Photocatalytic and bactericidal activity of mesoporous TiO$_2$–Ag nanocomposite particles

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Abstract

Mesoporous TiO$_2$–Ag composite particles with raspberry-like morphology were prepared by a two-step chemical route and their photocatalytic and bactericidal properties were examined. Ag nanoclusters of about 50 nm in diameter were decorated on surface of submicrometer, anatase TiO$_2$ particles with Ag concentration of 3.8 ± 0.4 at%; in which, the TiO$_2$ particles were mesoporous with an average pore diameter of 9.3 nm and a BET surface area of 147.5 m$^2$ g$^{-1}$. The composite particles enhanced the photocatalytic degradation of methylene blue (MB) dye in water under ultraviolet irradiation when compare to that of the bare TiO$_2$. Removal of the MB dye with an initial concentration of 1 × 10$^{-5}$ M was completed within an hour and the degradation rate of the MB dye was found independent of temperature employed. In addition, the composite particles imparted bactericidal activity against gram-negative Escherichia coli in aqueous solutions under dark condition, enabling hence bifunctional activities under both light and dark situations.

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1. Introduction

Metal-oxide composite particles consisting of specifically metallic silver (Ag) and titanium dioxide (TiO$_2$) have attracted considerable attention over the years owing to their promising use in heterogeneous photocatalysis, microbial disinfection, chemical and biological sensing for environmentally benign and clean energy-related applications [1–6]. Of particular interest of such composite particles includes microstructural features and synthetic methods affecting their synergistic, multifunctional performance. On the one hand, Ag nanoparticles which were either grafted on the TiO$_2$ surface [7] or being encapsulated within mesoporous TiO$_2$ cages [8] have been shown in our earlier works to give rise to unique photochemical and bactericidal activities, arisen mainly from the tailored microstructure of the composites. The microstructural feature, in particular, enables bifunctional bactericide and photocatalysis under both light and dark conditions, as well as a mitigated impact toward environmental and biological systems in practical use [8]. On the other hand, various synthetic strategies have been attempted with an aim that immobilization of the Ag nanoparticles on the TiO$_2$ host matrix becomes attainable with a desired hierarchical structure [9]. In view of the literature, preparation of the Ag-grafted TiO$_2$ composite particles with raspberry-like morphology often involves a preferential deposition of Ag nuclei followed then by growth of the Ag clusters into a discontinuous rough shell, or by a direct coating of the Ag nanoparticles on the surface-modified TiO$_2$ [7,10–13]. For example, Yang et al. [10] synthesized Ag nanoparticles decorated on TiO$_2$ nanorods with controllable Ag density and particle size through an in-situ reduction of Ag precursor. Preferential deposition and growth of the Ag nanoparticles were obtained by electrostatic interactions between the Ag precursor and the TiO$_2$ host. Choe et al. [11] examined mechanisms involved in growth and coalesce of the Ag clusters on the TiO$_2$ surface when electroless deposition was used for the composite fabrication.

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Similarly, Zhan et al. [12] also prepared decorative Ag nanoparticles on TiO$_2$-coated, magnetic Fe$_3$O$_4$-cenospheres through electroless deposition. A photodeposition method was used by Kowalska et al. [13] in which the TiO$_2$ surface was hybridized with either mono-metallic Ag, gold (Au), or bi-metallic Ag–Au nanoparticles. They found that the plasmonic effect exerted by the different metallic particles critically influences degradation of organic compounds in liquids under both ultraviolet (UV) and visible-light irradiations.

Chen et al. [14] recently prepared mesoporous TiO$_2$ anatase beads by a combined sol–gel and solvolithic process in which organic hexadecylamine (HDA) was used as a structure-directing template in a cooperative self-assembly route. By adjusting the HDA:Ti and water:Ti molar concentrations, they have demonstrated that mesoporous TiO$_2$ (denoted hereafter m-TiO$_2$) beads of submicrometer size can be obtained with tailored pore size, crystallite size, specific surface area, and bead diameter. Extension of the above process to the synthesis of mesoporous TiO$_2$–Ag nanocomposites with raspberry-like morphology (denoted hereafter m-TiO$_2$@Ag) and investigation of their photocatalytic and bactericidal activities remain yet limited [15], despite the clear importance of the composite particles from technological viewpoints. In this study, we report a two-step chemical route for the synthesis of m-TiO$_2$@Ag particles, in which the m-TiO$_2$ particles were first prepared by the method proposed by Chen et al. [14]. The particles were then subjected to coating of Ag nanoparticles via chemical means in order to prepare the m-TiO$_2$@Ag composite particles. We have examined the photocatalytic and bactericidal performance of the resultant m-TiO$_2$ and m-TiO$_2$@Ag particles by using methylene blue (MB) and Escherichia coli (E. coli) as the model material, respectively, under both light and dark conditions.

