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Highly effective photocatalysts based on carbon nanofibers decorated with TiO_2 and CdSe under visible light

Seung Hwa Yoo[a,1], Sung-In Lee[a,2], Han-Ik Joh[b], Sungho Lee[a,c,*]

[a] Carbon Composite Materials Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology, 92 Chudong-ro, Bongdong-eup, Wanju-gun, Jeollabuk-do 55324, Republic of Korea
[b] Department of Energy Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, Republic of Korea
[c] Department of Nano Material Engineering, Korea University of Science and Technology, 217 Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea

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ABSTRACT

A highly effective photocatalyst based on CdSe quantum dots (QDs) and TiO_2 nanoparticles well-dispersed on carbon nanofibers (CNFs), named as CdSe/TiO_2/CNF was synthesized by simple successive ionic layer adsorption and reaction (SILAR) method on TiO_2/CNF. It was verified by spectroscopic analysis that CdSe QDs were successfully synthesized and some aggregations and oxide phases existed in CdSe/TiO_2/CNF. The photocatalytic activity of CdSe/TiO_2/CNF was demonstrated for decomposition of methylene (MB) aqueous solutions. The tests were performed for different MB concentrations and light irradiation. It was found that CdSe/TiO_2/CNF showed high photocatalytic activity under visible light irradiation and even high MB concentrations.

Introduction

Photocatalysts work under lights, which are absorbed to provide electron-hole pairs with free radicals by reactions [1–3]. One of the mostly used photo-catalysts is titanium dioxide (TiO_2) because of its high catalytic performance to create hydroxyl radicals in water, leading to decomposition of organics by photo-oxidation [4,5]. It is well known that TiO_2 absorbs only ultraviolet (UV) light due to a large band gap energy (3.2 eV), which restrict more various and efficient usage under sunlight because sunlight consists of infrared of 49%, visible of 46% and UV light of 5% [6,7]. Therefore, maximizing photocatalytic activity by visible light has been studied with semiconducting inorganics, metal oxides or non-metal element doping which generate electron-hole pairs when visible light is absorbed [8–16].

Cadmium selenide (CdSe) has been used as semiconductor, having a band gap of 1.75 eV, which is much narrower with a higher conduction band-edge compared to TiO_2 [8,17]. These render CdSe to be an excellent candidate for transferring photo-generated electrons from CdSe to TiO_2 under visible light in CdSe decorated TiO_2, which enhance photo-catalytic activities. Wang et al. reported that CdSe quantum dots (QD) have higher energy level difference between each CdSe QD and TiO_2 conduction band-edges, compared to bulk CdSe [18,19]. Therefore, CdSe QD is more efficient in charge carrier separation by much faster electron transferring. There are several representative routes to synthesize CdSe-QD on TiO_2 such as ligand exchange [20], linker-assisted hybridization process [17,21], chemical bath deposition [22], and electrophoresis [23]. However, these methods require chemical synthesis to obtain CdSe QD using cadmium precursor and selenium powder and further steps to decorate QD on TiO_2. In this study, CdSe was simply deposited on TiO_2 supported on carbon nanofibers (CNFs), named as CdSe/TiO_2/CNF, and was utilized as a photocatalyst to decompose aqueous methylene blue as a model pollutant.

* Corresponding author at: Carbon Composite Materials Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology, 92 Chudong-ro, Bongdong-eup, Wanju-gun, Jeollabuk-do 55324, Republic of Korea.
E-mail address: sunghol@kist.re.kr (S. Lee).
[1] Current address: Biomedical Manufacturing Technology Center, Korea Institute of Industrial Technology, 59 Yangho-gil, Yeongcheon-si, Gyeongsangbuk-do 38822, Republic of Korea.
[2] Current address: LG Chem R&D Campus Daejeon, 188 Munji-ro, Yuseong-gu, Daejeon 34122, Republic of Korea.

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Experimental

Materials

Polyacrylonitrile (PAN), titanium isopropoxide, cadmium nitrate tetrahydrate, selenium dioxide, sodium borohydride, and dimethylformamide (DMF) were purchased from the Sigma Aldrich Co. All chemicals were analytical grade and used without purification.

Preparation of TiO_2/CNF

Solution preparation and electrospinning TiO_2 precursor/PAN nanofiber mat

8 w% PAN solution was prepared by dissolving 4 g of PAN in 46 g of DMF for 2 h at 60 °C. Separately, 4 g of titanium isopropoxide was mixed with 0.3 g of acetic acid dropwise, and the mixture was slowly added to as-prepared PAN solution. The final solution was rigorously stirred until it was completely dissolved.

