Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information for:

In situ synthesis of Bi_2S_3/Bi_2SiO_5 heterojunction photocatalysts with enhanced visible light responsive activity

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1. UV-vis diffuse reflectance spectra

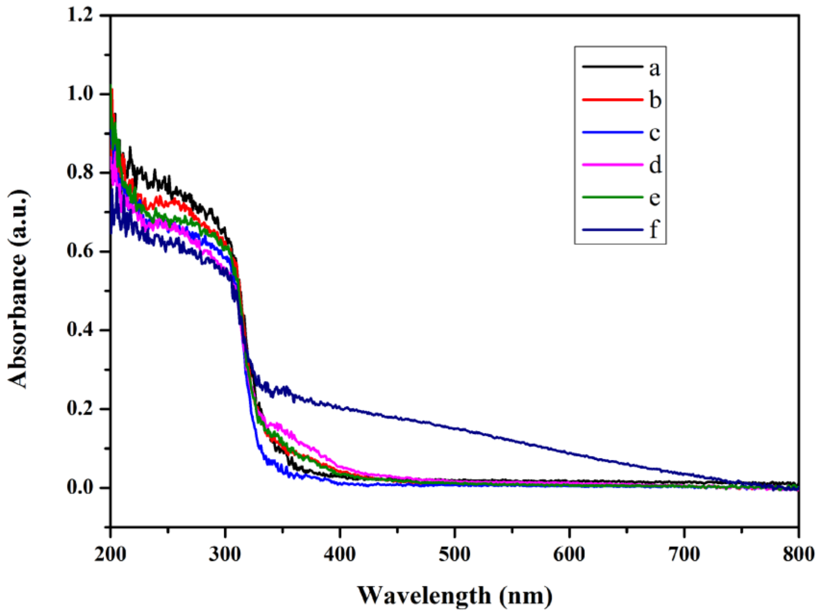


Fig. S1 UV-vis diffuse reflectance spectra (a) thiourea as sulfur source reacted with Bi_2SiO_5 at room temperature for 30 min, (b) thiourea as sulfur source reacted with Bi_2SiO_5 at 60 ℃ for 3 h, (c) pure Bi_2SiO_5, (d) cysteine as sulfur source reacted with Bi_2SiO_5 at 60 ℃ for 3 h, (e) cysteine as sulfur source reacted with Bi_2SiO_5 at room temperature for 30min and (f) TAA as sulfur source reacted with Bi_2SiO_5 at room temperature for 30 min.

Fig. S1 shows the UV-vis diffuse reflectance spectra of Bi_2S_3/Bi_2SiO_5 heterojunctions forming by different sulfur source and processing conditions. From the picture we can know even improving the reaction time and temperature, the visible light absorption of the samples using thiourea and cysteine as sulfur source is still very low. When TAA was used as sulfur source and the reaction was kept in a short time and room temperature, the visible light absorption of the samples is increased obviously. From the results, the speed of releasing S^{2-} can be concluded in the following order: TAA > cysteine > thiourea. So TAA is regarded as the appreciate sulfur source for the prpeparation of Bi_2S_3/Bi_2SiO_5 heterojunctions.

2. XRD pattern

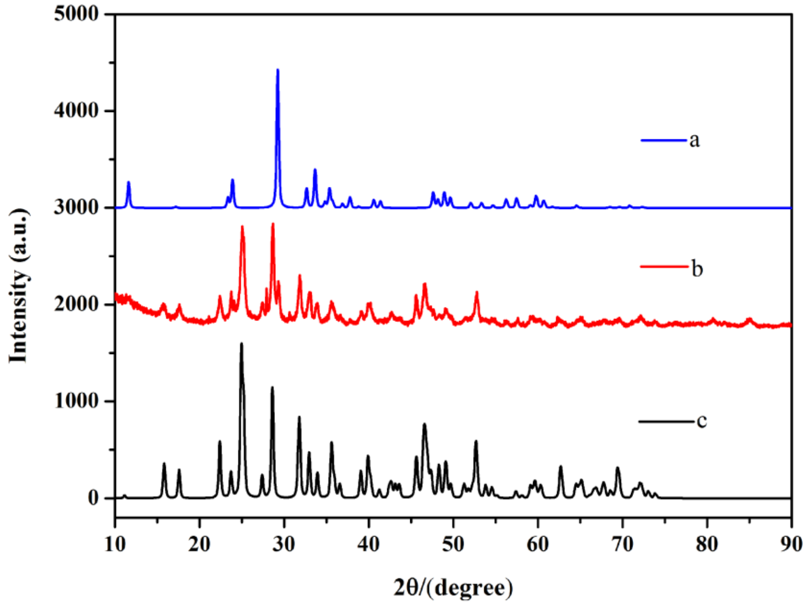
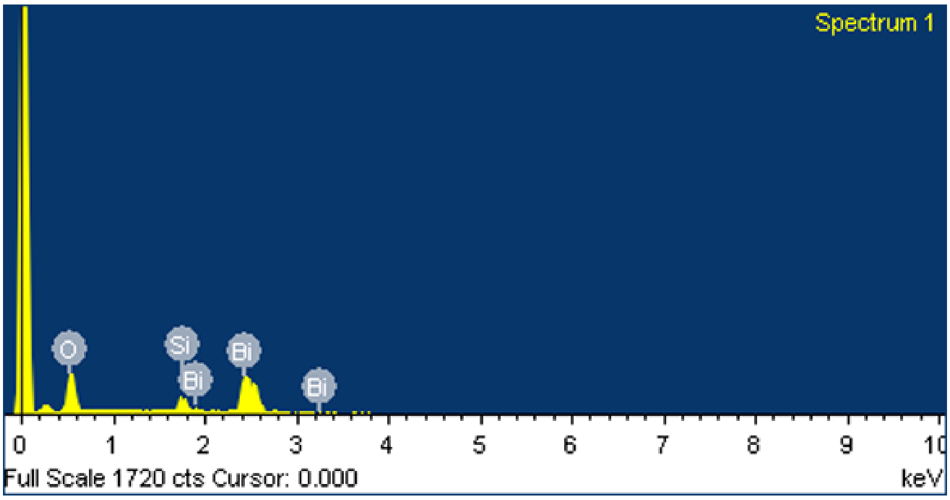


