Facile preparation novel SnO_2@UiO-66/rGO hybrid with enhanced photocatalytic activity under visible light irradiation

Xiaohua Zhao [a], Xiang Liu [b, c, *], Xin Liu [a], Wei Zhang [a], Zhenya Zhang [a]

[a] *School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China.*

[b] *Institute of Chemical and Materials Engineering, Zhenjiang College, Zhenjiang 212000, China.*

[c] *Biofuels Institute of Jiangsu University, Zhenjiang 212013, China.*

Email:liuxiang0222@126.com

Experimental section

Materials

All chemical reagents were of analytical grade and were used as received.

Preparation of ultrafine SnO_2 NPs

2~8 nm SnO_2 NPs was adopted the method reported by Wu's group.[1] Typically, lysteine (Lys, $C_6H_{14}N_2O_2$, > 99% purity, 10 mmol) was dissolved in 20 mL of deionized water to form solution A. $SnCl_4\cdot 5H_2O$ (Analytic reagent, AR, 2 mmol) was dissolved in 20 mL of deionized water to form solution B, followed by adding solution A into solution B with stirring for 12 h at room temperature. Then, the mixture was sealed into a 50 mL Teflon-lined autoclave, heated to 180 °C, and maintained at this temperature for 12 h. After the autoclavewas cooled down to room temperature naturally, the products were collected and washed with deionized water and then absolute alcohol, followed by drying at 60 °C for 4 h.

Preparation of PVP-stabilized SnO_2 NPs [2]

SnO_2 NPs were dipersed in 20 ml of chloroform (0.5 mg/ml). A solution of PVP (250 mg, Mw =10,000) in chloroform (10 ml) was then added. After the mixture was stirred for 24 hours, the PVP-stabilized SnO_2 NPs were precipitated with hexane and collected by centrifugation at 6,000 rpm for 5 minutes. The sample was cleaned with chloroform and hexane to remove the excess free PVP. Finally, the PVP-stabilized NPs were redispersed in methanol (0.25 mg/ml).

Preparation of SnO_2@UiO-66 composite

SnO_2@UiO-66 composite was prepared *via* a simply solvothermal method.

Tyically, $ZrCl_4$ (0.232 g, 1.0 mmol), terephthalic acid (0.166 g, 1.0 mmol) and acetic acid (3 mL) were dissolved in DMF (50 mL). Subsequently, 1 mL of the self-prepared PVP-stabilized SnO_2 NPs suspension was added, and the mixture was ultrasonically treated for about 15 min. Finally, the solution was transferred to a 100 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated in an oven at 120 ^oC for 24 h under autogenously pressure. After cooled naturally, the sample was purified with anhydrous methanol for several times.

Preparation of SnO_2@UiO-66/rGO composite

GO was prepared from purified natural graphite according to a modified Hummers' method.[3] The SnO_2@UiO-66/rGO composite was synthesized by solvothermal treatment. In a typical experiment, 25 mg of GO and the as-prepared 50 mg of SnO_2@UiO-66 were ultrasonically dispersed in 20 mL of EtOH/ ethylene glycol (V/V=9/1) for about 15 min. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated in an electric oven at 120 ^oC for 8 h, and then cooled to room temperature naturally. The product was collected by centrifugation and washed with alcohol three times.

Characterization

XRD patterns were obtained by a D/MAX 2500PC X-ray diffractometer equipped with Cu Kα radiation (λ = 1.54 Å). Raman measurements were performed with a DXR spectrophotometer at 514 nm laser excitation. The morphologies were observed using field emission scanning electron microscopy (FESEM, JSM-7001F), transmission electron microscopy (TEM, Philips Tecnai 12) and HRTEM (JEM-2100), respectively. The specific surface area was measured using a nitrogen gas sorption surface area tester (NOVA 3000e) and calculated by the Brunauer-Emmett-Teller (BET) method. The nitrogen adsorption and desorption isotherms were measured at 77 K. The samples were dried in vacuum at 80 ^oC for 5 h and then degassed at 150 ^oC for 8 h prior to determination. UV-vis diffuse reflection spectroscopy (DRS) was performed on a SHIMADZU UV-2550 spectrophotometer in the range from 200 to 800 nm equipped with an integrated sphere attachment and with $BaSO_4$ as the reference. Zeta potential analysis was performed on a Malvern zetasizer instrument (Nano ZS90). 20 mg of the samples were suspended in 50 mL deionized water and dispersed by sonication at room temperature before each point was measured. The photoluminescence (PL) spectra of the photocatalyst were obtained by a Fluorescence