Heat treatment to convert TiO_2 precursor/PAN to TiO_2/CNF nanofiber mat

The as-prepared polymeric nanofiber mat was stabilized followed by carbonization. For stabilization, the polymeric nanofiber mat was heated in air at 250 °C for 120 min in a forced convection oven. Then, the stabilized mats were carbonized at 1600 °C under N_2 atmosphere. The temperature was raised from 25 to 1600 °C at 5 °C/min rate with no holding time at the final temperature. Subsequently, the carbonized mats were activated in oxygen atmosphere with 60 min holding time at 500 °C.

Preparation of CdSe/TiO_2/CNF

CdSe/TiO_2/CNF was prepared through a successive ionic layer adsorption and reaction (SILAR) method. The as-prepared TiO_2/CNF mat was dipped into an ethanol solution containing 0.03 M cadmium nitrate tetrahydrate for 30 s to allow Cd^{2+} to be absorbed; then, it was rinsed with ethanol. Subsequently, the sample was dipped into an ethanol solution containing 0.03 M selenium dioxide and sodium borohydride for 30 s, where the pre-adsorbed Cd^{2+} reacted with Se^{2-} to form CdSe. After finishing the SILAR method, the treated samples were grounded with an agate mortar to finally give a powder form of CdSe/TiO_2/CNF.

Photocatalytic decomposition test

0.1 g of CdSe/TiO_2/CNF powder was added in 100 mL methylene blue (MB) solution of 50, 100, and 150 ppm initial concentration. The mixture of MB solution and CdSe/TiO_2/CNF powder was stirred for 2 h to achieve adsorption-desorption equilibrium. A Xe lamp (US 66983 Arc Lamp Source 200–500 W, Newport.) with a 420 nm cut-off filter (GG-420, 2″ Sq. Longpass Filter, Edmund optics.) was used for the photocatalytic decomposition tests by utilizing visible light. In case to utilize visible + UV light, the cut-off filter was eliminated to use the full spectrum of Xe lamp. At given time intervals (2 min), 3 mL of sample solutions were collected and CdSe/TiO_2/CNF powder was removed by filtration. The residual concentration of MB for each time intervals were measured with an UV–vis spectrometer (V670, JASCO Inc.).

Analysis of material properties

The morphology of CdSe/TiO_2/CNF was observed using a field emission scanning electron microscope (FE-SEM, NOVA Nano SEM 450) and a transmission electron microscope (TEM, Tecnai G2 F20, FEI). X-ray diffraction was carried out using a D/MAX2500 V PC X-ray diffractometer (Rigaku, Japan) with monochromated Cu Kα as a source between 2θ of 10 and 80° at a scan rate of 3°/min. X-ray photoelectron spectra were obtained (Thermo Scientific, K-alpha) using monochromated Al Kα (1486.6 eV) X-rays at a pressure less than 3×10^{-7} Torr.

Results and discussion

In our previous study, well-dispersed TiO_2 nanoparticles on carbon nanofibers (CNFs) were prepared, and a significantly

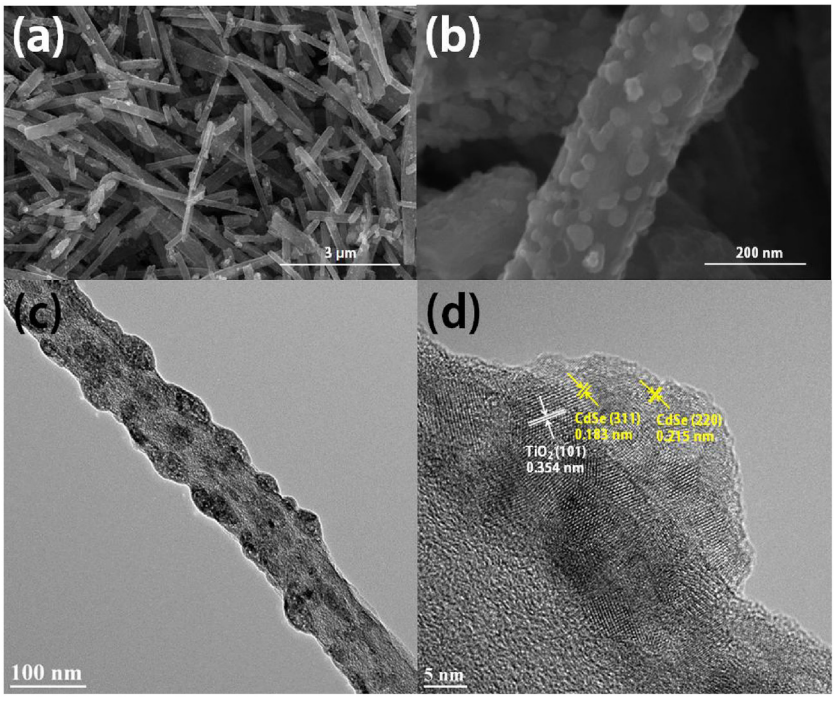

Fig. 1. (a, c) SEM and TEM images of CdSe/TiO_2/CNF powder. (b, d) Higher magnification of (a) and (c), respectively.

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