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Uniform dispersion of Au nanoparticles on TiO_2 film via electrostatic self-assembly for photocatalytic degradation of bisphenol A

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ABSTRACT

A simple electrostatic self-assembly method was developed to uniformly disperse ultra-fine Au nanoparticles (NPs) on TiO_2 film to improve the photocatalytic activity. Without any modification of TiO_2 surface with functional groups, negatively charged Au NPs could be spontaneously adsorbed on TiO_2 films with electrostatic attraction when the pH of Au colloids was lower than or close to the isoelectric point of TiO_2. Ultra high-resolution FESEM observation showed that Au NPs with diameter of 3–5 nm were physically separated and uniformly dispersed on TiO_2 film. The pH of Au colloids remarkably influenced the Au loading that was decreased at high pH. The average size of deposited Au NPs increased from 3.1 ± 1.3 nm at $-5\,^{\circ}C$ to 10.5 ± 3.1 nm at $40\,^{\circ}C$, indicating that growth of Au NPs was retarded at low temperature. The dispersed Au NPs on TiO_2 film enhanced the photocurrent generation with ~five folds and increased the photovoltage of ~115 mV, revealing that the recombination of electron–hole pairs was significantly reduced. The photocatalytic activity of the Au–TiO_2 nanocomposite film was improved with ~2.5 folds for degradation of bisphenol A, and no deactivation was observed during 10 cyclic tests. The key characteristics of deposited Au NPs, such as ultra-fine size, uniform dispersion, physical separation and high loading, were responsible for improved photocatalytic activity of the Au–TiO_2 film.

1. Introduction

Highly dispersed Au nanoparticles on TiO_2 surface exhibits extraordinary high activity for photocatalytic degradation of undesirable chemical contaminants [1–3]. It has been the focal point of numerous investigations particularly because of the reduction of hole–electron recombination in Au–TiO_2 composites [4–8]. In earlier studies, Au–TiO_2 composite powders were widely investigated [3,9–12]. However, one major drawback, i.e. large cost of separating Au–TiO_2 powder from water after treatment, hinders the practical application. To overcome this obstacle, many investigations are oriented towards immobilization of Au–TiO_2 composites on various supports [13–19].

Up to now, these Au–TiO_2 nanocomposite films have been prepared by both physical and chemical routes, including the RF-sputtering approach [13–15], sol–gel dip coating [16], deposition–precipitation [17,18] and photo-reduction method [19]. To prepare Au–TiO_2 porous films, typically precursor ions like $[AuCl_4]^-$ are first transferred into the pores in advance through adsorption, ion-exchange, or ultra-sonication, then Au precursors are in situ reduced with electrochemical deposition [20], UV irradiation [21] or other chemical methods [22–24]. Then, the reduced Au nanoparticles (NPs) are incorporated into pore channels or matrix of TiO_2 films. However, using these methods, it is difficult to control the morphology, size and distribution of deposited Au NPs due to the influence of oxide supports [25]. Because the photocatalytic activity of Au–TiO_2 composites highly depends on the shape, size, distribution, loading and chemical states of Au NPs [26–28], uniform dispersion of metallic Au NPs with ultra-fine size is vital to improve the photocatalytic activity of Au–TiO_2 composite films.

In recent years, some efforts have been made to uniformly disperse Au NPs on TiO_2 film via assembling pre-synthesized colloidal Au NPs onto the surface of TiO_2, thus the influence of oxide supports in determining the size and dispersion of Au NPs is minimized [29,30]. Additionally, it is much easier to control the size and monodispersity of Au NPs in colloidal solutions than in situ reduction on TiO_2 film [31]. Using the electrophoretic deposition, Patel et al. [25] successfully incorporated 3.1 nm Au NPs inside the mesochannels of TiO_2 film. However, severe agglomerated Au NPs with 20–30 nm diameter appeared on TiO_2 films reported by Kamat and co-workers [4,24]. To electrophoretically deposit Au NPs on TiO_2 films, the substrate must be electrically conductive and Au NPs need to be dispersed in organic medium. With a simple adsorption method, Kamat and co-workers transferred colloidal Au NPs onto the TiO_2 film, but significant agglomera-

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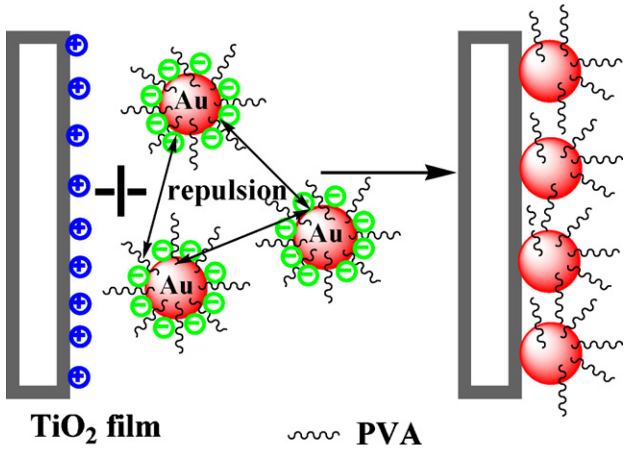

Fig. 1. Illustrative diagram of depositing negatively charged Au nanoparticles on TiO_2 film via electrostatic self-assembly.

tion and growth of Au NPs also occurred [5]. In order to attach colloidal Au NPs on the TiO_2 via self-assembly, the TiO_2 surface is usually modified with functional groups (e.g., SH group) having great affinity to Au NPs [10,32,33]. Although heating treatment can be used to remove these capping agents, the residual sulfur may poison active sites of both Au NPs and TiO_2 support [33,34]. In a word, efficient transfer of pre-synthesized Au NPs from colloidal solutions onto TiO_2 film still remains a great challenge up to now [29–31,33,35].

