method at 130 °C and then calcinated at 400 °C for 2 h. Ag nanoparticles were photo-deposited onto the TNTs for enhanced photodegradation of pentachlorophenol (PCP) under simulated solar light. The samples were characterized using transmission electron microscopy, physical adsorption of nitrogen, X-ray diffraction, X-ray photoelectron spectroscopy and UV–Visible diffuse reflectance spectroscopic techniques. The as-synthesized TNTs showed tubular structures with the outer and inner diameter of 9–10 and 5–6 nm, respectively. The results showed that metallic Ag nanoparticles were uniformly dispersed on the TNTs surface, and Ag/TNTs exhibited significant visible-light absorption. After 180 min irradiation, about 99% PCP was removed by Ag/TNTs (5.4 at.%), compared to 54.3% by P25 and 59.4% by pure TNTs. This is attributed to the synergistic effects between Ag nanoparticles acting as traps to effectively capture the photo-generated electrons, and the localized surface plasmon resonance (LSPR) of Ag nanoparticles promoting the absorption of visible light. The intermediates during the PCP photodegradation were systematically analyzed, ruling out the existence of high toxic polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Ag/TNTs showed excellent stability even after five cycles.

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1. Introduction

Pentachlorophenol (PCP) is regarded as a highly toxic halogenated aromatic compound because of its five chlorine substitutions. It is extensively used as herbicide, pesticide and bactericide in agriculture, and as common wood-preservation in industries [1]. It exists in water and soil, which can migrate to groundwater, thereby causing a potential risk to animals and human [2]. Many methods such as sorption [3–5], biodegradation [6–8], oxidation [9–15], photocatalytic degradation [16,17], and electrochemical methods [18–20] have been used to remove PCP from environment. Sorption only transfers pollutants from the aqueous phase to the surface of adsorbents, it does not eliminate pollutants. Biodegradation has several shortcomings, such as bad treatment effect, large area of devices taking up, long time of the treatment and easily influenced by seasons. Advanced oxidation processes (AOPs) possess a lot of advantages, such as no secondary pollution, and quick degrading rate, so they are extensively applied to treat PCP wastewater. The common methods among AOPs used to treat PCP include ozonation oxidation [13], photocatalytic oxidation [11], Fenton's oxidation [14], supercritical oxidation [12] and electrocatalytic oxidation [15]. In the AOPs above, photocatalytic degradation of PCP is more attractive. Among various photocatalytic materials, TiO_2 is one of the most used ones due to its excellent properties such as no toxicity, low cost, high activity and chemical stability [21].

Recently, there have been many studies on nanotubular materials because of their special physical and chemical properties [22]. Titania nanotubes of different microstructures and geometrical shapes have been fabricated using different techniques such as electrodeposition [23], sol-gel synthesis [24], freeze-drying [25] and chemical treatments of titania particles [26]. Among them, Kasuga's synthesis process is simple, which makes the practical application of TiO_2 nanotubes as catalyst or catalyst support a possibility. However, the photocatalytic activity of TNTs is limited by low absorption capability of the visible light and a high recombination rate of photo-generated electron-hole pairs formed in photocatalytic reactions. Consequently, many efforts have been made to improve the photocatalytic performance of TNTs, such as doping non-metal [27], metal ions [28] and coupling with semiconductor nanoparticles [29].

Noble metals, such as gold (Au) and silver (Ag), can absorb visible light due to the existence of localized surface plasmon resonance (LSPR) [30]. Moreover, these metals can act as electron traps in the metal- TiO_2 nanostructures and function as electron donors to promote electron transfer from metal to TiO_2 , thus minimizing the recombination of photo-generated electron-hole pairs in the surface of TiO_2 [30,31]. Wang et al. synthesized mesoporous Au/ TiO_2 microspheres [32], Au nanoparticles act as sensitizers which effectively promoted the separation of visible-light photo-generated electron-hole pairs because of their strong LSPR. The photocatalytic activity was improved, however, Au nanoparticles tend to aggregate to form large particles, which reduced the photocatalytic activity of Au/ TiO_2 . Furthermore, Au nanoparticles are costly, which is disadvantageous for practical applications. TiO_2 nanotubes have been considered as an effective support to control the particle size and guarantee a uniform dispersion of nanoparticles. This method can increase the utilization efficiency of noble metals and improve the catalytic performance. Compared with Au, Ag is a more suitable noble metal for industrial application due to its nontoxicity, low cost and easy preparation.

