Materials Letters 141 (2015) 362–365

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Synthesis of porphyrin sensitized TiO_2/graphene and its photocatalytic property under visible light

Chaohui Ruan [a], Longfei Zhang [a], Yeling Qin [a], Chen Xu [a], Xiaobo Zhang [a,*], Junmin Wan [a], Zhiguang Peng [b], Jianjun Shi [a], Xiaoyun Li [a], Lina Wang [a,*]

[a] Department of Physics, Zhejiang Sci-Tech University, Hangzhou 310018, PR China
[b] College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, PR China

ARTICLE INFO

Article history:
Received 28 August 2014
Accepted 19 November 2014
Available online 28 November 2014

Keywords:
Structural
Nanocomposite
Photocatalyst
Porphyrin
Graphene

ABSTRACT

A novel porphyrin sensitized TiO_2/graphene photocatalyst was synthesized via a simple method using TiO_2 nanowires, reduced graphene oxide and porphyrin. Reduced graphene oxide sheets are an excellent conductor that can inhibit the charge recombination and enhance the electron–hole separation of modified TiO_2 nanowires. Porphyrin sensitized on TiO_2 nanowires acts as a sensibilizer to increase the light absorption of the photocatalyst. The composite with a large superficial area shows improved photocatalytic property to decompose methylene blue under visible light irradiation.

1. Introduction

Since the discovery of photocatalytic water splitting reaction by Fujishima and Honda in 1972 [1], TiO_2 has been considered as one of the most attractive photocatalysts because of its low cost, non-toxicity and chemical stability. However, TiO_2 is a wide band gap semiconductor ($\sim$3.2 eV) and responds only to UV light which accounts for only 3–5% of solar light. Futhermore, photogenerated electron–hole pairs are easily recombined, which significantly diminishes the efficiency of the photocatalytic reaction [2]. As such, inhibiting the recombination of photogenerated electron–hole pairs and extending the optical absorption to visible light region are two key ways to improve the photocatalytic activity of TiO_2 under solar irradiation [3].

To inhibit the recombination of photo-generated electron–hole pairs in TiO_2, loading of graphene has attracted much attention owing to its superior electron mobility and high specific surface area [4]. Reduced graphene oxide sheets are an excellent conductor that can inhibit the charge recombination and enhance the electron–hole separation of modified TiO_2 nanowires [5]. Recently, TiO_2/graphene oxide or TiO_2/reduced graphene oxide composites have been investigated by many groups. For example Liu et al. [6] synthesized self-assembling TiO_2 nanorods on large graphene oxide sheets at a water/toluene interface. Due to the effective charge anti-recombination on graphene oxide, TiO_2 nanorods exhibit an improved photocatalytic performance. Zhang et al. [5] synthesized P25–graphene composites under hydrothermal conditions and the composites showed enhanced photocatalytic activity for degradation of methylene blue in aqueous solutions under visible light irradiation.

On the other hand, photosensitization is an effective method to extend the photo-response of TiO_2 into visible region [7]. Particularly, porphyrins and their metal complexes are widely used for spectral sensitization of wide band gap semiconductors [8]. Giuseppe Mele et al. [9] synthesized porphyrin impregnated polycrystalline TiO_2 powders for degradation of 4-nitrophenol in aqueous suspension that showed enhanced photocatalytic activity compared to bare TiO_2. Shabana Afzal et al. [10] synthesized porphyrin-sensitized TiO_2 coated on cotton fibers that exhibited superior visible-light self-cleaning performance.

In this work, porphyrin sensitized TiO_2/graphene composite was synthesized via a simple method using TiO_2 nanowires, reduced graphene oxide and porphyrin. Porphyrin sensitized on TiO_2 nanowires acts as a sensibilizer to increase the light absorption of the photocatalyst. Reduced graphene oxide sheets modified on TiO_2 nanowires improve superficial area of the composite and enhance the photocatalytic property of TiO_2 nanowires. Porphyrin sensitized TiO_2/graphene composite composite with a large superficial area can adsorb organic pollutants, indicating an enhanced photocatalytic property in degradation of methylene blue under visible light irradiation.

* Corresponding authors. Tel./fax: +86 575 86843222.
E-mail addresses: zzxiaobo@sina.com (X. Zhang), lnwang@zstu.edu.cn (L. Wang).

http://dx.doi.org/10.1016/j.matlet.2014.11.095
0167-577X/

2. Experimental section

Preparation of TiO_2 nanowire: A Ti plate was hydrothermally treated in a sealed Teflon-lined vessel containing 20 mL of 2.0 mol/L NaOH solution under 240 °C for 9.5 h, and then the as-prepared plate was rinsed with dilute acid three times and dried in air.

Reduced graphene oxide (rGO) sheets incorporating with TiO_2 nanowire: Graphene oxide(GO)was prepared according to a Hummers method [11], then GO was dispersed in ethanediol by solvothermal and the GO was reduced. The deposition of rGO nanosheets on TiO_2 nanowire was carried out on a DYY-6D electrophoretic instrument as a home-built two-electrode cell containing 100 mL of 0.02 mg/mL graphene nanosheets suspension with TiO_2 nanowire martix on a Ti plate as the working electrode and a platinum plate as the counter-electrode. The current (voltage) was in the range of 0.1–5 mA and the voltage was 20 V at room temperature for 20 min.