In this paper, an alternative simple approach is presented that is based on electrostatic self-assembly of colloidal Au nanoparticles (NPs) on prefabricated TiO_2 film (Fig. 1). This strategy provides a completely solution-based method for uniformly dispersion of Au NPs on TiO_2 film. There are several reasons for us to propose this strategy: (1) the ultra-fine size, well-distribution and tailored loading of Au NPs can be obtained by easily controlling over the pH and temperature of Au colloids and assembly time. (2) Physical separation of individual Au NPs can maximize the transfer efficiency of photo-generated electrons from TiO_2 to Au NPs. (3) Due to the ease of fabrication, this route is low cost and scalable to fabricate various Au–TiO_2 nanocomposite films with no restrictions on the size, shape or composition of the supports.

Bisphenol A (BPA) is widely used as a major component for manufacturing polycarbonate resins, epoxy and polyester-styrene resins [36,37]. And it is a well-known endocrine disrupting chemical (EDC) due to its estrogenic activity [38]. Thus, the inevitable discharge of BPA from plastic products has caused severe water pollution. Effective treatment of BPA has been required as part of water remediation efforts. In this work, BPA is adopted as a model compound to evaluate the photocatalytic activity of the prepared Au–TiO_2 film.

2. Experimental

2.1. Chemicals

All chemicals were used as received without further purification. Polyvinyl alcohol (PVA, 99.0%, average molecule weight 1750), sodium borohydride, tetrabutylorthotitanate, acetyl acetone, *n*-propanol, hydrocholoric acid and sodium hydroxide were purchased from Beijing Chemical Reagent Company. Hydrogen tetrachloroaurate trihydrate ($HAuCl_4{\cdot}3H_2O$) and bisphenol A were from Sigma–Aldrich. Ultra-purity water from Thermo Barnstead Nanopure Diamond UV^{TM} was used in all experiments.

2.2. Synthesis of Au–TiO_2 nanocomposite film

TiO_2 film was prepared with a sol–gel dip-coating method similar to our previous study [39]. Tetrabutylorthotitanate, acetyl acetone, water and *n*-propanol were mixed with a volumetric ratio of 1:0.3:0.4:7. The titanium sheet, pretreated with 10 wt% hot oxalic acid solution, was dipped into the above sol and withdrawn at a speed of 1 mm s^{-1}. The dried gel film was annealed in air at 500 °C for 1 h at a heating rate of 2 °C min^{-1}. After four cycles of the dip-coating process, the film with optimized TiO_2 loading was coated on the Ti substrate.

The typical procedure for depositing Au nanoparticles (NPs) on the TiO_2 film is given as follows. 354 mg PVA was dissolved into $HAuCl_4$ aqueous solution (0.3 mM, 200 mL). Then, the PVA/$HAuCl_4$ solution was kept at low temperature in a water bath, into which a fresh $NaBH_4$ solution (0.07 M, 10 mL) was rapidly added with simultaneous ultra-sonication and vigorous stirring for 1 min. The color of the mixture immediately turned from pale yellow to dark brown, indicating the formation of Au NPs. A piece of prefabricated TiO_2/Ti sheet, 150 mm × 120 mm, was rolled up and completely immersed into the freshly prepared Au colloids. By adjusting the pH of Au colloids, the Au NPs were adsorbed on the TiO_2/Ti sheet via electrostatic self-assembly at low temperature in a static manner. After assembly of 5–90 min, the TiO_2/Ti sheet was withdrawn, washed with boiling water for 3 times, and then annealed in air at 300 °C for 1.5 h to remove the capped PVA. Thus, the Au–TiO_2 nanocomposite films with various Au loadings were prepared.

2.3. Characterization

The morphology of Au–TiO_2 film was observed using an ultra high-resolution field-emission scanning electron microscope (FESEM, S-5500, Hitachi, second electron resolution: 0.4 nm/30 kV) performed at an accelerating voltage of 5.0 kV. X-ray from the SEM microscope probe was used to determine the deposited Au amount. High-resolution transmission electron microscopy (HRTEM) images were recorded using a JEM 2010 microscope with an electron diffractometer. The zeta potentials of Au colloids and TiO_2 films were measured as a function of pH using a zeta potential analyzer (ZetaPALS, 32BIT, Brookhaven). The UV–Vis absorption spectra of Au colloids were recorded using a UV-Vis Recording Spectrophotometer (UV-2401PC, Shimadzu). TiO_2 and Au–TiO_2 powders for recording TEM images and zeta potentials were scratched from the Ti substrate. X-ray diffraction (XRD) analysis of the TiO_2 and Au–TiO_2 films was carried out with a Rigaku D/max-RB using Cu Kα radiation (λ = 0.15418 nm), operated at 40 kV and 100 mA.

Chemical states of surface elements of the films were investigated by X-ray photoelectron spectroscopy (XPS, PHI-5300, ESCA) at a pass energy of 50 eV, using Al Kα as an exciting X-ray source. The spectra were calibrated with respect to the C1s line of adventitious carbon at 284.8 eV. Elemental analysis of Au–TiO_2/Ti was conducted with an inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP). The Au–TiO_2/Ti sheets with a size of 150 mm × 120 mm were first dissolved in aqua regia for 24 h. The solution containing Au ions was then analyzed to determine the Au loading.

2.4. Photoelectrochemical measurements

The photoelectrochemical measurements were performed by using a CHI 660B electrochemical workstation in a classical three-electrode electrochemical cell with reference (saturated calomel electrode, SCE)) and counter (platinum foil) electrodes. The TiO_2/Ti or Au–TiO_2/Ti sheet, with area of 2 cm^2, acted as the working electrode. The electrolyte was N_2-saturated 0.05 M Na_2SO_4 solution.