Based on the above considerations, we fabricated Ag nanoparticles loaded anatase TiO_2 nanotubes by reduction of Ag ions using

UV irradiation. The obtained photocatalyst was used to remove PCP under simulated solar light ($\lambda > 400 \text{ nm}$) irradiation. The correlation of the catalytic performance with the structural properties and the promoting effect of the Ag modifications are also discussed in the paper.

2. Experimental

2.1. Photocatalyst synthesis

The alkaline hydrothermal method [33,34] was used to synthesize the titanate nanotubes materials. Typically, commercial TiO_2 (Degussa P25, 0.5 g) was dispersed in 40 mL of an aqueous solution of NaOH (10 M) and placed into a Teflon-lined stainless steel autoclave. The autoclave was statically heated at 130°C for 24 h. White precipitate was separated through filtration and washed with ultra pure water until the pH value of the supernatant attained a value close to 9.0. In a second step, an aqueous suspension containing the precipitate was neutralized using a 0.1 M HCl solution until a pH value of 7.0 was reached. To ensure that all Na^+ is removed, a second washing with 1.0 M HCl solution and 500 mL of ultra pure water followed by a filtration were carried out. Finally, the sample was dried at 30°C under vacuum for 48 h, and then calcined at 400°C in air for 2 h to form anatase TiO_2 TNTs.

The Ag-deposited TiO_2 TNTs were fabricated by the photodeposition method. Typically, 1 g/L of calcined TiO_2 TNT were dispersed in an equal volume ratio of methanol-water mixture under vigorous stirring, and a certain number of AgNO_3 was added into the solution. The mixture was exposed to a 400 W high pressure Hg lamp for 4.0 h in nitrogen atmosphere under stirring, and the obtained Ag-deposited TiO_2 TNTs were harvested by filtration, washed with ultra pure water, and dried under vacuum at 30°C for 48 h. No Ag ion was detected in the filtrate indicating that all Ag ions had been completely loaded onto the TiO_2 TNTs. Different volumes of AgNO_3 solution with a concentration of 0.1 M were used to vary the loading of Ag. The samples thus obtained are denoted as Ag/TNTs ($x \text{ at.}\%$), where $x \text{ at.}\%$ indicates the atom percentage of Ag on the nanocomposites. Ag nanoparticles (NPs) were synthesized using the same method except adding TiO_2 TNTs. For all the characterization, Ag/TNTs (5.4 at.%) was used.

2.2. Characterization methods

The crystalline phase of the synthesized samples were determined by X-ray diffraction (Phillips PW 1050-3710 Diffractometer) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), operated at a tube current of 40 mA and a voltage of 45 kV. Data were collected over 2θ values from 10° to 80° , at a scan speed of $1^\circ/\text{min}$. The surface morphology and particle size were observed by transmission electron microscopy (HRTEM, JEM-2011), with an accelerating voltage of 200 kV. The BET specific surface area and pore volume analysis of the samples were determined using a N_2 physisorption technique, the samples were degassed at 180°C for 3 h before the actual measurement. The UV-vis diffuse reflectance spectra were obtained using a Perkin Elmer Lambda 750S UV/Vis spectrometer equipped with an integrating sphere assembly. The spectra were recorded at room temperature in air from 250 to 600 nm. X-ray photoelectron spectroscopy was performed using a Perkin-Elmer RBD upgraded PHI-5000C ESCA system with monochromatic Mg K α excitation and a charge neutralizer was used to investigate the surface electronic states of the samples. All the bonding energies were calibrated to the C 1s internal standard peak (284.8 eV) of surface carbon.

