Supplementary Material

Efficient adsorption and full spectrum photocatalytic degradation of low concentration PPCPs promoted by graphene/TiO_2 nanowires hybrid structure in 3D hydrogel networks

Yajie Hu[1], Yanan Yang[1], Jiejing Zhang, Shengnan Jin, Hong Zheng*

Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China

1 The first coauthors

1. Experimental section

1.1 Preparation of graphene oxide (GO) and TiO_2 nanowires

GO was prepared using the modified Hummers' method.[1] Briefly, natural flake graphite powder (3 g), $NaNO_3$ (1.5 g) and $KMnO_4$ (9 g) were successively added to concentrated H_2SO_4 (46 mL) under stirring, while the temperature was kept at 0 ◦C using an ice bath. The mixture was continued to stir for 30 min until the solution became dark green. Then the system was heated up to 30 ℃ under stirring and kept for 30 min. 140 mL of deionized water was slowly added the mixture and the mixture was stirred at 90 ℃ for 15 min. After that, the color of mixture changed from dark green to brown or golden brown with the addition of 10 mL H_2O_2 (30%). Finally, the mixture was centrifuged and washed for several times, the obtained precipitate was filtered, and dried to obtain GO. GO was sonicated for 30 min to obtain exfoliated GO before use.

TiO_2 nanowires was prepared using hydrothermal method reported by Pan et al.[2] with a small modification. 2.4g P25 TiO_2 nanopowders were added into 80 mL of 10 M KOH aqueous solution and stirred for 30 min, and the homogeneous suspension was transferred to a Teflon-lined stainless-steel autoclave (100 mL capacity). Then the autoclave was sealed and kept at 200 °C for 24 h. After cooled down naturally to room temperature, the obtained products were immersed in 0.1 M HCl aqueous solution under stirring for 5 min. After that, the sample was quickly washed until the pH value was equal to 7. After being recovered by vacuum filtration, the wet products were dried at 70 °C for 6 h, then heated at the heating rate of 5 °C/min and kept at 550 ℃ for 2 h in a muffle furnace to obtain TiO_2 nanowires.

1.2 Characterization of the samples

The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 advance diffractometer with Cu Kα radiation (λ= 0.15418 nm) at 40 kV and 100 mA. The Raman spectra were collected on a laser confocal Raman spectrometer (Invia, Renishaw, UK) with 2 cm^{-1} acquisition resolution, using Ar^+ laser (532 nm) as the excitation light source. TEM image of GNW was obtained on a Hitachiht 7700 transmission electron microscope (TEM) operated at 100kV. The morphologies of rGO hydrogel, rGO/P25, and rGO/GNW were recorded on a JSM-7001F field-emission scanning electron microscopy (FESEM, Japan) operated at 10.0 kV. UV-Vis DRS spectra were recorded using a Hitachi UV-3100 spectrophotometer in the range of 200-800 nm. The FT-IR spectra were acquired on a PerkinElmer Frontier infrared spectrometer. The spectral range was recorded in the range of 4500-400 cm^{-1} by the KBr pellet technique. The surface elemental composition and chemical states of the samples were examined by an X-ray photoelectron spectrometer (ESCA PHI-5300 XPS) with a pass energy of 50 eV and an X-ray excitation source of Al Kα. The values of binding energies were calibrated with respect to C1s peak at 284.80 eV. Nitrogen adsorption-desorption data of the samples were obtained at 77.35 K using a Quantachrome ASIQM0002-4 BET analyzer, and their pore size distribution was acquired from the N_2-desorption branch using the BJH method. The photoluminescence (PL) spectra of the samples were obtained on a Hitachi F-4600 florescence spectrophotometer with the excitation wavelength of 430 nm. Electrochemical impedance spectroscopy (EIS) was collected via an electrochemical analyzer (CHI760E, China) in the standard three-electrode system using as-prepared samples as the working electrode, a silver chloride electrode as reference, a platinum wire parallel as a counter electrode and 0.1 M sodium sulfite as electrolyte.

