Supporting Information

Heterostructured Bi$_2$S$_3$@NH$_2$-MIL-125(Ti) nanocomposite as a bifunctional photocatalyst for Cr(VI) reduction and rhodamine B degradation under visible light

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S1. Synthesis of Bi$_2$S$_3$ and NH$_2$-MIL-125(Ti)

Bi$_2$S$_3$ was synthesized according to the previous report.$^1$ In typical, 1.82 g Bi(NO$_3$)$_3$·3H$_2$O was first dissolved into 25 mL ethylene glycol (EG) under nitrogen bubbling and obtained solution A. Meanwhile, 1.35 g Na$_2$S was dissolved in a mixed solvent of 10 mL EG and 20 mL deionized water under stirring for 15 min, which denoted as solution B. Then solution B was added dropwise to solution A under magnetic stirring, along with plenty of black suspended matter. Subsequently, 1.92 g carbamide and 20 mL deionized water were added to the mixture and stirred for another 30 min. The mixed solution was then transferred into a Teflon-lined stainless steel autoclave and maintained at 180 °C for 24 h. After cooling to room temperature, the precipitate was collected by vacuum filtration, and washed successively by ethanol and water for several times. Finally, the obtained products were dried under vacuum at 60 °C for obtaining the Bi$_2$S$_3$.

NH$_2$-MIL-125(Ti) was synthesized using a solvothermal method.$^{2,3}$ The H$_2$BDC-NH$_2$ (2.2 g), DMF (36 mL), methanol (4.0 mL), and Ti(OC$_4$H$_9$)$_4$ (2.4 mL) were mixed and dispersed with magnetic stirring for 5 mins to form a homogeneous solution. Then, the solution was poured into a Teflon-lined stainless-steel autoclave for 48 h at 150 °C. After cooling to room temperature, the obtained precipitate was separated by centrifugation, following by being washed repeatedly with DMF and methanol and dried at 60 °C overnight. As such, the NH$_2$-MIL-125(Ti) was obtained.
S2. XPS spectra of the samples

Fig. S1. XPS survey spectra of (i) NH$_2$-MIL-125(Ti), (ii) Bi$_2$S$_3$, (iii) Bi$_2$S$_3$@NM-10, (iv) Bi$_2$S$_3$@NM-50, and (v) Bi$_2$S$_3$@NM-100 nanocomposites.

Table S1. Atomic percentage of NH$_2$-MIL-125(Ti), Bi$_2$S$_3$, and Bi$_2$S$_3$@NM nanocomposites.

| Samples          | Atomic percentage |       |       |       |       |       |       |
|------------------|-------------------|-------|-------|-------|-------|-------|-------|
|                  |                   | C 1s  | N 1s  | O 1s  | Ti 2p | Bi 4f | S 2p  |
| NH$_2$-MIL-125(Ti) | 55.39             | 7.33  | 30.37 | 6.91  | -     | -     | -     |
| Bi$_2$S$_3$       | 9.75              | -     | -     | -     | 6.1   | 84.15 |       |
| Bi$_2$S$_3$@NM-10 | 62.33             | 10.56 | 22.74 | 4.16  | 0.04  | 0.18  |       |
| Bi$_2$S$_3$@NM-50 | 61.60             | 10.34 | 22.93 | 4.46  | 0.06  | 0.61  |       |
| Bi$_2$S$_3$@NM-100| 59.89             | 9.98  | 23.11 | 4.86  | 0.19  | 1.98  |       |
Fig. S2. (a) Ti 2p, (b) C 1s, (c) N 1s, and (d) O 1s high resolution XPS spectra of NH$_2$-MIL-125(Ti).

Fig. S3. (a) Bi 4f and S 2p, and (b) S 2s high resolution XPS spectra of Bi$_2$S$_3$. 
**Fig. S4.** N 1s and O 1s high resolution XPS spectra of (a) Bi$_2$S$_3$@NM-10, (b) Bi$_2$S$_3$@NM-50, and (c) Bi$_2$S$_3$@NM-100 nanocomposites.
S3. Surface morphologies of the NH$_2$-MIL-125(Ti) and Bi$_2$S$_3$ samples

Fig. S5. Low- and high-magnification FE-SEM images of (a, b) NH$_2$-MIL-125(Ti) and (c, d) Bi$_2$S$_3$.
**Fig. S6.** (a, b) TEM images of NH$_2$-MIL-125(Ti) and (c, d) TEM and HR-TEM images of Bi$_2$S$_3$ (the inset in (d) is the corresponding SAED pattern).
S4. Nitrogen adsorption-desorption isotherms of the samples

