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TiO_2/cyclized polyacrylonitrile hybridized nanocomposite: An efficient visible-light photocatalyst prepared by a facile “in situ” approach

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ABSTRACT

TiO_2/cyclized polyacrylonitrile (CPAN) hybridized nanocomposites (h-TCP) were obtained via an “in situ” method. TiO_2 sol–gel was prepared initially in the presence of polyacrylonitrile (PAN). Then the prepared TiO_2/PAN gel was heat-treated for simultaneous crystallization of TiO_2 and cyclization of PAN to obtain h-TCP nanocomposites. The as-prepared nanocomposites were characterized and compared with TiO_2 nanoparticles surface-modified by CPAN (sm-TCP) and neat TiO_2. Results show that CPAN molecular chains existing around TiO_2 nanocrystals play a good role in partition to TiO_2 nanocrystals, which decreases the mean size of TiO_2 crystals in h-TCP, alleviates the aggregation of h-TCP nanocomposites, and increases their specific surface areas. The electron–hole pair separation efficiency and interface charge transfer efficiency are also improved compared with neat TiO_2 and sm-TCP. The h-TCP nanocomposites possess excellent visible-light photocatalytic activity and stability for photodegradation of methyl orange and phenol. The visible-light photocatalytic mechanism of h-TCP has been discussed.

1. Introduction

Semiconductor-mediated heterogeneous photocatalysis powered by the abundant solar energy has been continuously developed as a potentially promising alternative for the environmental contaminants treatment, water splitting, and photoelectrochemical conversion [1–6]. Among the various semiconductor materials, TiO_2 is by far the most widely researched photocatalyst due to its excellent photodecomposition ability, high chemical and thermal stability, non-toxicity, low cost, abundant resource, and environment friendly advantages [7]. Unfortunately, some intrinsic characteristics of TiO_2 limit its practical applications. The wide band gap of TiO_2 (3.2 eV for the anatase phase) makes it be activated only by high-energy UV light irradiation (<387 nm), resulting in its low-efficiency in the utilization of the solar energy. Furthermore, the fast recombination rate of photogenerated electron–hole pairs on the surface or in the lattice of TiO_2 remarkably hinders its photocatalytic activity and commercialization. Thereby, considerable methods such as crystal growth control [8,9], noble metal depositing [10], metal ion or non-metal atoms doping [11–13], and semiconductor coupling [14–16] have been developed to shift the light absorption towards visible light region and/or decrease the recombination probability of the photogenerated electron–hole pairs for improving the photocatalytic activity of TiO_2.

Owing to the unique electrical and optical properties, such as strong absorption in visible light region, high mobility of charge carriers, and excellent environmental stability [17,18], the conjugated polymers with spatially extended π-bonding system have attracted growing research attention on the modification of semiconductor photocatalysts. Polyaniline [19–22], polypyrrole [23–25], polythiophene [26–28], and their derivatives [29,30] have been used to modify TiO_2 nanoparticles, which exhibit higher visible-light photocatalytic activities than that of neat TiO_2. In addition, the conjugated polymers can also be obtained from the non-conjugated ‘precursor polymers’ from which π-electron structures can be introduced in a controlled way [31], which seems to offer an attractive route to a commercially exploitable material, particularly when the precursor is a readily available and well characterized polymer [32]. Some conventional polymers such as polyvinyl chloride [33], polyisoprene [34], polyvinyl alcohol [35], and polyacrylonitrile [36] have been successfully used to prepare conjugated polymer derivatives through controlled thermal treatment for the modification of TiO_2 nanoparticles. Unfortunately, most of the above-mentioned nanocomposite materials were prepared via the modification of the conjugated polymers on the surface of pre-synthesized TiO_2 nanoparticles, e.g., the commercial TiO_2 P25. Due

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to the high surface energy of nanoparticles, the aggregation of TiO_2 nanoparticles is inevitable and difficult to be completely dispersed in the preparation process of sm-TCP. This implies that CPAN may be compounded on the surface of aggregative TiO_2 nanoparticles, leading to the decrement of their specific surface areas. This is disadvantageous to the photocatalytic activity of the modified TiO_2 materials. Therefore, it is an interesting investigation to modify TiO_2 nanoparticles with both high specific surface area and high visible-light photocatalytic activity using conjugated polymers.

In this paper, we prepared TiO_2/cyclized polyacrylonitrile (CPAN) hybridized nanocomposites (h-TCP) with both high specific surface area and high visible-light photocatalytic activity by a facile “in situ” method. Firstly, TiO_2 sol–gel was prepared in the presence of polyacrylonitrile (PAN), and then both the crystallization of TiO_2 and the cyclization of polyacrylonitrile were simultaneously performed in situ via a single heat-treatment, which could be beneficial to the excellent dispersion of CPAN on TiO_2 surface and intimate contact between CPAN and TiO_2 nanocrystals. The as-prepared nanocomposites were characterized by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and so on. Their visible light photocatalytic activities were evaluated by the photodegradation of methyl orange (MO) and phenol under visible light irradiation.

2. Experimental

2.1. Materials

Tetrabutyl titanate, glacial acetic acid, absolute ethanol, and dimethyl sulfoxide were obtained from Tianjin Wing Tai Chemical Reagent Co., Ltd., China. All these reagents were of AR grade and used without further purification. Potassium persulfate (Tianjin Damao Reagents Company, China) was purified by recrystallization from water. Polyacrylonitrile (PAN) was prepared using a traditional deposition polymerization [37] with acrylonitrile (Zhengzhou Piney Chemical Reagent Co., Ltd., China, purified by the vacuum distillation) as the monomer. Deionized water was used in all experiments.

