Electronic Supplementary Information

A room-temperature solid-state route for the synthesis of graphene oxide-metal sulfide composites with excellent photocatalytic activity

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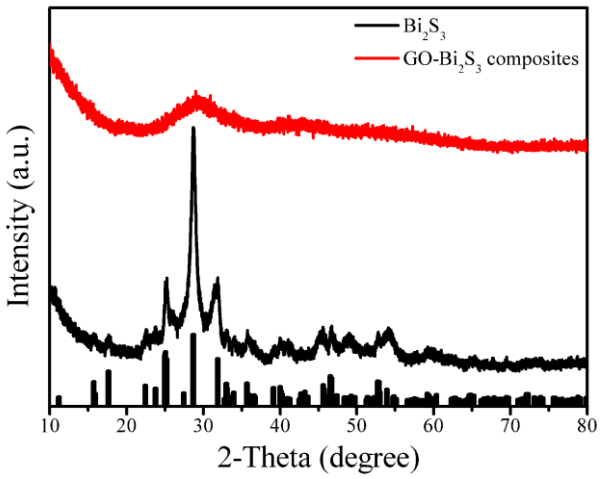

Fig. S1 XRD patterns of Bi_2S_3 and GO-Bi_2S_3 composites.

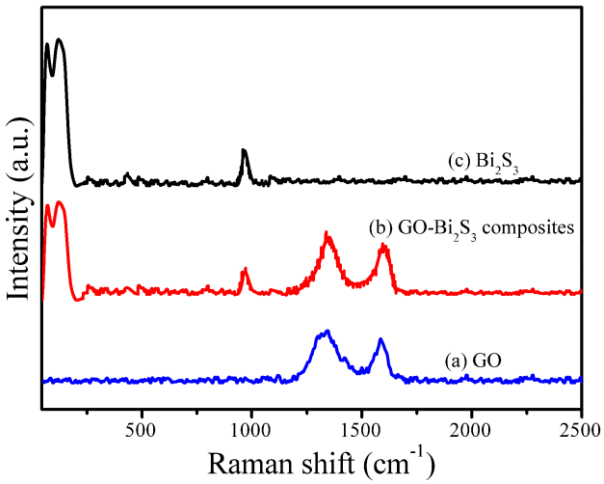

Fig. S2 Raman spectra of GO, Bi_2S_3 and GO-Bi_2S_3 composites.

The XRD, Raman characterizations of Bi_2S_3 and GO-Bi_2S_3 composites were also investigated. As shown in Fig. S1, the characteristic diffraction peaks of Bi_2S_3 are in good agreement with that of orthogonality Bi_2S_3 (JCPDS card no. 65-2431). The obtained GO-Bi_2S_3 composites displays similar XRD pattern to Bi_2S_3, indicating the formation of Bi_2S_3. However, a broad diffraction peak at 29.0° was observed, implying the relatively small crystallite sizes of Bi_2S_3 nanoparticles in the composites.[50]

As presented in Fig. S2, features corresponding to the D and G band of GO and GO-Bi_2S_3 composites were observed. The typical bands of GO can be found at 1341 cm^{-1} and 1581 cm^{-1}, corresponding to the D and G bands, respectively. Whereas the G

band for the GO-Bi_2S_3 composites shifted to 1597 cm^{-1}, indicating the chemical interaction GO and Bi_2S_3.[51] The Raman spectra of GO-Bi_2S_3 composites and pure Bi_2S_3 show similar features in the range of 45-1000 cm^{-1}, indicated the presence of Bi_2S_3 in the GO-Bi_2S_3 composites. On the other hand, the calculated $I_{(D)}/I_{(G)}$ ratios for GO and GO-Bi_2S_3 composites were 1.13 and 1.20, respectively. The increased $I_{(D)}/I_{(G)}$ ratio of the GO-Bi_2S_3 composites is a clear indication of the increase of reduction level, which is in agreement with the Raman results of the GO-ZnS composites.

