Electrochimica Acta 261 (2018) 284–288

Contents lists available at ScienceDirect

Electrochimica Acta

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

Preparation and enhanced visible-light photoelectrocatalytic activity of ternary TiO_2–ZnO/RGO nanocomposites

Xinying Pan [a, b, 1], Pan Yang [b, 1], Hui Nan [a], Lijun Yang [b], Huiyuan Chen [a, **], Xiaochong Zhao [b, *]

[a] *School of Chemical Engineering, Qinghai University, Xining 810016, China*
[b] *Institute of Materials, Chinese Academy of Engineering Physics, Jiangyou 621908, China*

ARTICLE INFO

Article history:
Received 19 September 2017
Received in revised form
13 November 2017
Accepted 22 December 2017
Available online 24 December 2017

Keywords:
Photocatalytic
Charge transfer
Hydrothermal method

ABSTRACT

TiO_2–ZnO/RGO nanocomposite was successfully synthesized via a hydrothermal method. The morphology, structure and photocatalytic performance were characterized by XRD, TEM, XPS, FT-IR, UV–vis DRS, CV and EIS. The photocatalytic performance of ZnO, TiO_2, TiO_2–ZnO and TiO_2–ZnO/RGO for degradation of methyl orange (MO) were explored under visible-light irradiation. Results showed that the TiO_2–ZnO/RGO nanocomposite exhibited the best photocatalytic activity due to the improved light utilization and charge transfer property, which is consistent with the EIS results of the charge-transfer resistance of $TiO_2 > TiO_2$–ZnO > TiO_2–ZnO/RGO > ZnO. Meanwhile, for TiO_2–ZnO/RGO nanocomposite in the decomposition of methyl orange (MO) under visible-light irradiation, the degradation kinetics was faster than the other samples, which could be completed within 100 min. The results suggested that TiO_2–ZnO/RGO nanocomposite has a promising in practice for applications in water and wastewater treatment.

1. Introduction

Water pollution is a common environmental concern worldwide, many approaches have been developed to degrade pollutants in water. Photocatalysis based on semiconductor such as TiO_2 and ZnO has been intensively investigated to degrade organic pollutant in water due to their low-cost, high efficiency and non-toxicity [1–10]. However, commercial application of these kinds of wide band-gap semiconductors (3.37 eV for ZnO and 3.2 eV for TiO_2) have been restricted by two challenging issues [11,12]: the high recombination rate and poor response in visible light range. These issues can be addressed by coupling semiconductor, Otieno Benton et al. [13] reported that TiO_2/ZnO nanocomposites could extend the light adsorption spectrum and reduce the recombination of photogenerated electron/hole pairs. Recently, carbonaceous materials hybridized with semiconductors have attracted much attention [14–17]. Among various carbonaceous materials, graphene is a unique material due to its high electron conductivity, specific surface area and unique optical properties. Yang et al. [18] and Chen et al. [19] demonstrate that reduced graphene oxide (RGO)–TiO_2 and RGO-ZnO hybrids can effectively increase the photocatalytic activity due to reduced recombination.

In this study, the TiO_2–ZnO nanocomposites were first synthesized by hydrothermal method, and then reduced graphene oxide (RGO) were introduced in TiO_2–ZnO nanocomposite to be the ternary TiO_2–ZnO/RGO nanocomposites to improve the light utilization and charge transfer property. The morphology, structure, composition and photoelectrocatalytic activity of the nanocomposites were analyzed by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), UV–vis diffuse reflectance spectra (UV–vis DRS), cyclic voltammograms (CV) and electrochemical impedance spectroscopy (EIS). The results showed that TiO_2–ZnO/RGO nanocomposites exhibited enhanced photocatalytic activity in the decomposition of methyl orange (MO) under visible-light irradiation. The degradation kinetics was fast, which could be completed within 100 min. Thus the hybrid semiconductor nanostructures promising in practice for applications in water and wastewater treatment.

---

* Corresponding author. Xiaochong Zhao

** Corresponding author. Huiyuan Chen

E-mail addresses: huiyuanchen97@163.com (H. Chen), zhaoxiaochong_2013@tsinghua.org.cn (X. Zhao).

[1] These authors contributed equally to this work and should be considered co-first authors.

https://doi.org/10.1016/j.electacta.2017.12.143

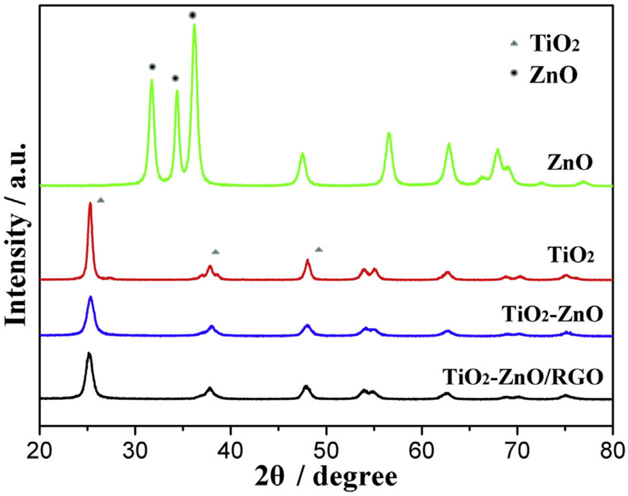

Fig. 1. XRD pattern of TiO_2, ZnO and as-synthesized nanocomposites.

