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COMMUNICATION

Nanotube-confinement induced size-controllable g-C_3N_4 quantum dots modified single-crystalline TiO_2 nanotube arrays for stable synergetic photoelectrocatalysis

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Abstract
Size-controllable g-C_3N_4 quantum dots (QDs) were *in-situ* synthesized and grafted onto single-crystalline TiO_2 nanotube arrays (TiO_2-NTAs) based on nanotube-confinement effect. This photoelectrocatalyst exhibited high activity in synergetic H_2 evolution and organic pollutant degradation. The g-C_3N_4 QDs, together with TiO_2-NTAs due to multiple light reflections, promoted light harvesting owing to the narrow energy band gap and upconversion from quantum size effect of g-C_3N_4 QDs. Meanwhile, the single-crystal TiO_2 *in-situ* formed during the g-C_3N_4 synthesis process favored the photoelectron transfer, and the g-C_3N_4/TiO_2 heterojunctions further promoted separation of photoelectrons from holes. Moreover, the strong g-C_3N_4-TiO_2 interaction and the confinement effect of TiO_2 nanotubes efficiently inhibited self-gathering and leaching of g-C_3N_4 QDs, leading to excellent stability in photoelectrocatalysis.

Introduction

Quantum dots (QDs) and their composites have been widely investigated due to their unique quantum size effects and potential applications in photoelectric devices, photocatalysis, and sensor areas, among others [1–4]. Currently,

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the most important problems are how to prepare uniform size-controllable QDs and how to inhibit their self-gathering and/or leaching from composites. Solar energy has attracted increasing global attention due to the increased energy crisis [5]. Although solar cells can directly convert solar energy into electric power, their low conversion rate, high cost and environmental pollution limit practical applications. One of the most promising approaches is the use of sunlight-driven photocatalytic water splitting to produce H_2 for utilization as a clean energy fuel [6,7]. To improve the H_2 production efficiency, synergetic water splitting processes have been developed with organic pollutant degradation and photoelectrocatalytic (PEC) techniques [8]. The key to advancing these techniques is the design of powerful photoelectrocatalysts [9].

Recently, TiO_2 nanotube arrays (TiO_2-NTAs) were reported to show higher photoelectrocatalytic activity than immobilized TiO_2 films [10]. Good electrical conductivity promotes photoelectron transfer and also facilitates photoelectron-hole separation to reduce recombination. However, unique morphologies and porous channels with high surface area facilitate both light harvesting *via* multiple-reflections and reactant adsorption [11-13]. Additionally, TiO_2 can only be activated by high-energy light due to the large energy band gap, thus limiting the use of sunlight, which contains less than 5 % UV light [14-16]. Various efforts have struggled to deliver visible-light photocatalysts by doping TiO_2 with ions [17], coupling with noble metals [18,19] and forming hybrids with metal sulfides [20] *etc*. Since Wang et al. reported the visible-light photocatalytic performance of g-C_3N_4 in 2009 [21], g-C_3N_4 has been widely studied in both H_2 production *via* water splitting and in environmental cleaning by mineralizing organic pollutants under visible-light irradiation [22]; however, the application of this process is still quite limited by low efficiency. To date, both g-C_3N_4 single-layered QDs [23] and low-molecular-weight carbon nitrides (oligomers) [24] have been reported to display high photocatalytic activity and excellent stability in visible-light driven photocatalysis. However, notable tiny g-C_3N_4 nanoparticles are difficult to recycle and are easily leached during photocatalytic reaction.

Herein, for the first time, we report the incorporation of g-C_3N_4 QDs implanted on the inner wall of single-crystal TiO_2 nanotube arrays *via* chemical vapor deposition. The nanotube structure plays a crucial role in retarding the growth of g-C_3N_4 nanoparticles through the confinement effect and inhibiting the leaching of g-C_3N_4 nanoparticles. The as-prepared g-C_3N_4/TiO_2-NTAs displayed strong adsorption of visible light with longer wavelength due to both the narrow energy band gap and the quantum size effect of g-C_3N_4 QDs [23,25]. In addition to the single-crystal structure, the quantum-sized g-C_3N_4 is able to upgrade the lowest unoccupied molecular orbital (LUMO) of g-C_3N_4 [23], which could promote the transfer of photoelectrons. Meanwhile, the heterojunctions between g-C_3N_4 QDs and TiO_2 could efficiently inhibit photoelectron-hole recombination. As a result, it exhibited high photoelectrocatalytic activity and stability in synergetic H_2 evolution from water splitting and degradation of organic pollutants under visible-light irradiation.

Experimental section

Preparation of g-C_3N_4/TiO_2-NTAs electrode

Titanium sheets (0.3 mm thick, 99.5%) were purchased from Shanghai Right Titanium Industry Co., Ltd., and melamine, ammonium fluoride, phosphoric acid, acetone and ethanol of analytical grade were obtained from the Aladdin Company and used without further purification. All solutions were prepared with deionized water.

In a typical process, a pure TiO_2 nanotube array electrode was fabricated by the electrochemical anodic oxidation technique, as previously described [26]. The 0.3-mm-thick polished titanium sheet was cut into 33×20 mm^2 pieces. The titanium pieces were cleaned with ultrasonic irradiation for 15 min in acetone, ethanol and deionized water. The titanium plate and platinum foil were used as the anode electrode and cathode electrode, respectively. An aqueous solution containing 0.2 mol/L NH_4F and 0.1 mol/L H_3PO_4 was used as the electrolyte solution for anodic oxidation of titanium. Under a constant voltage of 20 V supplied by DC constant voltage power, amorphous TiO_2-NTAs was formed after 7 h of reaction. The as-obtained sheets were rinsed with deionized water and dried in air. Deposition of g-C_3N_4 into TiO_2 nanotube arrays was performed in a chemical vapor deposition (CVD) process with melamine as a precursor. Different quantities of melamine were placed on the bottom of a ceramic crucible with a cover. A TiO_2 nanotube film was placed top-down 3 cm away from the bottom of the crucible. The crucible was heated up to 550 °C (5 °C/min) in a muffle furnace. After holding at 550 °C for 4 h, g-C_3N_4 QDs were deposited onto the surface of TiO_2-NTAs. At the same time, certain g-C_3N_4 powders were also obtained in the bottom of crucible. The as-obtained g-C_3N_4/TiO_2-NTAs electrodes were labeled as CTX, where *X* represents the mass (X=0, 1, 3, 5, and 7 g) of the melamine in the crucible before the CVD process. The as-produced samples were denoted as CT0, CT1, CT3, CT5, and CT7.

Characterization

X-ray diffraction measurements were carried out in parallel mode (2θ varied from 10° to 60°) using a Rigacu Dmax-3C Advance X-ray diffractometer (Cu Kα radiation, λ=1.5406 Å). Transmission electronic microscopy (TEM) images and selected area electron diffraction (SAED) images were collected on a JEM-2010 instrument. The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000). All of the binding energy values were calibrated using C1 s=284.8 eV as a reference. Raman spectra and UV-vis diffuse reflectance spectra (UV-vis DRS) were collected on Dilor Super LabRam II and MC-2530 instruments, respectively. The FT-IR spectra of pellets of the samples mixed with KBr were recorded on a Nicolet Magna 560 FT-IR spectrometer at a resolution of 4 cm^{-1}. The photoluminescence (PL) spectra were recorded on a Varian Cary-Eclipse 500. Thermogravimetric analysis (TGA) was performed on a DTG-60H thermogravimetric analyzer with a heating speed of 5 °C/min in air. To test the upconversion property of the g-C_3N_4 QDs, CT5 was dissolved in a strong