2.2. Photocatalyst preparation

A typical procedure to prepare h-TCP nanocomposites is described as follows. Deionized water (4 mL), absolute ethanol (6 mL) and glacial acetic acid (6 mL) were mixed under stirring and labeled as solution A. Tetrabutyl titanate (10.0 g), glacial acetic acid (2 mL) and dimethyl sulfoxide solution of PAN (2 mL) were respectively added into absolute ethanol (13 mL) under continuous stirring at room temperature, and the obtained solution was labeled as solution B. Solution A was added dropwise into solution B under vigorous magnetic stirring for 30 min at 30 °C. Then the as-obtained mixture would turn into gel after continuous stirring for 60–90 min. The resultant gel was aged at room temperature for 3 d and dried at 100 °C for 36 h. After that, the product was ground in a mortar and then calcined at 300 °C for 1 h. According to this method, a series of hybridized nanocomposites were synthesized and labeled as h-TCP (m:1), where m:1 means the mass ratio of TiO_2 to PAN. As references, neat TiO_2 nanoparticles were prepared in absence of PAN under the same conditions (labeled as LT-TiO_2). In addition, common TiO_2 nanoparticles calcined at 450 °C for 2 h were marked as HT-TiO_2. The TiO_2 nanoparticles surface-modified by CPAN with the mass ratio of TiO_2 to CPAN as **300:1**, signed as sm-TCP **(300:1)**, were obtained according to the preparation method described in our previous work [36].

2.3. Photocatalyst characterization

The X-ray diffraction (XRD) patterns of the samples were recorded in the region of 2θ from 5° to 100° by a Rigaku D/MAX-2500 diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm) operated at 40 kV and 150 mA. High-resolution transmission electron microscopy (HRTEM) measurements were carried out on a G2 F20 electron microscopy instrument (Tecnai Co., Holland) using an accelerating voltage of 200 kV. Raman spectra were recorded at a resolution of 2 cm^{-1} by a Nicolet 6700 Raman microspectrometer using the 514.5 nm line of an Ar ion laser as the excitation source. The specific surface areas of the photocatalysts were determined by Brunauer–Emmett–Teller (BET) analysis on a Micromeritics Tri-Star II 3020 surface area and porosity system with nitrogen as an adsorptive gas at 77 K. UV–vis diffuse reflectance spectra (UV–vis DRS) were performed by a Shimadzu-2550 Scan UV–vis system equipped with an integrating sphere attachment over a range of 200–800 nm with $BaSO_4$ as a reference. X-ray photoelectron spectroscopy (XPS) analysis was investigated by a PHI 5000C ESCA System with Al Kα radiation ($h\nu = 1486.6$ eV). The X-ray anode was run at 250 W and the high voltage was kept at 15.0 kV with a detection angle of 54°. Photoluminescence (PL) emission spectra were recorded on a Fluorescence spectrophotometer (F-4600 FL Spectrophotometer, Hitachi, Japan) using a Xenon lamp as the excitation source. The excitation wavelength was 250 nm. Cyclic voltammetry measurements were performed on an electrochemical system (CHI660E, China). CPAN was deposited as a film on a 1.0 cm × 0.5 cm indium-tin-oxide conducting glass to obtain the working electrode. Ag/AgCl and Pt were employed as the reference electrode and counter electrode, respectively. The electrolyte was 0.1 mol L^{-1} $(NH_4)_2SO_4$ solution. Electrochemical impedance spectra (EIS) were detected on an electrochemical system (Solartron 1255B frequency response analyzer and Solartron SI 1287 electrochemical interface) with 0.1 mol L^{-1} KCl solution as the electrolyte, FTO/h-TCP or FTO/TiO_2 electrode as the working electrode, Pt as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode, respectively. The h-TCP and TiO_2 films were coated on the FTO substrates (fluorine-doped SnO_2, 15 Ω/sq) using a doctor-blade method.

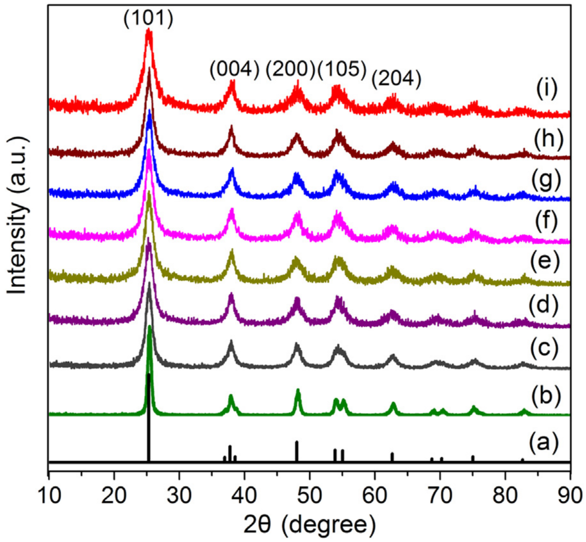

Fig. 1. XRD patterns of anatase TiO_2 (PDF# 01-072-7058) (a), sm-TCP (300:1) (b), LT-TiO_2 (c), h-TCP (500:1) (d), h-TCP (400:1) (e), h-TCP (300:1) (f), h-TCP (200:1) (g), h-TCP (100:1) (h), and h-TCP (50:1) (i).