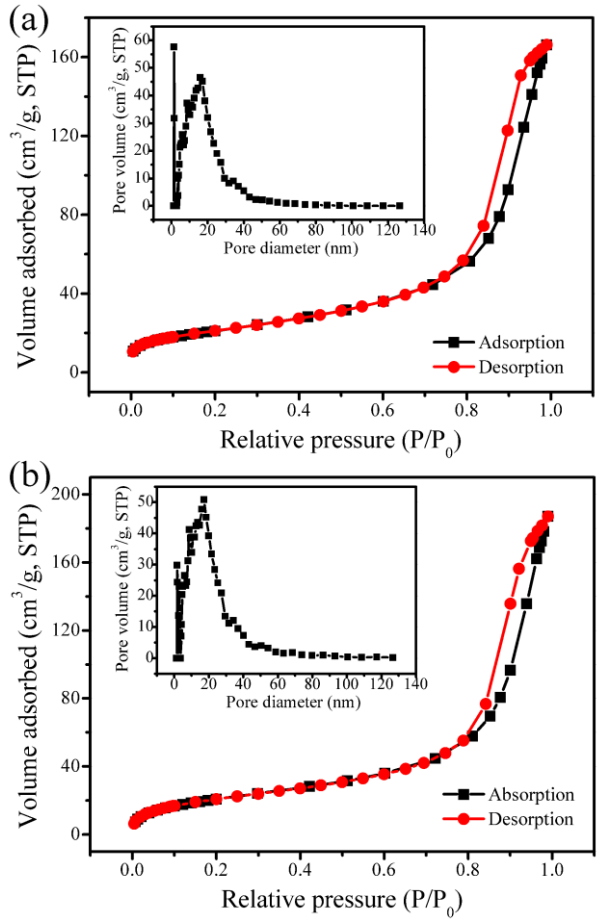

Fig. S3 Nitrogen adsorption-desorption isotherms and the corresponding DFT pore size distributions (insets) of CdS (a) and GO-CdS composites (b).

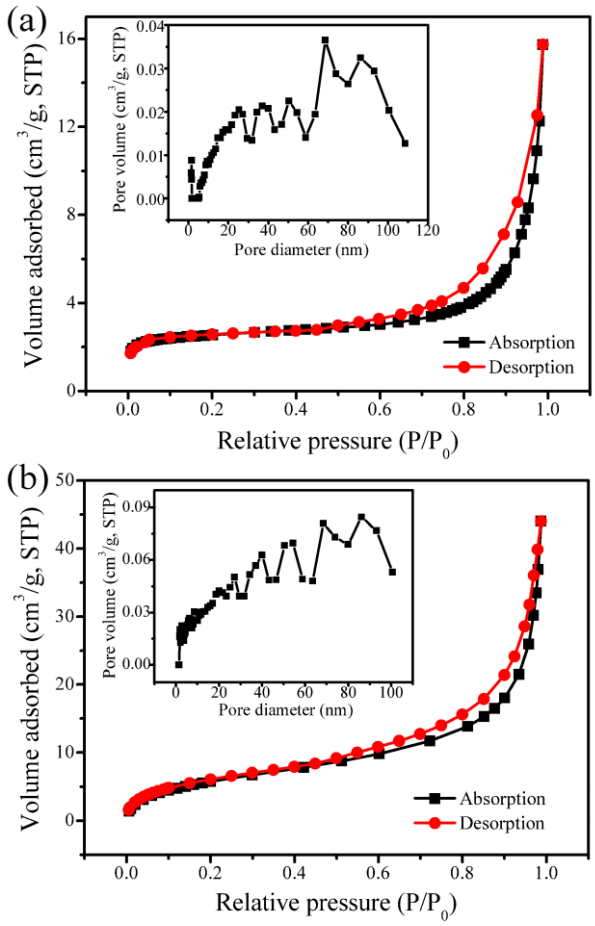

Fig. S4 Nitrogen adsorption-desorption isotherms and the corresponding DFT pore size distributions (insets) of Bi_2S_3 (a) and GO- Bi_2S_3 composites (b).

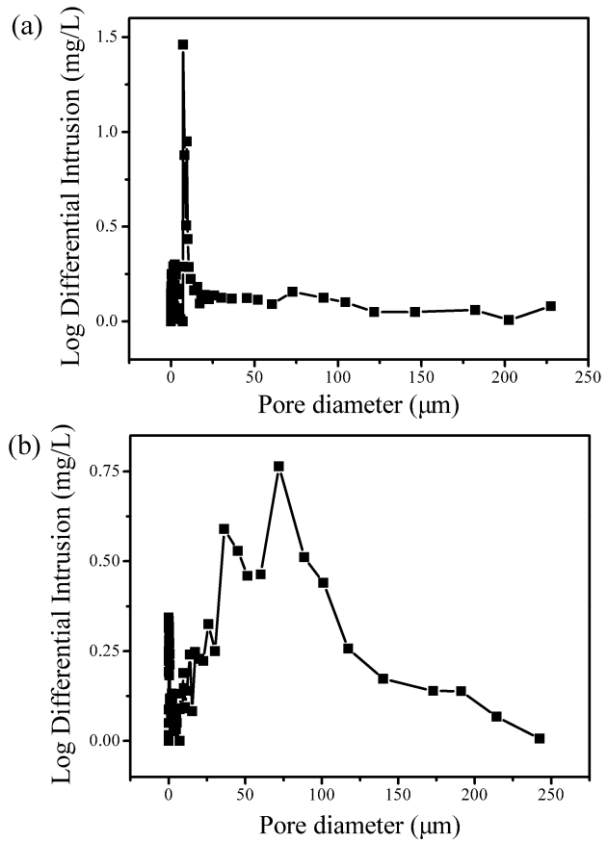

Fig. S5 Pore size distributions of Bi_2S_3 (a) and GO-Bi_2S_3 composites (b) tested by the high pressure of mercury.

