

Supporting Information for the manuscript

A low-temperature and one-step method for fabricating ZnIn₂S₄-GR nanocomposites with enhanced visible light photoactivity

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Synthesis of graphene oxide (GO). In detail, 2 g of graphite powder (supplied from Sinopharm Chemical Reagent Co., Ltd., China) was put into a mixture of 12 mL of concentrated H₂SO₄, 2.5 g of K₂S₂O₈, and 2.5 g of P₂O₅. The solution was heated to 80 °C in an oil-bath kept stirring for 24 h. The mixture was then carefully diluted with 500 mL of deionized (DI) water, filtered, and washed until the pH of rinse water became neutral. The product was dried under ambient condition overnight. This pre-oxidized graphite was then subjected to oxidation described as follows. In a typical procedure, pre-oxidized graphite powder was added to a mixture of 120 mL of concentrated H₂SO₄ and 30 mL HNO₃ under vigorous stirring, and the solution was cold to 0 °C. Then, 15 g of KMnO₄ was added gradually under stirring and the temperature of the mixture was kept to be below 20 °C by cooling. Successively, the mixture was stirred at room temperature for 96 h, and then diluted with 1 L of DI water in an ice bath to keep the temperature below 50 °C for 2 h. Shortly after the further diluted with 1 L of DI water, 20 mL of 30% H₂O₂ was then added to the mixture and a brilliant yellow product was formed along with bubbling. The mixture was filtered and washed with 1:10 HCl aqueous solution to remove metal ions followed by DI water to remove the acid. The filter cake was then dispersed in water by a mechanical agitation. Low-speed centrifugation was done at 1000 rpm for 2 min. The supernatant then underwent two more high-speed centrifugation steps at 8000 rpm for 15 min to remove small GO pieces and water-soluble byproduct. The final sediment was redispersed in water with mechanical agitation or mild sonication using a table-top ultrasonic cleaner, giving a solution of exfoliated GO. The GO separated in the form of a dry, brown powder. It is well documented to utilize GO as the precursor of graphene (GR) to synthesize the reduced graphene oxide (RGO)-semiconductor composite photocatalysts.^{S1-S5}

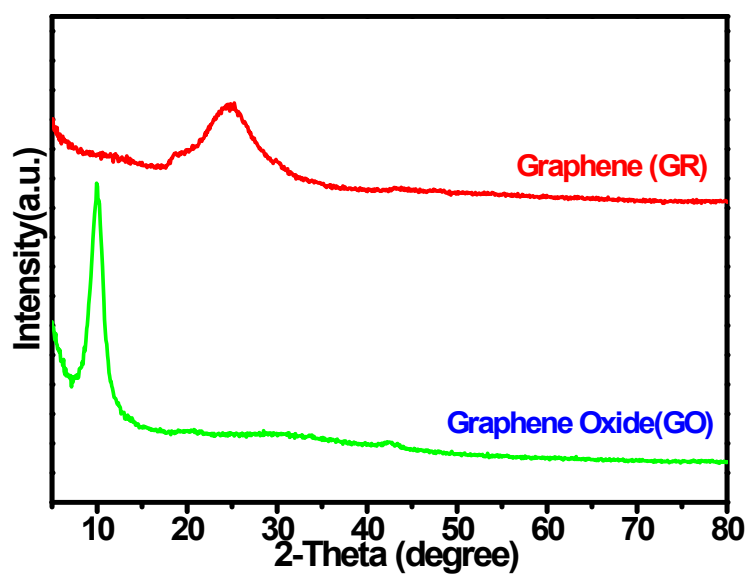


Fig. S1 XRD patterns of the samples of GO and GR obtained from the reduction of GO.

