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Gold-plasmon enhanced photocatalytic performance of anatase titania nanotubes under visible-light irradiation

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ABSTRACT

[3-Aminopropyl]trimethoxysilane-modified titania nanotubes decorated with Au nanoparticles (APTMS/(TNTs-Au)) nanocomposites were synthesized using a deposition-precipitation process. The results showed that Au nanoparticles (NPs) in the metallic state were firmly adhered to the surface of the anatase TNTs. APTMS/(TNTs-Au) exhibited great photocatalytic activities which were evaluated from the degradation rate of methylene blue aqueous solution under visible light irradiation. 3D finite-difference time domain simulation was performed to estimate the electromagnetic field distribution at the interface between TNTs and Au NPs. The visible photocatalytic activity of APTMS/(TNTs-Au) was largely attributed to the surface plasmon absorption of metallic Au NPs, which generated and transferred hot electrons to the CB of TNTs. In addition, the hot electrons on the surface of TNTs also suppressed the radiative electron–hole recombination and consequently enhanced the photocatalytic activity.

1. Introduction

Water pollution has become one of the most severe and widespread environmental problems in recent years. Many methods have been used to purify water, for instance, ultraviolet radiation, distillation and activated carbon adsorption [1–3]. Among these strategies, TiO_2, first reported by Fujishima and Honda [4] as a kind of semiconductor-based photocatalysts, has attracted many attentions owing to its advanced properties of non-toxicity, low cost, long-term physical, the most efficient photocatalytic activity and chemical stability [5–7]. There are many morphologies of TiO_2 nanomaterials, such as nanoparticle, nanoflower, nanosheet, nanotube and nanobelt [8–12]. The intriguing prospect of titanium dioxide nanotubes (TNTs) as effective photocatalyst has become noticeable for its characteristics regarding the pertinent high electron mobility and larger specific surface area [13]. However, its intrinsic property of the large band gap of 3.2 eV limits its utilization to the ultraviolet band, which composes only 3% of the total solar spectrum [14]. Therefore, many efforts have been made to extend the photo response of TiO_2 into the visible-light region, such as doping metal and nonmetal elements [15,16].

Noble metallic nanomaterials such as gold (Au) nanoparticles (NPs) which exhibit a wide absorption of visible light as a result of the surface plasmon resonance (SPR) effect have attract huge attention [17]. Au NPs are comparatively stable under irradiation of light during the catalytic process. Anchoring Au NPs on the surface of TNTs not only ensures TiO_2 active in visible light, but also facilitates charge transport and reduces the charge recombination process [18]. For depositing Au on the surface of TiO_2, various methods have been attempted e.g. physical mixing, electrolysis, UV photoreduction, core–shell formation and chemical reduction [19–22]. These existing methods are often complex, or with loose connections with TiO_2.

In the present work, we propose a deposition–precipitation method to synthesize [3-aminopropyl]trimethoxysilane (APTMS)-modified TNTs decorated with Au NPs (APTMS/(TNTs-Au)). Au NPs with the average diameter of ~10 nm are homogeneously deposited on the surface of TNTs with anatase phase. The photocatalytic activity of APTMS/(TNTs-Au) is studied by measuring the degradation of methylene blue (MB) in aqueous suspensions under irradiation of visible light. APTMS/(TNTs-Au) exhibites much higher photocatalytic efficiency compared with that of TiO_2 NPs, pure TNTs and APTMS-modified TNTs. The electromagnetic field distribution at the interface between TNTs and Au NPs are estimated by the 3D finite-difference time domain (FDTD) simulation. The enhanced photoactivity of APTMS/(TNTs-Au) in visible region can be attributed to the high specific surface area of composites, the surface plasmon absorption (SPR) of Au NPs

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and the unique electron transport between Au NPs and TNTs. By analyzing the enhancement effect of the nanocomposites, the origin of the enhancement mechanism in the system is investigated and a deeper understanding on the overall photocatalytic enhancement effect has been achieved.

2. Experimental

The morphology of catalysts was characterized using field emission scanning electron microscopy (SEM; Hitachi S-4800, Japan) with an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) images were obtained using H-800 microscope (Hitachi, Japan) to provide the morphology detail. The phase compositions of the catalysts were determined by X-ray diffraction (XRD, BRUKER) with a diffractometer with Cu Kα radiation (k= 0.15406 nm). X-ray photoelectron spectroscopy (XPS) analysis was carried on a PHI Quantera (PHI, Japan) and the energy calibrations were made against the C 1s peak to eliminate the charging of the sample during analysis. The specific surface areas of the samples were determined through nitrogen adsorption at 110K on the basis of the BET equation using a V-Sorb 2800P instrument (Gold APP, China). UV–visible (UV–vis) absorption spectrum was measured with UV-310IPC spectrophotometer (Shimadzu, Japan). 3D FDTD simulation was performed to investigate the electromagnetic field distribution in the light-illuminated materials on a commercial software package (Lumerical FDTD Solution 8.1, Inc., Canada). The TiO_2 dielectric constant we used is from Tompkins [23], and the constant of Au we used is from Johnson and Christy [24]. The grid was set to a 0.1 nm cubic in our calculation.