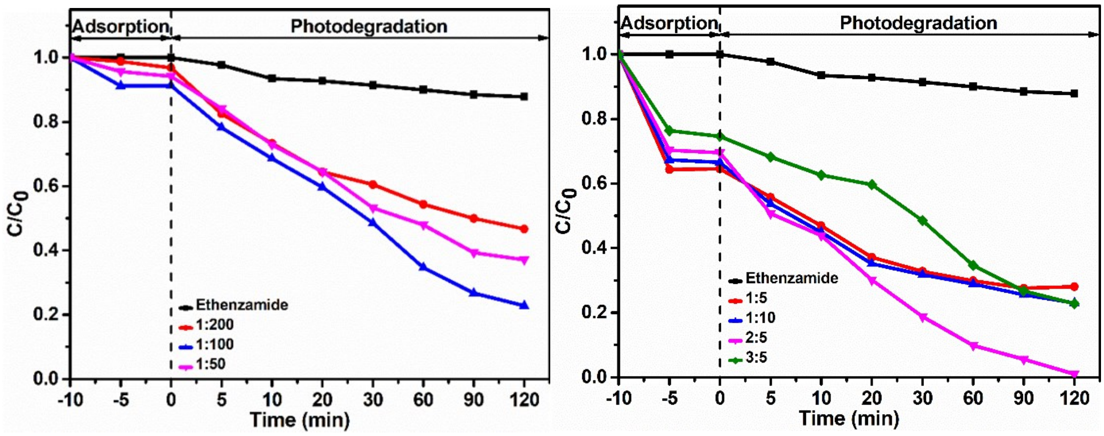

Fig. S1 The effects of mass ratios of rGO to TiO_2 (a) and rGO to GNW (b) on the photocatalytic degradation of ethenzamide by GNW and rGO/GNW under UV irradiation, respectively.

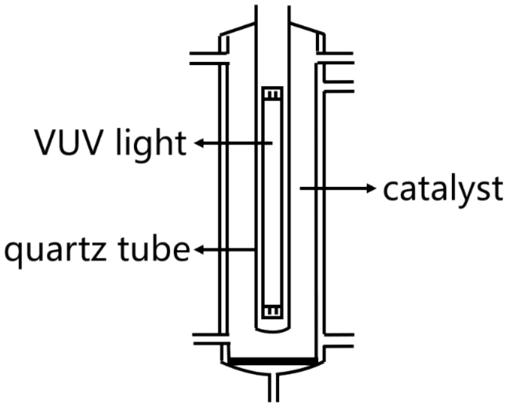

Fig. S2 VUV photocatalytic reactor.

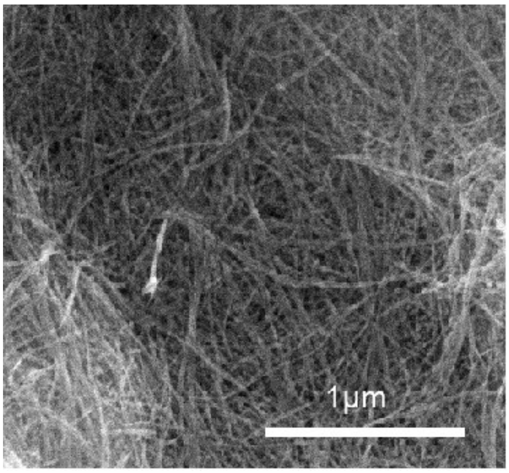

Fig. S3 FESEM image of TiO_2 nanowires.

Fig. S4 The picture of the as-prepared rGO/GNW.