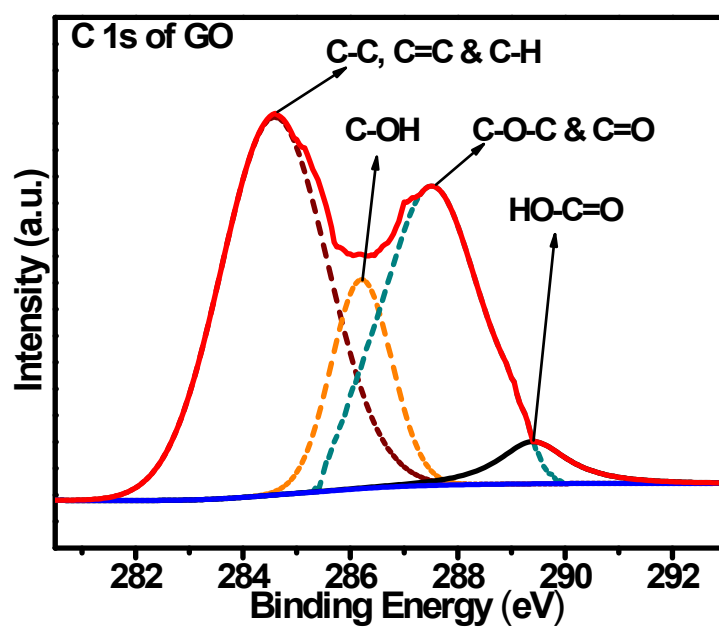


Fig. S2 C1s XPS spectrum of GO.

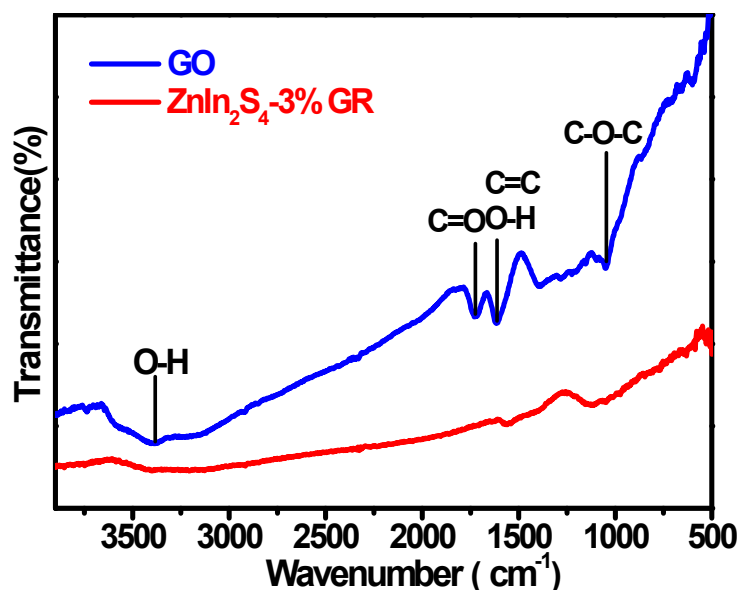


Fig. S3 The Fourier transformed infrared spectra (FT-IR) of original GO and ZnIn₂S₄-3%GR nanocomposite at different range of wavenumber.

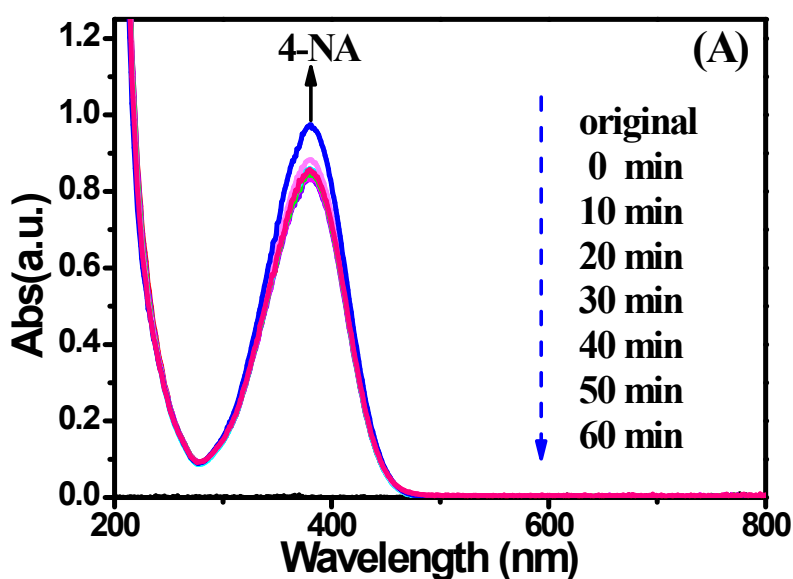


Fig. S4 UV-vis absorption spectra of 4-NA aqueous solution over ZnIn₂S₄-3%GR nanocomposite under visible light irradiation ($\lambda > 420$ nm) with the addition of ammonium formate as quencher for photogenerated holes in the absence of N₂.

Note: The intensity of the main absorbance of 4-NA solution around 380 nm slightly decreases as the irradiation time is increased and no other new peak appears, initially implying that no other products are formed at the same time.