Lifetime Spectrometers (QuantaMaster™ 40) at room temperature with excitation wavelength of 305 nm. The electrochemical impedance spectra (EIS) were performed at a Versatile Multichannel Potentiostat 2/Z (VMP2) electrochemical workstation. This measurement was performed on a round three-electrode system, in which, saturated Ag/AgCl worked as the reference electrode, the platinum wire worked as the counter electrode, and the as-prepared photocatalysts modified indium-tin oxide (ITO) glass worked as the working electrode. The working electrode was modified as follows: 10 mg SnO_2@UiO-66 and SnO_2@UiO-66/rGO composites dispersed in 0.5 ml DMF with ultrasonic bath for 30 min, respectively. The as-prepared slurry was dripped on the 1×1 cm^2 ITO glass and dried at 60°C for 4 h, the content of the SnO_2@UiO-66 slurry dripped on the ITO glass was same with SnO_2@UiO-66/rGO, and the working electrode was thus obtained. The working electrodes were immersed in a 0.2 M Na_2SO_4 aqueous solution without any additive for 30 s before measurement. EIS was applied at open circle voltage with amplitude of 10 mV in a frequency range of 100 kHz to 0.1 Hz. The potential of the working electrode against a Pt counter electrode was set at 0.0 V.

The evaluation of photocatalytic activities

The photocatalytic activities were evaluated by the degradation of RhB dyes under visible light. In a typical experiment, 40 mg of the photocatalyst was suspended in 100 mL aqueous solution of RhB (50 mg L^{-1}). Before being exposed to any form of illumination, the suspensions were stirred in the dark for 1 hour to ensure that adsorption-desorption equilibrium of RhB on the sample surface was established. The suspensions of catalyst and RhB dye were then irradiated by a 300 W Xe lamp (300 W, PLS-SXE300). To measure the photocatalytic activity under visible irradiation, a 420 nm UV-cutoff filter was used to provide the visible-light. During the illumination process, about 5 mL of suspension was taken out at an interval of 30 min and centrifuged to separate the photocatalysts. The degradation process was monitored by concentration changes of the RhB at its typical absorption wavelength (553 nm), using the DU 800 UV-vis spectrophotometer. The percentage of degradation is reported as C/C^0, where C is the absorption of the dye solutions taken at each time interval at the maximum absorption peak, and C^0 is the absorption of the initial concentration of the dye solution. We also studied the recyclability of the SnO_2@UiO-66/rGO catalysts with the best photocatalytic efficiency. The photocatalysts were separated and washed by centrifugation with ethanol and deionized water for 3 times to remove the residual organic species, and reused for the next run.