2. Experimental procedure

2.1. Preparation of the m-TiO$_2$ particles

Amorphous TiO$_2$ particles were prepared from a sol–gel route in which titanium(IV) isopropoxide (Ti(OCH(CH$_3$)$_2$)$_4$, 97%, molecular weight 284.22, Sigma Aldrich, U.S.A.) of 0.568 ml was added into a solution mixture consisting of 20.27 g ethanol (CH$_3$CH$_2$OH, 99.9%, J.T. Baker, U.S.A.), 0.1 g potassium chloride solution (0.1 M, KCl, Riedel-deHaen, U.S.A.), and 0.25 g HDA (CH$_3$(CH$_2$)$_8$NH$_2$, ≥ 90%, molecular weight 241.46, Sigma Aldrich, U.S.A.) at room temperature under vigorous stirring for 4 h. Whitish powders were found during the sol-to-gel reaction. The amorphous TiO$_2$ powders were then centrifuged and washed by ethanol repeatedly for three times before being dried in ambient atmosphere.

Crystallization of the amorphous TiO$_2$ beads was obtained by mixing the dried amorphous TiO$_2$ particles of 0.1 g with 20.2 g ethanol (95%, molecular weight 46.07, Choney Pure Chemical, Taiwan) and 12.5 ml de-ionized water before being transferred altogether into a Teflon-lined stainless steel autoclave (Series-4793, Parr Instrument Co., U.S.A.). The de-ionized water used was from Millipore Super-Q Plus system with an electrical resistivity of 18.2 MΩ cm at 25 °C. The powder mixtures were heated to 160 °C with an isothermal holding of 1 h. The particles after the mild solvothermal treatment were washed in ethanol for three times and were then dried in oven at 65 °C to obtain the anatase-structured m-TiO$_2$ particles ready for the subsequent Ag decoration.

2.2. Preparation of the m-TiO$_2$@Ag particles

In brief, de-ionized water of 100 ml was adjusted to pH = 3 by addition of a few drops of 2 M HCl solution. Anhydrous tin chloride (SnCl$_2$, reagent grade, 98%, Alfa Aesar, U.S.A.) of 0.034 g was then added into the acidic solution followed then by addition of the m-TiO$_2$ of 0.05 g along with a vigorous agitation for 30 min. The Sn$^{2+}$-treated m-TiO$_2$ particles were centrifuged and washed in de-ionized water, respectively, in order to remove the weakly adsorbed Sn$^{2+}$ ions on the particle surface. The particles were then re-dispersed in 100 ml de-ionized water to form m-TiO$_2$ suspension for subsequent use.

Freshly prepared Tollens’ reagent consisting of [Ag(NH$_3$)$_2$]$^{+}$ complex in the solution mixture was added into the Sn$^{2+}$-modified m-TiO$_2$ suspension slowly. Tollens’ reagent containing 0.31 M silver complex was prepared by slowly adding 10 g of 8.2 M sodium hydroxide solution (NaOH, 98%, Alfa Aesar, U.S.A.) to aqueous solution consisting of reagent-grade silver nitrate (99%, Sigma Aldrich, U.S.A.) of 1.27 g in de-ionized water of 5.5 ml. The presence of OH$^-$ ions in the solution quickly converted the silver complex into brown silver oxide precipitates. Aqueous ammonia (25%, Choney Pure Chemical, Taiwan) of 8 ml was then added into the solution to dissolve the silver oxide into the [Ag(NH$_3$)$_2$]$^{+}$ complex. When Tollens’ solution was added into the Sn$^{2+}$-modified m-TiO$_2$ suspension, Sn$^{2+}$ ions were oxidized favorably to generate electrons so that the nearby [Ag(NH$_3$)$_2$]$^{+}$ would gain the electrons and reduce to atomic Ag$^{0}$ at locations preferably on the m-TiO$_2$ surface, resulted in the m-TiO$_2$@Ag composite particles with raspberry-like morphology.