2.1. Chemical reagents

Degussa-TiO_2 (P25) was purchased from Evonik industries, Germany. [3-aminopropyl]trimethoxysilane (APTMS) was purchased from Sigma, USA. Tetrachloroauric acid ($HAuCl_4$), sodium hydroxide (NaOH), ammonia, and hydrochloric acid (HCl) were purchased from Beijing Chemical factory and, used without further purification. All other chemicals used in this work were of analytical grade.

2.2. Synthesis of APTMS/(TNTs-Au) nanocomposites

The APTMS/(TNTs-Au) nanocomposites were prepared by deposition-precipitation method. This approach is depicted in Fig. 1. The titania nanotubes (TNTs) were synthesized through a hydrothermal reaction process [25]. In a typical experimental procedure, 2 g P25 powders was added into 70 mL of NaOH aqueous solution (10 M), and stirred for 30 min until a homogeneous suspension was obtained. The suspension was transferred to a 100 mL Teflon lined stainless steel autoclave and put into a muffle furnace to undergo a hydrothermal treatment at 150 °C for 24 h. The obtained precipitate was washed through centrifugation with deionized water and HCl aqueous solution (0.1 M) several times until the pH was readjusted to about 7. The final product was obtained by drying under vacuum at 90 °C.

The APTMS functionalization on TNTs (APTMS/TNTs) was carried out as follows. Briefly, 1 g of TNTs was added in a mixture of 1.2 mL water, 0.8 mL of ammonium hydroxide (25 wt.%) and 30 mL ethanol. After being stirred for 30 min, 0.5 mL of APTMS was added dropwise into the above dispersion. The mixture was sufficiently dispersed via ultrasonication and stirred for 12 h. Then, the APTMS/TNTs was washed with ethanol and dried at 60 °C for 2 h.

Finally, the APTMS/(TNTs-Au) nanocomposites were prepared by the deposition–precipitation method. 100 mL of $HAuCl_4$ aqueous solution (4.2×10^{-3} M) was heated to 80 °C, and the pH value of the solution was carefully adjusted to 7 using NaOH aqueous solution (1 M) under continuous magnetic stirring. 1 g of APTMS/TNTs was added into the solution and pH value was adjusted to 7 with NaOH aqueous solution (1 M) again. After vigorously stirred at 80 °C for 2 h, the APTMS/(TNTs-Au) nanocomposites were centrifuged and washed with warm distilled water for 10 min. This procedure was repeated for six times and the resultant product was dried at 90 °C for 5 h.

2.3. Photocatalytic activity test

Photocatalytic experiments were carried out at room temperature (25 °C). 30 mg catalysts (P25, TNTs, APTMS/TNTs and APTMS/(TNTs-Au)) were added into four quartz test-tubes with 60 mL 0.04 g/l aqueous solution of methylene blue (MB), respectively. The samples were positioned in a circle with a Xe lamp (300 W, equipped with a 420 nm filter) symmetrically. In order to reach the adsorption-desorption equilibration, four tubes of suspensions were magnetically stirred in darkness for 1 h. Then, the suspension was stirred under visible irradiation for 2 h. 5 mL suspension was taken from each test-tube regularly as samples, and the substances were instantly eliminated by centrifugation at 8000 rpm for 15 min. The photocatalytic activity of the catalyst was estimated by measuring the reduction of the absorption maximum (664.5 nm) of MB aqueous solution. The absorbance was measured with UV-310IPC spectrophotometer.

3. Results and discussion

SEM is used to characterize the prepared TNTs and APTMS/(TNTs-Au). As shown in Fig. 2a, the surface of TNTs is quite smooth and the length is about 300 nm. Fig. 2b shows the SEM image of APTMS/(TNTs-Au). It illustrates that the small Au NPs are firmly stuck to the TNTs, indicating the modifying of TNTs with APTMS are

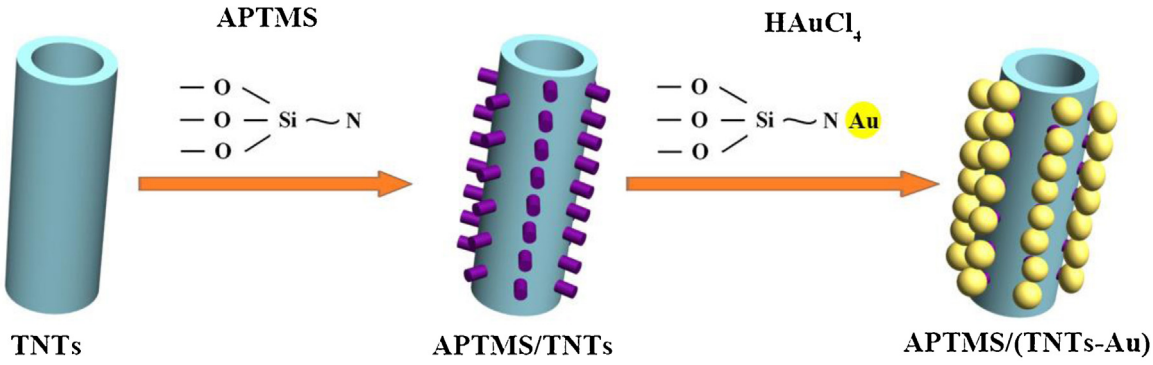

Fig. 1. Schematic depiction of the formation of APTMS/(TNTs-Au).