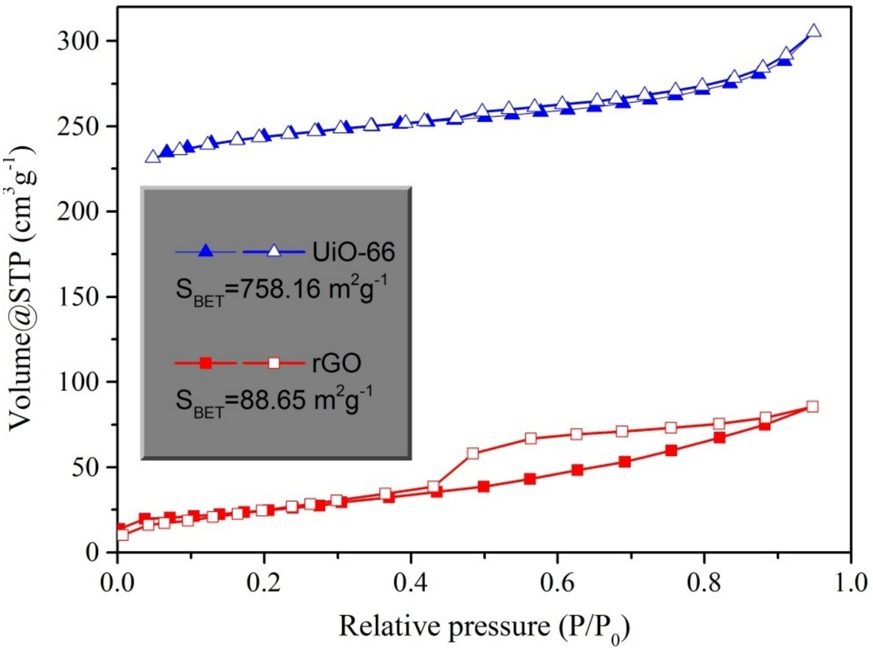
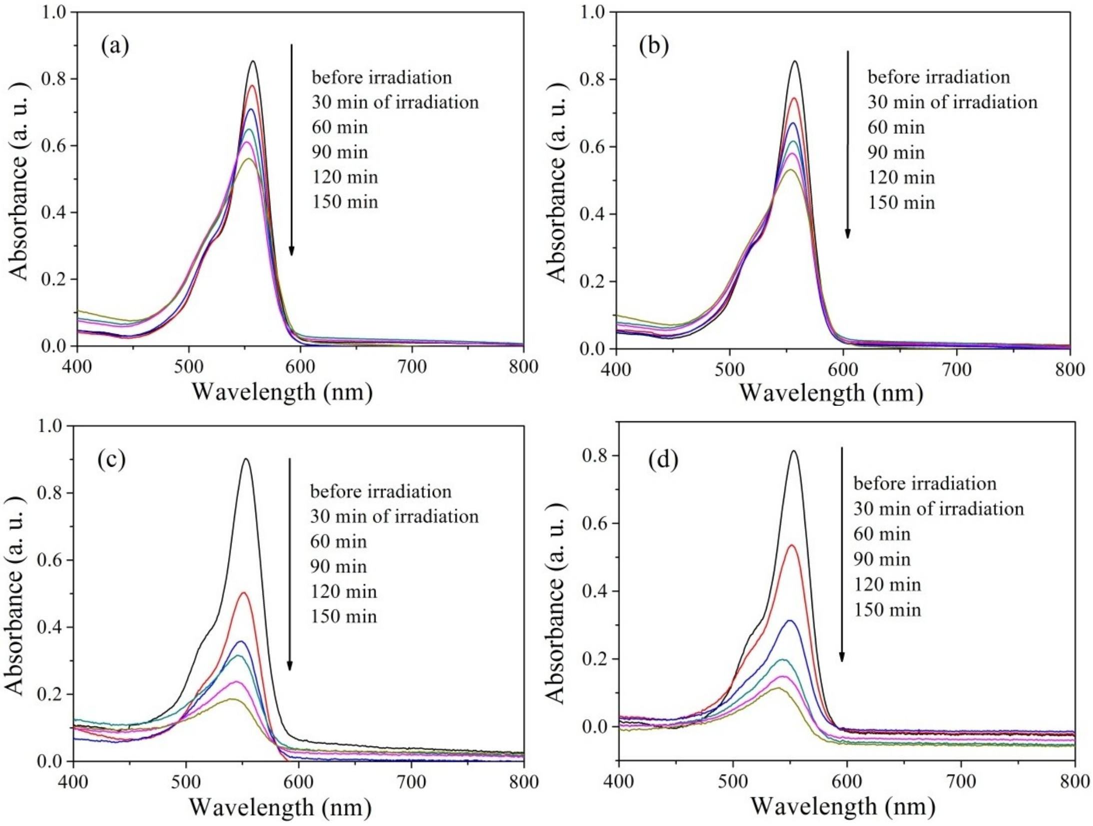


Fig. S1 N_2 adsorption-desorption isotherms of UiO-66 and rGO



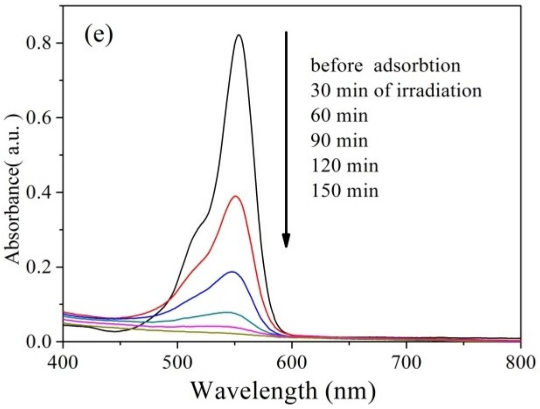


Fig. S2 Absorptiono spectra of the adsorptive RhB aqueous solutions with time in the presence of (a)SnO_2, (b)P25 TiO_2, (c) SnO_2@UiO-66, (d) SnO_2@rGO and (e) SnO_2@UiO-66/rGO catalysts under visible-light irradiation

References:

1. S. S. Wu, H. Q. Cao, S. F. Yin, X. W. Liu, X. R. Zhang, J. Phys. Chem. C 113 (2009) 17893-17898.
2. G. Lu, S. Z. Li, Z. Guo, O. K. Farha, B. G. Hauser, X. Qi, Y. Wang, X. Wang, S. Han, X. Liu, J. S. Duchene, H. Zhang, Q. Zhang, X. Chen, J. Ma, S. C. J. Loo, W. D. Wei, Y. Yang, J. T. Hupp, F. W. Huo, Nature Chem., 4 (2012) 310-316.
3. W. S. Hummers, R. E. Offeman, J. Am. Chem. Soc., 80 (1958) 1339-1339.