As shown in Fig. S4, the nitrogen adsorption-desorption isotherms of Bi_2S_3 and GO-Bi_2S_3 composites were measured to find the information about the specific surface area. It can be seen that Bi_2S_3 and GO-Bi_2S_3 composites possess a Type IV adsorption-desorption isotherms curves, as previously reported.[52] The isotherms curves revealed type H3 hysteresis loops, which are typical for open slit-shaped capillaries with wide bodies and narrow necks.[53] In addition, the corresponding pore size distributions from DFT method (insets of Fig. S4) show a distribution ranging from 2 to 100 nm, while the pore size distributions tested by the high pressure of mercury suggest the existence of macropores for the samples (Fig. S5). The above results indicated that there are mesopores and macropores in the materials. The determined specific surface area of GO-Bi_2S_3 composites is 21.9 m^2 g^{-1}, larger than that of Bi_2S_3 (8.6 m^2 g^{-1}), which can probably enhance the photocatalytic activity of GO-Bi_2S_3 composites.

In addition, the degradation kinetic of MO was also investigated. The first-order model[55] can be expressed as follows, In (C_0/C) = kt, where, C_0 and C are the dye concentration at time 0 and t min, respectively, k is the first order reaction rate constant. Fig. S6, S7 and S8 depict the photocatalytic degradation kinetics of MO. It can be seen that the curves of In (C_0/C) versus irradiation time approach to linear, indicating a rather good correlation to the first-order reaction kinetic. The determined k values for ZnS, GO-ZnS composites, CdS, GO-CdS composites, Bi_2S_3 and GO-Bi_2S_3 composites are 0.00609 min^{-1}, 0.02558 min^{-1}, 0.00481 min^{-1}, 0.01362 min^{-1}, 0.00734 min^{-1} and 0.01204 min^{-1}, respectively. It indicates that the k values of GO-ZnS composites, GO-CdS composites and GO-Bi_2S_3 composites are higher than that of ZnS, CdS and Bi_2S_3 (The higher k value means a higher degradation ratio of MO), respectively. The results suggest that GO-ZnS composites, GO-CdS composites and GO-Bi_2S_3 composites possess higher photocatalytic activity than that of ZnS, CdS and Bi_2S_3, which is consistent with the conclusions of photocatalytic degradation curves presented in Fig. 6a, Fig. 9a and 10a.

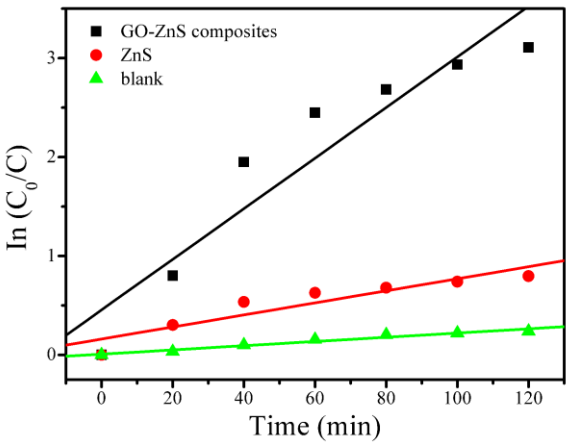

Fig. S6 In (C_0/C) versus irradiation times for the degradation of MO.

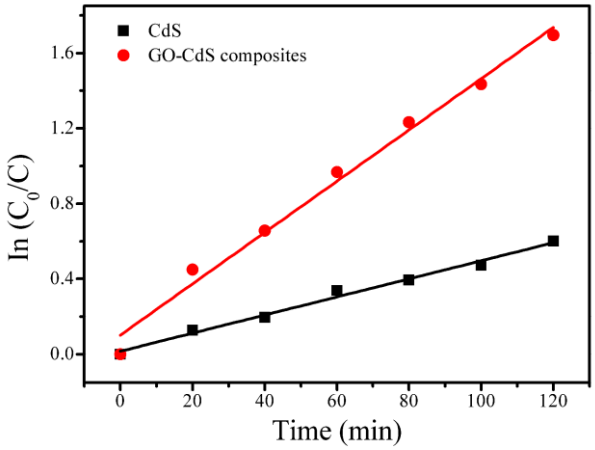

Fig. S7 In (C_0/C) versus irradiation times for the degradation of MO.

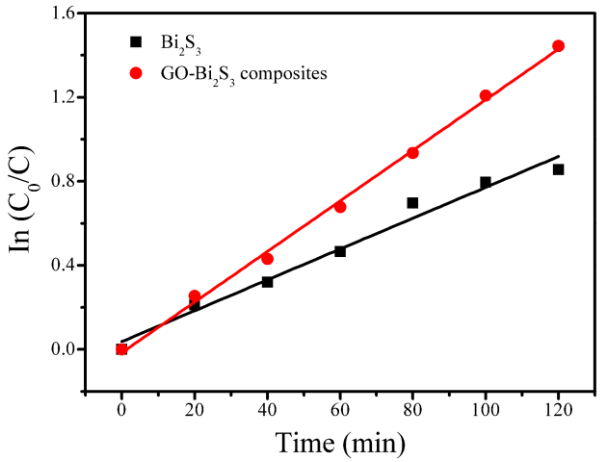

Fig. S8 In (C_0/C) versus irradiation times for the degradation of MO.

Notes and references

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