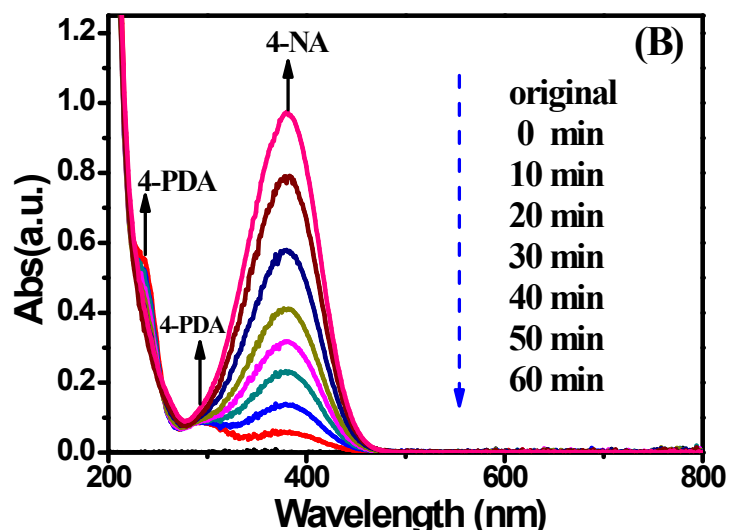


Fig. S5 UV-vis absorption spectra of 4-NA aqueous solution over ZnIn_2S_4 -3%GR nanocomposite under visible light irradiation ($\lambda > 420 \text{ nm}$) with the addition of ammonium formate as quencher for photogenerated holes under N_2 purge.

Note: The absorption at 380 nm decreases and absorption at 240 nm and 300 nm increases concomitantly, which can be ascribed to the reduction of 4-NA and the formation of 4-PDA, respectively. No other absorption changes demonstrate that there are only two principal species, 4-NA and 4-PDA and no other products are formed at the same time.

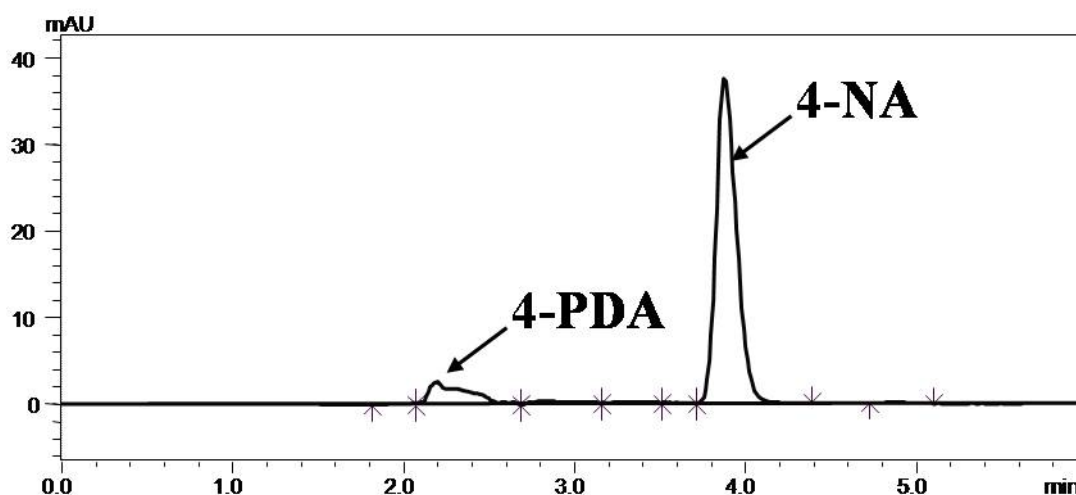


Figure S6 HPLC analysis images of the products in the aqueous phase over the ZnIn_2S_4 -3%GR nanocomposite under visible light irradiation ($\lambda > 420 \text{ nm}$) with the addition of ammonium formate as quencher for photogenerated holes in the absence of N_2 .

Note: In the absence of N_2 , only a trace amount of 4-NA is reduced to 4-PDA, which is too slight to be detected in UV-vis spectral change in **Fig. S4**, and no other products can be observed, further indicating that no other products are formed.