2.3. Structure and property characterizations

Crystalline structure of the m-TiO$_2$ and m-TiO$_2$@Ag beads was determined by X-ray diffractometry (XRD, MAC MXP III, Japan) using Cu Kα radiation with a characteristic wavelength of 1.5406 Å. Microstructure of the particles was examined by field-emission scanning (FE-SEM, JSM-6700F, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM, JEM-2010, JEOL, Tokyo, Japan), respectively. Elemental information was obtained by an energy-dispersive spectroscopy (EDS, Oxford Inca Energy 400, UK) equipped along with the FE-SEM, and the elemental Ag concentration in the composite particles was estimated semi-quantitatively by the ZAF analysis. Pore structure and Brunauer–Emmett–Teller (BET) surface area of the m-TiO$_2$ and m-TiO$_2$@Ag particles were determined from nitrogen gas sorption–desorption (ASAP 2020, Microneritics, Norcross, GA, U.S.A.) at the boiling point of liquid nitrogen (77.4 K). Pore-size distribution of the synthesized particles was derived from the adsorption
branch of the sorption–desorption isotherms based on the Barrett–Joyner–Halenda (BJH) model. Additional chemical information of the m-TiO2@Ag particles was determined by field-emission electron spectroscopy for chemical analysis (ESCA/XPS, ULVAC-PHI, PHI 5000 Versa Probe, Japan). Photocatalytic experiment was conducted in aqueous solutions by a UV irradiation using a 200 W mercury lamp (wavelength of 365 nm) as the light source with exposure duration up to 120 min. Initial weight of the m-TiO2 and m-TiO2@Ag particles used in the solutions was held at 0.25 g L⁻¹ and the initial MB concentration was 1 x 10⁻⁵ M. The solution temperature was controlled over a temperature range from 25 to 45 °C by a circulating water pump. All the solutions were kept in darkness for 30 min to establish an adsorption–desorption equilibrium prior to the UV exposure. Some samples were then siphoned out from the reaction solutions after different exposure times and quickly centrifuged to separate the particles from the solutions. The supernatant solutions were immediately characterized by UV–vis spectrophotometry (Lambda 800, PerkinElmer, U.S.A.) to determine the absorption change over a range of wavelengths from 200 to 900 nm. Change of the absorption intensity at a characteristic wavelength of 664 nm was compared in order for determination of the residual MB concentration in the solution. A five-point calibration curve over the range of temperature and time used in the study was established from different solutions of known MB concentrations prior to the test.

Antibacterial activity of the m-TiO2@Ag particles was carried out against E coli by the plate-counting Luria Bertani broth (LB) method. As described in our earlier reports [7,8], the particles of 1 mg were weighed and added into 7 ml of a phosphate buffer solution containing the bacteria. The powdered solutions (pH ~ 7.5) were incubated at 37 °C under vibration agitation for up to 24 h. Some of the solutions (0.5 ml) were then cultured on an agar plate and incubated at 37 °C for additional 18 h, and the exact number of discrete colonies was counted as the number of remaining bacteria. Two parallel tests by using the m-TiO2 particles and one without the presence of any particle were also conducted for comparison purposes.