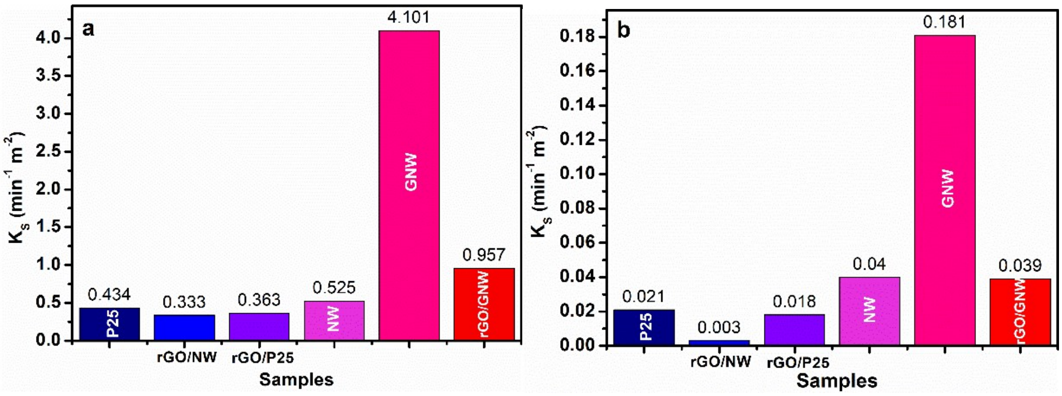

Fig. S5 The rate constant normalized to the specific surface area under (a) VUV and (b) UV irradiation.

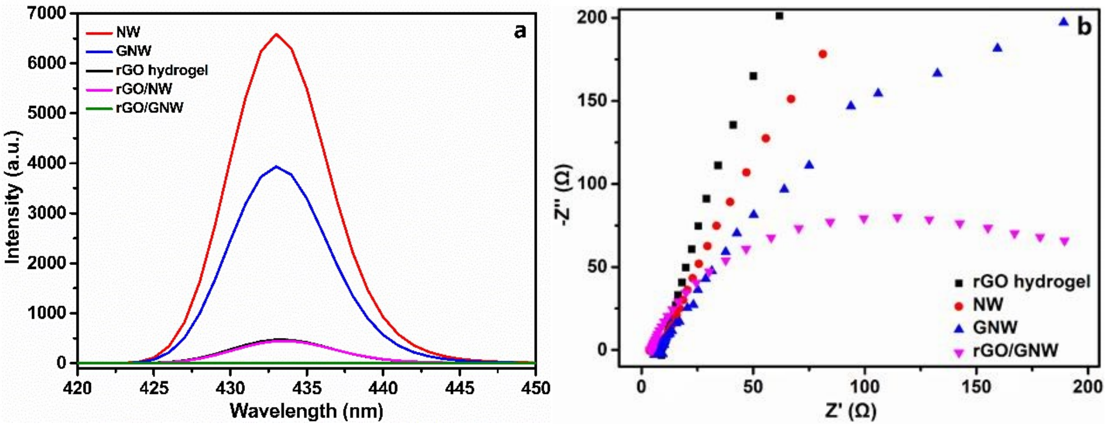

Fig. S6 PL (a) and EIS spectra (b) of the samples.

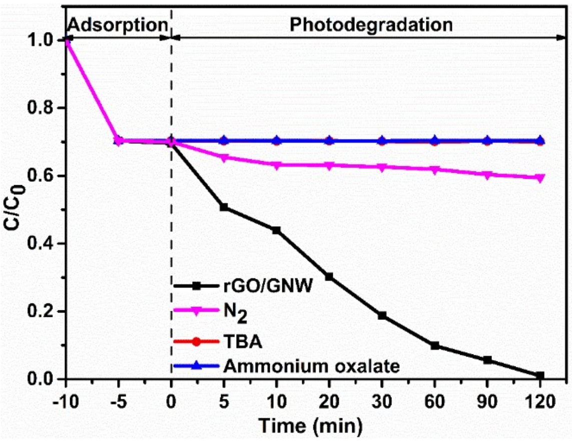

Fig. S7 The effects of different capture agents on the photocatalytic degradation of ethenzamide by the as-prepared rGO/GNW under UV light irradiation.

References

1. M. Nawaz, W. Miran, J. Jang and D.S. Lee, *Appl. Catal. B: Environ.*, 2017, **203**, 85-95.
2. X. Pan, Y. Zhao, S. Liu, C.L. Korzeniewski, S. Wang and Z. Fan, *Acs Appl. Mater. Interfaces*, 2012, **4**, 3944-3950.