2.3. Photocatalytic activity measurements

Pentachlorophenol (PCP) was used as a model pollutant to test the photocatalytic performances of Ag/TNTs. A 500 W xenon lamp (CHF-XQ-500 W, Beijing Changtuo Co., Ltd.), with the photon flux of 100 mW/cm² served as the light source to simulate solar light irradiation. The lamp was placed inside a cylindrical vessel surrounded by a jacket with circulating water for cooling, and the distance between the PCP solution and the lamp was about 15 cm. The UV light with wavelength shorter than 400 nm was removed with a glass filter. 0.5 g Photocatalyst was mixed with 10 mg/L PCP (500 mL). Prior to irradiation, the mixture was stirred magnetically for 30 min in the dark to reach an adsorption–desorption equilibrium. The photocatalytic reaction was stopped by removing the photocatalysts from the suspension through centrifuging and filtering with a Millipore membrane (0.22 μm), and then the supernatant solution was analyzed with TOC-VCPN analyzer (Shimadzu) (determining the concentration of total organic carbon (TOC)) and high-performance liquid chromatography (HPLC, LC-20AT, Shimadzu) (determining the concentration of PCP). For the analysis of PCP, a C-18 reverse phase column was equipped for separation. The mobile phase was composed of methanol and 0.15% acetic acid aqueous solution (V:V = 4:1) with a flow rate of 0.8 mL/min [2]. The detection wavelength was set at 254 nm. Intermediates identification was conducted by a typical procedure as follows. 50 mL of the degraded suspension was taken out and filtered, and then the supernate was concentrated to 2 mL by a rotary evaporator for the subsequent analysis on a HPLC–MS (API2000, AB SCIEX). Ion chromatography (Metrohm 861 Advanced Compact IC) was used to detect the released chloride ions. The mobile phase was an aqueous solution of NaHCO₃ (1.7 mmol)–Na₂CO₃ (1.8 mmol) with a flow rate of 1.0 mL/min.

3. Results and discussion

3.1. Characterization

3.1.1. XRD

The phase composition and crystal structure of the samples were evaluated by X-ray diffraction. As shown in Fig. 1, XRD pattern revealed that the crystal structure of the protonated titanate nanotubes obtained during the hydrothermal treatment was similar to that of hydrogenotitanate (H₂Ti₂O₅·H₂O or

H_{2–x}Na_xTi₂O₅·H₂O), which can be obtained through the following reactions [35]:

Ionic exchange could take place during the acid washing and calcination process:

The peaks (Fig. 1a) at $2\theta = 24.5^\circ$, 27.8° and 48.4° reveal the presence of hydrogenotitanate nanotubes “H₂Ti₂O₅·H₂O” phase [35]. After calcinations at 400 °C for 2 h, phase transformation can be observed from Fig. 1b. The layered structure slowly reconstructed into anatase by the reactions (3) and (4). The peaks at $2\theta \approx 25.2^\circ$, 37.8° , 48.1° , 53.8° , 55.1° , 62.7° , 68.9° , 70.1° , and 75.1° , are corresponding to the (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystalline planes of the anatase phase (JCPDS no. 21-1272). As can be seen in Fig. 1c, the peaks at 2θ values of 38.1° , 44.3° , 64.4° , and 77.4° can be indexed to (111), (200), (220), and (311) diffractions of cubic structured Ag. The other peaks in Fig. 1c can be assigned to anatase phase of TiO₂. The existence of the diffraction peaks of Ag and anatase phase of TiO₂ suggests that the synthesized Ag/TNTs are composed of both phases.

3.1.2. TEM

TEM was used to characterize the surface morphology of Ag NPs, TNTs and Ag/TNTs. Fig. 2a shows that the diameters of Ag nanoparticles were 15–25 nm. Fig. 2b and c shows that the as-synthesized TNTs showed tubular structures, the outer and inner diameters of the as-prepared TNTs were 9–10 nm and 5–6 nm, respectively. In addition, the TEM and HRTEM images of TNTs exhibited uniform diameters along with the length. As can be seen in Fig. 2c, the well-crystallized Ag nanoparticles with diameters less than 30 nm are uniformly dispersed on the surface of TiO₂ nanotubes.

3.1.3. BET

Fig. 3 shows the nitrogen adsorption–desorption isotherms and pore size distribution of the as-synthesized TNTs and Ag/TNTs. The adsorption isotherm (Fig. 3a) of TNTs and Ag/TNTs showed a typical type IV isotherm with H3 hysteresis loop in the relative pressure (P/P_0) range of 0.5–0.95, indicating the characteristics of mesoporous materials [36]. The pore size distributions (Fig. 3b) of TNTs and Ag/TNTs, derived from the BJH method, showed that the average pore diameters were 5.4 and 4.7 nm, respectively. It is noteworthy that the surface area of TNTs and Ag/TNTs were 343.34 and 289.71 m²/g, respectively. This can be due to the blocking of the pore channels of TNTs by Ag NPs.