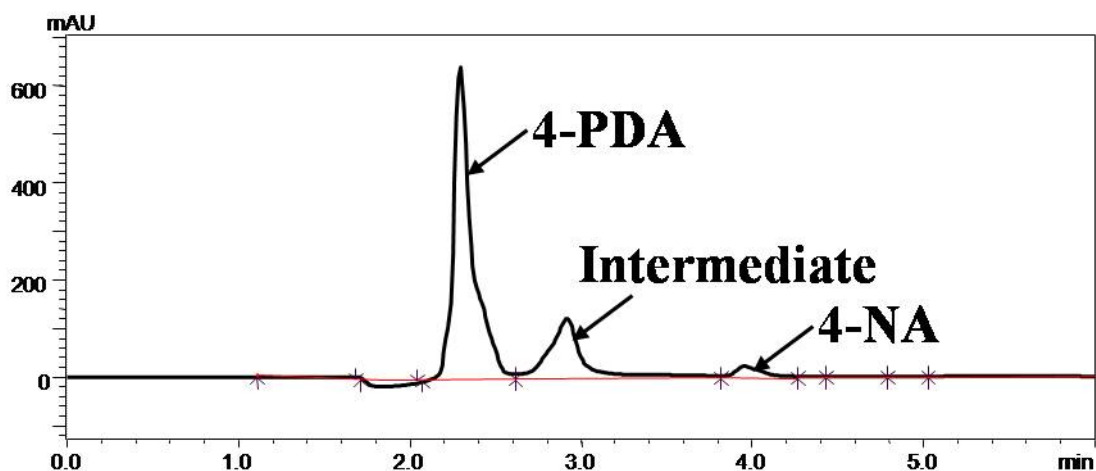


Figure S7 HPLC analysis images of the products in the aqueous phase over the ZnIn₂S₄-3%GR nanocomposite under visible light irradiation ($\lambda > 420$ nm) with the addition of ammonium formate as quencher for photogenerated holes under N₂ purge.

Note: 4-NA is largely reduced to 4-PDA, and the primary product of 4-PDA is detected. In addition, a minor peak observed around 3 min could be ascribed to intermediate products^{S6}.

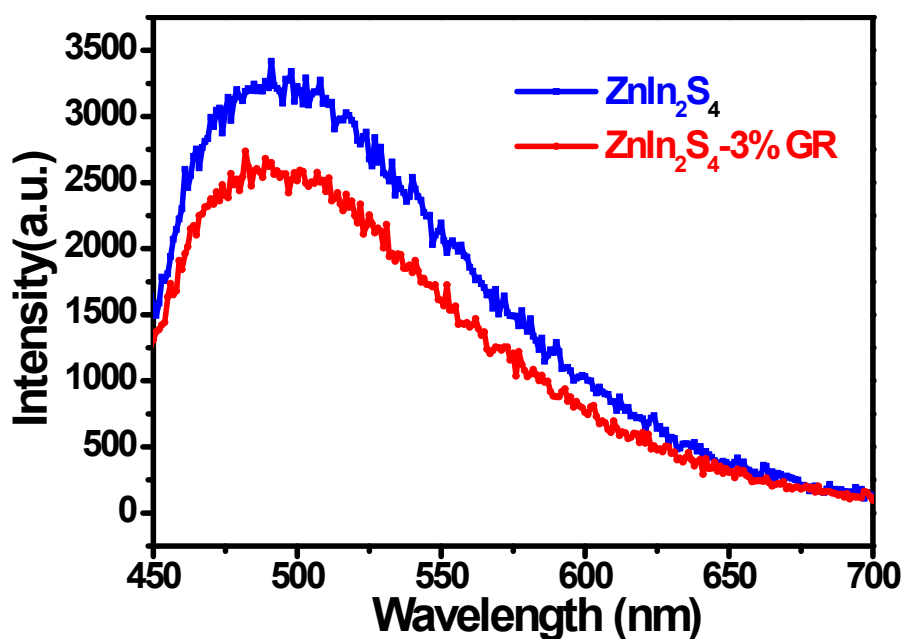


Fig. S8 Photoluminescence (PL) spectra of blank ZnIn₂S₄ and ZnIn₂S₄-3%GR nanocomposite.

Table S1 BET surface area of blank ZnIn₂S₄ and ZnIn₂S₄-GR nanocomposites with different weight addition ratios of GR

Samples	ZnIn ₂ S ₄	ZnIn ₂ S ₄ -1%GR	ZnIn ₂ S ₄ -3%GR	ZnIn ₂ S ₄ -5%GR	ZnIn ₂ S ₄ -10%GR
S _{BET} (m ² /g)	40	46	50	54	63

References

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