3. Results and discussion

Fig. 1 shows microstructure of the m-TiO2 and m-TiO2@Ag particles. In Fig. 1a and b, the m-TiO2 particles show spherical or elliptical morphology without notable agglomeration. According to Chen et al. [14], the presence of HDA would serve as a structure-directing agent in the sol–gel process by preferentially anchoring the amino groups of the HDA molecules with the hydrolyzed metalorganic Ti[OCH(CH3)2]₄(OH)ₓ species and oligomers in the solvent mixture via hydrogen-bonding interactions. The resultant organic–inorganic hybrids with long-chain alkyl groups were hydrophobic in character. This hence facilitated the molecules to self-organize into hybrid micelles with a well-defined spherical geometry of submicrometer size as the titanium species and oligomers further polymerized, which led to a condensed, near-spherical amorphous structure with time. The amorphous structure evolved toward anatase, wormhole-like structure upon subjected to the mild solvothermal treatment while the bead morphology remained intact [14]. On the other hand, the
decoration of Ag nanoparticles on the m-TiO2 beads was first carried out by sensitization of the TiO2 surface with Sn2+ ions followed by redox transmetalation in which the aqueous Ag+ ions were used to replace the surface-adsorbed Sn2+ ions by formation of Ag0 atoms through difference in their reduction potentials. With the Sn2+ modification and the subsequent treatment with Tollens’ solution, Ag nanoparticles with a cluster size under 50 nm were found to deposit preferentially on the m-TiO2 surface, resulted in the raspberry-like m-TiO2@Ag particles in Fig. 1c and d. The inset of EDS spectrum in Fig. 1c confirms the presence of Ag. In addition, the EDS–ZAF analysis revealed that Ag concentration of about 3.8 ± 0.4 at% was present in the host TiO2 matrix. It may be interesting to note that some Sn might still be present after the redox transmetalation, i.e., some Sn2+ ions were not completely exchanged by the formation of Ag0. This hence suggests that Ag content in the composite particles may be further increased by increasing the Ag(NH3)2+ concentration or by treating with a longer reaction time. In Fig. 1c and d, distribution of the Ag nanoparticles on the m-TiO2 surface was found quite uniform but agglomeration did exist. Nevertheless, some “free” Ag nanoparticles were found occasionally, suggesting that the Ag clusters may separate from the m-TiO2 surface due presumably to weak adhesion between the dissimilar phases. This is anticipated to become more pronounced when the Ag concentration or the degree of Ag agglomeration increases [7]. It may be interesting to note that when the as-prepared m-TiO2 particles were treated directly by Tollens’ solution without the Sn2+ modification, no apparent coating of the Ag nanoparticles was resulted on the m-TiO2 surface, i.e., the morphology resembled to that in Fig. 1a and b. This indicates that the presence of Sn2+ sites is critically important to the preferential deposition and growth of the Ag nanoparticles on the m-TiO2 surface in order for the subsequent redox transmetalation to take place at the Sn2+ sites. As shown in Eq. (1), the Sn2+/Sn4+ reduction potential is about −0.151 V vs. the standard hydrogen electrode (SHE) [16]. This is substantially lower than that of the Ag/Ag+ pair (0.799 V) in Eq. (2). Therefore, the adsorbed Sn2+ ions would be in favor of giving away electrons spontaneously when encountering the Ag+ ions in the solution. This electrochemical potential difference facilitated a selective redox transmetalation to occur so that a sequential Ag0 deposition was resulted on the m-TiO2 surface (Eq. 3). In view of the literature, similar operation has been exploited in both aqueous and organic media for synthesis of bimetallic films and composites of various chemical compositions without use of reducing agent [17–19].

\[
\begin{align*}
\text{Sn}^{2+} & \rightarrow \text{Sn}^{4+} + 2e^- \\
\text{Ag}^+ + e^- & \rightarrow \text{Ag} \\
\text{Sn}^{2+} + 2\text{Ag}^+ & \rightarrow \text{Sn}^{4+} + 2\text{Ag}
\end{align*}
\]

In Fig. 2, the anatase structure is the predominant phase of the m-TiO2 particles from the XRD analysis. Minor amount of Ag is found for the m-TiO2@Ag particles with a relatively weak diffraction intensity, which is in good agreement with that of the ZAF finding. Both particles present a type IV isotherm along with an apparent hysteresis loop at relative pressure \(P/P_0 = 0.60–0.85\) in Fig. 3. This reveals the presence of interparticle non-uniform pores existing in the particles [14]. The specific BET surface area and pore volume of the m-TiO2 particles were 147.5 m² g⁻¹ and 0.349 cm³ g⁻¹, respectively. The high specific surface area and large pore volume are ascribed to the mesoporosity of the m-TiO2 particles with an average pore diameter of ca. 7.5 nm. In comparison, a substantially larger portion of smaller pores with a pore diameter under 10 nm was found in the inset of Fig. 3. In addition, the presence of Ag nanoparticles on the m-TiO2 particles appeared to reduce both the specific BET surface area (117.5 m² g⁻¹) and pore volume (0.284 cm³ g⁻¹) of the m-TiO2@Ag particles when compared to that of the m-TiO2. The average pore diameter yet remained about the same (8.0 nm). This finding further reveals that the Ag nanoparticles with a primarily particle size smaller than ca. 10 nm (Fig. 1d) would tend to block the surface pores of the m-TiO2 so that gas molecules failed to penetrate into some of the mesopores, resulted in the reduced BET and pore volume accordingly. This in turn suggests that some of the mesopores in the m-TiO2 particles became closed pores during the solution treatment of the Sn2+ sensitization and/or the redox transmetalation. The ESCA/XPS analysis in Fig. 4 indicates that Ag2O was present on surface of the Ag nanoparticles. This is believed attributable to the aqueous solution used in Tollens’ reagent and the transmetalation process.