3.1.4. XPS

The elemental composition and chemical status of Ag/TNTs were analyzed by XPS. Fig. 4a indicates that Ag/TNTs contain three elements O, Ti, Ag. The C element was attributed to the adventitious carbon-based contaminant. The Ag 3d spectra (Fig. 4b) of Ag/TNTs shows two obvious peaks, which are centered at about 373.6 and 367.6 eV and can be ascribed to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively. A spin–orbit separation of 6.0 eV can be observed, this is characteristic of metallic silver (Ag⁰) [37]. No other valence of Ag could be observed, indicating that the Ag⁺ are reduced to metallic Ag⁰ in the Ag/TNTs during the UV light irradiation. Furthermore, two peaks of Ti 2p_{3/2} and Ti 2p_{1/2} are observed at the binding

Fig. 1. XRD patterns of the as-prepared protonated titanate nanotubes (a), anatase TiO₂ nanotubes (calcinations of (a) at 400 °C in air for 2 h) (b) and Ag/TNTs (5.4%) (c).

Fig. 2. TEM imagings of Ag NPs (a), TNTs (HRTEM in the inset) (b) and Ag/TNTs (c).

Fig. 3. Nitrogen adsorption-desorption isotherms (a), and pore size distribution (b) of TNTs and Ag/TNTs.

energies of 459.2 and 465.1 eV (Fig. 4(c)), which are in good agreement with the Ti^{4+} state [38]. These results further confirm the formation of Ag/TNTs nanocomposites.

3.1.5. UV-vis diffuse reflectance spectra

The optical behavior of photocatalysts can be studied by measuring their UV-vis absorption. The characteristic absorption band of P25 and pure TiO_2 TNTs should be assigned to the intrinsic transition from the valence band (VB) to the conduction band (CB). As shown in Fig. 5, the absorption edge of P25 and pure TiO_2 TNTs is observed at about 400 nm, which is corresponding to the band-gap energy of 3.2 eV. After the deposition of Ag nanoparticles on pure TiO_2 TNTs, the Ag/TNTs showed significant visible-light absorption. It is apparent that a small and broad absorption peak centered close to 470 nm can be observed in visible region, which is attributed to the surface plasmon resonance effect of spatially confined electrons in Ag nanoparticles [39].

3.2. Photocatalytic degradation of pentachlorophenol under simulated solar light illumination

The photocatalytic activity of the samples was evaluated by degradation of PCP under simulated solar light irradiation, and the results are shown in Fig. 6. Without adding catalyst, no significant decomposition of PCP was observed under simulated solar light irradiation, which confirms the high stability of PCP in solution. The photocatalysts were added to the PCP solutions and stirred magnetically for 30 min in the dark in order to reach adsorption equilibrium. Less than 10% PCP could be removed by the adsorption of photocatalysts for all samples. About 54.3% PCP could be degraded by P25 in 180 min, which was probably attributed to its wide band gap energy (3.2 eV). As for pure TNTs, 59.4% PCP can be decomposed in 180 min, whereas using 5.4 at.% and 8.5 at.% Ag/TNTs, the degradation efficiencies increase to approximately 99.0% and 93.0%, respectively. You et al. [40] found that

Fig. 4. XPS analysis results of Ag/TNTs: the full XPS spectrum (a), high-resolution spectra of Ag 3d (b) and Ti 2p (c).

Fig. 5. UV-vis absorption spectra of P25, TNTs and Ag/TNTs.

the Ag particle sizes increased as increasing of Ag loading, the size of Ag nanoparticles increased to about 16 nm for 4.0 wt% Ag/TiO₂, and 2.0 wt% Ag/TiO₂ showed the highest photocatalytic activity. There was an optimum amount of the silver loaded, if the content of Ag is too low, the photo-generated charge carriers are not separated efficiently due to the insufficient contact between them. If the content of Ag is too high, there is an increased possibility for the capture of holes by the large number of Ag nanoparticles, excessive coverage of Ag nanoparticles on the surface of TNTs increases the reflection of the incident light and may also decrease the possibility of holes reacting with the adsorbed species at the surface of Ag/TNTs [40–42], which are adverse for photocatalytic reaction.