Preparation of TiO_2/graphene modified with TNO_2PP: TiO_2/graphene modified with meso-tetra (4-nitrophenyl) porphyrin (TNO_2PP) was prepared by mixing 0.5 g of TiO_2/graphene and 25 mg of TNO_2PP in DMF, and DMF was heated to reflux for 5 h. The TNO_2PP modified TiO_2/graphene were filtered, washed with DMF until the filtrate was colorless, then washed five times with distilled water, and dried to obtain samples of porphyrin sensitized TiO_2/graphene.

Characterizations: The morphology of the as-synthesized TiO_2 nanowires, TiO_2/graphene, and porphyrin sensitized TiO_2/graphene hybrid structures was characterized by a field-emission scanning electron microscope (FESEM; HITACHI S-4800, Japan) and a transmissionelectron microscope (TEM). X-ray diffraction (XRD) experiment was conducted to identify the crystalline phase of GO, rGO, using a Siemens/Bruker AX S D5005 X-ray diffractometer. FT-IR spectra were recorded on Nicolet Avatar 370 using a KBr pellet technique.

Measurement of photocatalytic activity: The catalytic process was carried out at room temperature in open environment. The visible light was generated from a 200 W fluorescence xenon lamp ($\lambda > 420$ nm), which was placed 10 cm above the bottom of the solution. Typically, 27 mg of photocatalyst was suspended in 150 mL of MB (methylene blue) solution (9.2 mg/L). Prior to photocatalytic reaction, the suspension was allowed to reach adsorption equilibrium with the photocatalyst in darkness. Then the solution was transferred to the light source. Samples of 4 mL were withdrawn from the suspension every 60 min during the irradiation. The photocatalysts were separated from the solution by centrifugation and the quantitative determination of MB was performed by measuring its absorption at 664 nm with a U-3900 UV–vis spectrophotometer.

3. Results and discussion

Characterization of GO and rGO: TEM image of the rGO (shown in Fig. 1a) shows that the rGO products were well-synthetized and presented in a form of two-dimensional sheets with micrometre-long wrinkles and large surface area. XRD patterns of the as-prepared GO and rGO samples are shown in Fig. 1b. For GO, the XRD peak at 11.3° corresponds to the (001) interlayer spacing of 0.78 nm, revealing that a great amount of oxygen atoms were intercalated into the interlayer space. Regarding rGO, the peak at 10.7° disappeared and a broad peak arose at around 22.4°, implying that the oxygen-containing functional groups of GO were removed and the rGO was successfully synthesized.

Porphyrin sensitized TiO_2/graphene catalyst: The porphyrin sensitized TiO_2/graphene was identified by a Fourier transform infrared (FT-IR) technique (Fig. 2) [12]. For TiO_2 nanowires, the vibrations at 3426 cm^{-1} and 1630 cm^{-1} observed correspond to the stretching vibrations and bending vibration of –OH on the surface of TiO_2, respectively. It is indicated that a large amount of hydroxyls were incorporated in the TiO_2. The stretching vibrations of C=C around 1400 cm^{-1}, C–H around 2920 cm^{-1} were observed in porphyrin sensitized TiO_2/graphene, indicating that porphyrins were modified on the surface of TiO_2. On the other hand, the peaks corresponding to the stretching vibrations of hydroxyl groups in porphyrin sensitized TiO_2/graphene samples became narrower and weaker, which indicated the decrease in the hydroxyl groups on TiO_2 surface due to the weak interaction between –OH and porphyrin.

Fig. 3a shows a typical scanning electron microscope (SEM) image of the as-made TiO_2 nanowires, which was observed to be abundant in quantity and pretty tidy with smooth surface, with the diameter of about 100 nm and length of about 10 μm. When

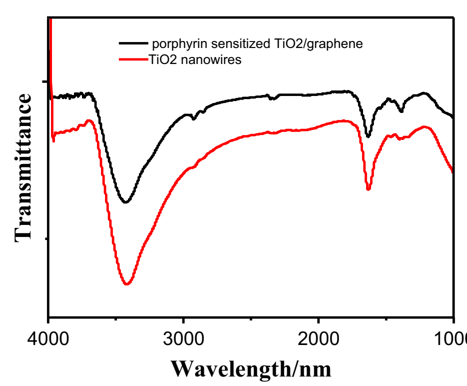

Fig. 2. FT-IR spectra of TiO_2 nanowires and porphyrin sensitized TiO_2/graphene.

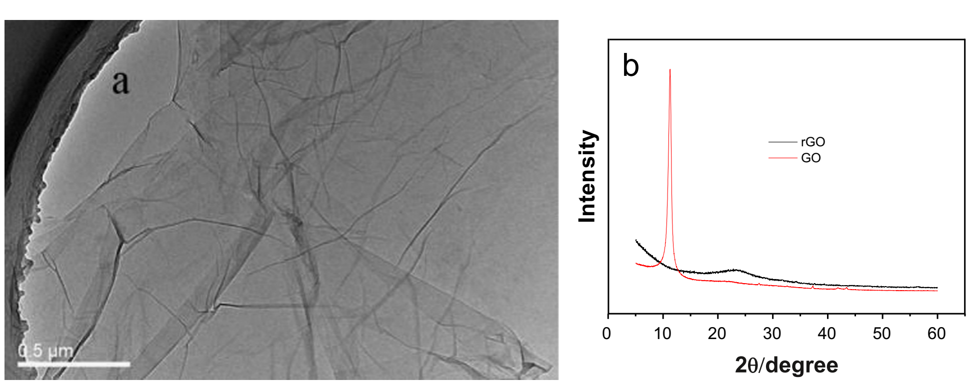

Fig. 1. TEM images of rGO (a) and XRD patterns of GO and rGO (b).