Fig. 5a shows degradation of the MB dye under UV irradiation when the m-TiO2 was present in the solution. Removal of the MB dye molecules required a UV irradiation time greater than 1 h to complete the degradation. In comparison, an irradiation time of 1.5 h was required to remove only half of the MB dye in aqueous solution of similar initial concentration (5 × 10⁻⁵ M) when commercial TiO2 submicrometer particles were used [7]. This is attributable to the mesostructure involved in the m-TiO2 with a substantially greater BET value. In addition, the degradation rate in Fig. 5a appears to be temperature dependent and the degradation ratio increases generally as the employed temperature was increased. On the contrary, the m-TiO2@Ag particles show a
much enhanced UV photocatalytic performance in which the MB dye molecules were almost fully removed from the solution within an hour under the identical UV exposure (Fig. 5b), despite the anatase TiO2 amount responsible for the UV photocatalysis was indeed fewer than that of the bare m-TiO2 case because of powders of the same weight were used for the test (Fig. 5a). The MB degradation compares favorably with that of our earlier work [7], in which only 70% of the MB molecules were degraded after the same UV-irradiation time on the Ag-decorative commercial TiO2 particles. The superior enhancement of photocatalytic performance is believed to stem primarily from the synergistic mesostructure of TiO2 and grafting of Ag nanoparticles without substantial agglomeration. It may also be interesting to note that the degradation was relatively independent of the temperature employed for the m-TiO2@Ag. This suggests that the minor presence of Ag is able to reduce the electron–hole recombination effectively under the UV exposure so that the temperature effect to the photocatalytic performance became negligible. In comparison to the ESCA/XPS result (Fig. 4), the presence of Ag2O appears not to influence conduction of the electrons and holds generated by the UV irradiation so that the UV photocatalysis of the composite particles showed a substantial enhancement.

Fig. 3. Isothermal N2 gas sorption–desorption curves of the m-TiO2 and m-TiO2@Ag particles. The inset shows BJH pore-size distribution from the sorption branches. The open and close symbols represent those of the N2 sorption and desorption, respectively.

Fig. 4. ESCA/XPS spectrum shows high-resolution scan of the Ag 3d region of the m-TiO2@Ag particles.

Fig. 5. Photodegradation of MB dye under UV irradiation with presence of (a) m-TiO2 and (b) m-TiO2@Ag particles in the solution. The temperature was held over a range of 25–55 °C.

The bactericidal property of the m-TiO2 and m-TiO2@Ag particles against the E. coli in dark condition is shown in Fig. 6. The control sample was carried out in parallel for comparison reasons without use of the particles. Under dark situation without the use of UV irradiation, the m-TiO2 sample did not show notable antibacterial activity when compared to that of the control sample. The survival colony of similar concentration resulted even when the incubation time was increased to 24 h. The m-TiO2@Ag sample yet showed a remarkably diminished number of the bacterial colony at the incubation time of 1 h, and the E. coli became completely extinct when the incubation time was further increased to 24 h. This sterilization of the gram-negative E. coli stems primarily from the release of Ag ions from the m-TiO2@Ag particles [7,8], despite the low Ag concentration (ca. 3.8 at%) and the presence of oxide layer on the Ag nanoparticles. The decoration of Ag nanoparticles on the m-TiO2 particles hence renders bi-functional UV photocatalysis and bactericide activities of the composite particles.

4. Conclusions

Both UV photocatalysis and bactericide activities of the mesoporous TiO2 particles were enhanced substantially with the decoration of Ag nanoparticles. MB dye with an initial concentration of $1 \times 10^{-5}$ M can be removed completely
within an hour and the removal rate is temperature independent. The composite particles also render bactericidal activity against gram-negative \textit{E coli} in aqueous solutions under dark condition. In addition, the grafting of Ag nanoparticles on the m-TiO$_2$ submicrometer particles can be prepared by a facile redox–transmetalation route in which Sn$^{2+}$ ions were adsorbed on the m-TiO$_2$ surface followed then by Ag$^+$ in aqueous solution that replaced the surface-adsorbed Sn$^{2+}$ by formation of Ag$^0$ atoms spontaneously through difference in their electrochemical reduction potentials without use of any reducing agent. The process is general and is suitable for the synthesis of other chemical compositions with similar composite structure.

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