The conduction band electrons can transfer to Ag nanoparticles that are dispersed on the TNTs, because the Fermi level of Ag is

Fig. 6. Degradation of PCP without a catalyst, over P25, TNTs, Ag/TNTs (5.4 at.%) and Ag/TNTs (8.5 at.%) under simulated solar light irradiation.

lower than that of TiO₂. Therefore, the Ag nanoparticles act to trap the photo-generated electrons, which can inhibit the fast recombination of photo-generated electrons and holes, and thus enhance the photocatalytic performance under simulated solar light irradiation [37]. Ingram and Linic [43] verified that electrons on the Ag/TiO₂ composite surface can be scavenged by the existing O₂ molecules to generate reactive oxygen radicals (O₂⁻), leading to strong photocatalytic activities, at the same time, the valence band holes can react with the absorbed OH⁻ and/or H₂O molecules to produce hydroxyl radicals (·OH) which possess high oxidizability [44]. The generated hydroxyl radicals may attack organic contaminants like PCP. Therefore, the TiO₂ photocatalysts combined with Ag nanoparticles exhibited enhanced photocatalytic performance. In addition, metal Ag can absorb visible light due to its LSPR [37].

It can be seen that the improved solar light driven photocatalytic performance can be ascribed to the synergistic effects of Ag NPs and TNTs, and the LSPR of Ag nanoparticles.

The decrease of TOC concentration is used to evaluate the mineralization level of PCP in the experiment. As can be seen in Fig. 7 and 43.2% (lower than PCP degradation efficiency) of TOC was removed in 180 min, indicating that some intermediates derived from PCP decomposition remained in solution. Through HPLC–MS analysis, the detected intermediates include 3,5-dichlorophenol and 2,3,5-trichloro-1,4-hydroquinone (3,5,6-trichloro-1,2-pyrocatechol or 3,4,5-trichloro-1,2-pyrocatechol), which is consistent with the results of Su et al. [2] Ion chromatography was used to measure chlorine ions generated during the photodegradation of PCP. As can be seen from Fig. 7, chlorine ion concentration increased during the photodegradation of PCP under simulated solar light irradiation, verifying the photocatalytic dechlorination of PCP. The dechlorination efficiency was calculated to be about 20% (by dividing the total chlorine ions amount in the solution with the initial amount of chlorine in PCP), which was much less than the removal efficiency (99.0%) of PCP, suggesting that some chlorinated intermediates formed during the PCP photodegradation process. This phenomenon is consistent with the analysis results of HPLC–MS. Fortunately, some high toxic polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans were not detected in the intermediates, revealing that this

Fig. 7. The photodegradation efficiency of PCP, TOC and dechlorination during PCP photodegradation over Ag/TNTs (5.4 at.%) under simulated solar light irradiation. $[Cl^-]$ is the concentration of chloride ions by ion chromatography, while $[Cl^-]_0$ is the initial stoichiometric concentration of organic chlorine.

Fig. 8. Recycling of Ag/TNTs for photodegradation of PCP under simulated solar light irradiation.

simulated solar light driven photocatalytic degradation of PCP over Ag/TNTs is an effective and green method to remove highly toxic PCP.

The stability of the photocatalyst is very important for practical applications. Fig. 8 shows that there was no obvious decrease in photocatalytic activity for Ag/TNTs after five cycles, indicating its high stability and durability. Therefore, the recycling of Ag/TNTs is possible, Ag/TNTs should be a promising photocatalyst for effective treatment of organic contamination.

4. Conclusions

In this study, Ag nanoparticles were loaded on the anatase TiO_2 nanotubes, and the obtained Ag/TNTs were used for photodegradation of PCP under simulated solar light. Ag existed mainly in metallic form, Ag/TNTs showed significant visible-light absorption, indicating the possibility for the utilization of visible light. Ag nanoparticles are uniformly dispersed on TNTs, and Ag/TNTs exhibited excellent solar light driven photocatalytic activity for the degradation of PCP. The obvious enhancement of photocatalytic activity can be attributed to the strong LSPR of the Ag nanoparticles and the intimate contact between Ag nanoparticles and TNTs, which favors the separation of photo-generated charge carriers. The intermediates during PCP photodegradation were analyzed, ruling out the existence of high toxic polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Ag/TNTs showed high stability and high photocatalytic activity even after five recycles, this is advantageous for practical applications.

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