2. Experimental

2.1. Synthesis of TiO_2–ZnO and TiO_2–ZnO/RGO nanocomposite

The TiO_2–ZnO nanoparticles were synthesized via a hydrothermal method using titanium tetrachloride and zinc sulfate heptahydrate. $TiCl_4$ and $ZnSO_4·7H_2O$ (1:1ratio) were dispersed in alkaline solution, completely disperse the components in the solvent by stirring. Later, the suspension was sealed in a teflonlined autoclave followed by heating at 180 °C for 10 h in blast oven. The resulting solution was centrifuged and thoroughly washed by deionized water and ethanol and dried at 60 °C for 10 h for further characterizations.

The preparation of graphene was referenced to the Hummers improved method [20,21]. Graphene oxide (GO, 2 mg) was dispersed in a mixed solution of deionized water(20 mL) and ethanol(10 mL), and sonicated for 1 h to obtain flaky homogeneous GO. Followed by the addition of TiO_2–ZnO nanocomposites (0.1 g), the suspension was obtained after stirring for 5 h. Then the suspension was placed in a Teflon autoclave at 160 °C for 8 h in blast oven. Finally, similar to our previous works, the resulting solution was centrifuged and thoroughly washed by deionized water and dried at room temperature for 10 h for future characterizations.

2.2. Characterizations

The crystal structure of the as-prepared catalysts were observed using XRD (Bruker D8, Japan), operating at 40 kV and 40 mA with Cu-Ka monochromatic radiation, in Bragg's angle range of 20 to 80°. The morphology was recorded on TEM (JEM 2010, Japan). XPS experiments was performed on a VG MultiLab 2000 system with a monochromatic Al Ka X-ray source. The chemical characteristics of samples were analyzed using FT-IR model Nicolet 380 (Thermo Fisher Scientific, Waltham, MA, USA). The optical absorption spectra was carried out on a UV–vis DRS (LUH 4150, Japan). The CV analysis was performed in the presence of a 0.1 M KOH solution at a scan rate of 20 mV s^{-1} in the potential range of −2 V to 2 V. The EIS measurements were also performed in the presence of a 0.1 M KOH solution by applying an AC voltage with 10 mV amplitude in the frequency range of 10 Hz–100 kHz under open circuit potential conditions. The CV and EIS were collected at ZAHNER Zennium (Germany).

3. Results and discussion

3.1. The analysis of morphology and structure performance

Fig. 1 shows XRD pattern of TiO_2, ZnO and as-synthesized TiO_2–ZnO/RGO nanocomposites. The peaks at 2θ values of 25.16°, 37.96° and 47.98° can be indexed to the (101), (004) and (200) planes of anatase TiO_2 and the peaks at 2θ values of 31.74°, 34.3° and 36.2° can be indexed to the (100), (002) and (101) crystal planes of ZnO [22–24]. The XRD pattern of TiO_2–ZnO nanocomposite shows diffraction peaks at 25.16°, 38.83° and 47.67°, it is similar to TiO_2–ZnO/RGO nanocomposites, no obvious diffraction peaks of ZnO and RGO are observed due to the low content of ZnO and RGO in the nanocomposites.

Fig. 2(a) is TEM image of prepared RGO, which reveals flexible and wrinkled sheet of RGO. Fig. 2(b) is TEM image of TiO_2–ZnO/RGO nanocomposites that gives clear evidence for the formation of the nanocomposite. It could be expected that an intimate interfacial contact exist in TiO_2–ZnO/RGO nanocomposites which might contribute an excellent conductivity [25].

XPS analysis was performed to investigate the surface composition and chemical states of materials. Fig. 3 is the XPS spectrum of TiO_2–ZnO/RGO nanocomposite and Zn 2p region is inserted. The C 1s, Ti 2p and O 1s can be observed in the full spectra. The binding energy of the C 1s and O 1s regions exhibited peaks at 284.7 and

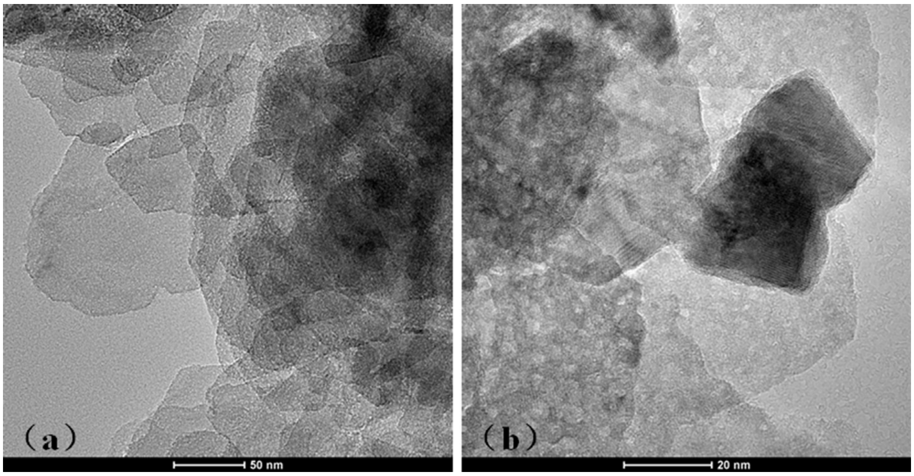

Fig. 2. TEM images of (a) RGO and (b) TiO_2–ZnO/RGO nanocomposite.