To evaluate the pore structures and specific surface areas, N\textsubscript{2} adsorption–desorption measurements of all samples were performed, as shown in Figure S7. The NH\textsubscript{2}-MIL-125(Ti) sample illustrated type I isotherms at 77 K with no hysteresis, indicating its typical microporous structure. The Bi\textsubscript{2}S\textsubscript{3} exhibited type IV isotherms with a hysteresis loop in the higher relative pressure (P/P\textsubscript{0}, 0.9–1.0) range, which implies the presence of capillary condensation in the mesoporous and macroporous. N\textsubscript{2} adsorption-desorption isotherms of Bi\textsubscript{2}S\textsubscript{3}@NM samples exhibit hybrid type I/IV isotherms with hysteresis loop at P/P\textsubscript{0} = 0.45–1.0, confirming the presence of both of micropores and mesopores.\textsuperscript{4} It illustrated that the specific surface area of NH\textsubscript{2}-MIL-125(Ti), Bi\textsubscript{2}S\textsubscript{3}@NM-10, Bi\textsubscript{2}S\textsubscript{3}@NM-50, and Bi\textsubscript{2}S\textsubscript{3}@NM-100 were determined to be 622.9, 485.7, 560.9, and 416.7 m\textsuperscript{2}·g\textsuperscript{-1} using Brunauer–Emmett–Teller (BET) method. The pore size distributions were obtained from the Barrett–Joyner–Halenda (BJH) method and Horvath-Kawazoe (HK) method. An extremely little specific surface area was observed for Bi\textsubscript{2}S\textsubscript{3}, only 12.5 m\textsuperscript{2}·g\textsuperscript{-1}, with a wide distribution centered around 40-65 nm (Figure S7b). The NH\textsubscript{2}-MIL-125(Ti) and Bi\textsubscript{2}S\textsubscript{3}@NM samples (Figure S7c-d) revealed narrow distributions centered at 0.5–1 nm and narrow distributions ranged from 3–5 nm, which were associated with the microporous and mesoporous structure.
**Fig. S7.** (a) Nitrogen adsorption–desorption isotherms of NH$_2$-MIL-125(Ti), Bi$_2$S$_3$, and Bi$_2$S$_3$@NM nanocomposites. (b) Barrett-Joyner-Halenda (BJH) mesopore size distributions of Bi$_2$S$_3$. (c) Horvath-Kawazoe (HK) micropore size distributions and (d) Barrett-Joyner-Halenda (BJH) mesopore size distributions of NH$_2$-MIL-125(Ti) and Bi$_2$S$_3$@NM nanocomposites.

**S5. Photocatalytic activity of the samples**
Fig. S8. UV-vis absorption spectra for reduction of Cr (VI) with (a) blank, (b) NH₂-MIL-125(Ti), (c) Bi₂S₃, (d) Bi₂S₃@NM-10, (e) Bi₂S₃@NM-50, and (f) Bi₂S₃@NM-100 catalysts. (g) Reaction rate constant (k) of various samples (initial concentration of Cr(VI): 10 mg·L⁻¹, photocatalyst dosage: 100 mg·L⁻¹, pH = 7.0).
**Fig. S9.** UV-vis absorption spectra for degradation of RhB with (a) blank, (b) NH$_2$-MIL-125(Ti), (c) Bi$_2$S$_3$, (d) Bi$_2$S$_3$@NM-10, (e) Bi$_2$S$_3$@NM-50, and (f) Bi$_2$S$_3$@NM-100 catalysts. (g) reaction rate constant ($k$) of various samples (initial concentration of RhB: 20 mg·L$^{-1}$, photocatalyst dosage: 100 mg·L$^{-1}$, pH = 7.0).
Fig. S10. Photocatalytic degradation of RhB with and without of Cr(VI) using the Bi$_2$S$_3$@NM-100 sample (initial concentration of RhB: 5 mg·L$^{-1}$, Cr(VI): 10 mg·L$^{-1}$, photocatalyst dosage: 200 mg·L$^{-1}$, pH = 3.0).

S6. The reusability and stability of the photocatalyst
Fig. S11. (a) FT-IR spectra, (b) XRD patterns, (c) XPS survey spectra and of the (i) pristine Bi$_2$S$_3$@NM-100, and recycled sample after (ii) Cr(VI) reduction and (iii) RhB degradation. (d) High-resolution XPS spectrum of Cr 2p for the recycled Bi$_2$S$_3$@NM-100 after photocatalytic reduction of Cr(VI).
Fig. S12. FE-SEM images of the recycled Bi$_2$S$_3$@NM-100 after (a) Cr(VI) reduction and (b) RhB degradation.

S7. Mott–Schottky analysis
Fig. S13. Mott-Schottky plots of (a) NH$_2$-MIL-125(Ti), (b) Bi$_2$S$_3$, (c) Bi$_2$S$_3$@NM-10, (d) Bi$_2$S$_3$@NM-50, and (e) Bi$_2$S$_3$@NM-100 nanocomposites measured in 0.5 M Na$_2$SO$_4$ aqueous solution at a frequency of 100 Hz in the dark.

Table S2. The values of flat-band, conduction band, valence band, and $E_g$ for various
samples.

| Samples       | Flat band (V vs. Ag/AgCl) | Flat band (V vs. NHE) | Conduction band (V vs. NHE) | Valence band (V vs. NHE) | $E_g$ (eV) |
|---------------|---------------------------|-----------------------|-----------------------------|--------------------------|-----------|
| NH$_2$-MIL-125(Ti) | -0.70                     | -0.49                 | -0.59                       | 2.09                     | 2.68      |
| Bi$_2$S$_3$   | -0.07                     | 0.14                  | 0.04                        | 1.36                     | 1.32      |
| Bi$_2$S$_3$@NM-10 | -0.57                     | -0.36                 | -0.46                       | 2.20                     | 2.66      |
| Bi$_2$S$_3$@NM-50 | -0.43                     | -0.22                 | -0.32                       | 2.32                     | 2.64      |
| Bi$_2$S$_3$@NM-100 | -0.29                     | -0.08                 | -0.18                       | 2.41                     | 2.59      |
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