Fig. S2 (a) XRD pattern of pure Bi_2SiO_5 (JCPDS. 36-0287), (b) XRD pattern of Bi_2SiO_5 reacted with TAA solution at 80 ℃ for 3 h, (c) XRD pattern of pure Bi_2S_3 (JCPDS. 17-0320).

From the picture we can see the diffraction peaks of Bi_2S_3 (JCPDS. 17-0320) appear obviously. This result indicates that the Bi_2SiO_5 can react with TAA to form Bi_2S_3/Bi_2SiO_5 composites, and increased reaction time and temperature can promote the Bi_2S_3 formation.

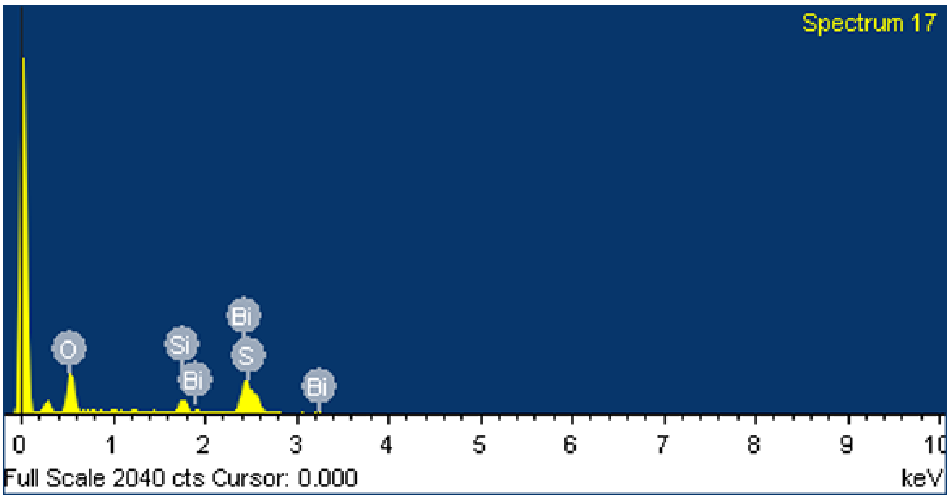
3. The chemical composition and of composite materials

From the EDS spectrum and detailed chemical composition of composite materials of Bi_2S_3/Bi_2SiO_5 composites, the atomic percentage of Bi, O, Si (Bi : O : Si = 2.15 : 1 : 6.19), is approximately corresponded with the stoichiometric ratio of Bi_2SiO_5. The atomic ratio of sulfur are 0.330%, 0.740% and 1.280% for Bi_2S_3/Bi_2SiO_5-15 min, Bi_2S_3/Bi_2SiO_5-30 min, and Bi_2S_3/Bi_2SiO_5-60 min, respectively. Therefore, the actual molar content of Bi_2S_3 are 0.110%, 0.247% and 0.427%, respectively.



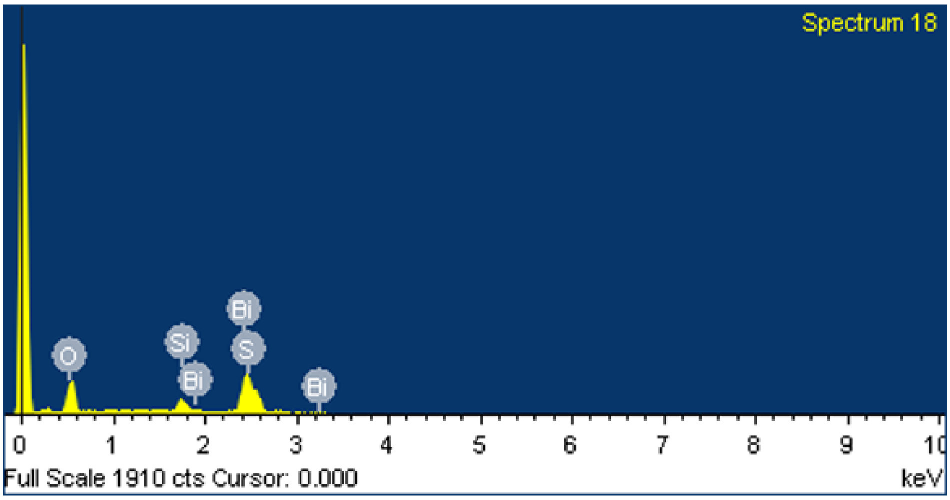
Element	Weight%	Atomic%
O K	17.13	66.22
Si K	4.86	10.70
Bi M	78.01	23.08
Totals	100.00	

Fig. S3 EDS spectrum and detailed chemical composition of composite materials of Bi_2SiO_5.



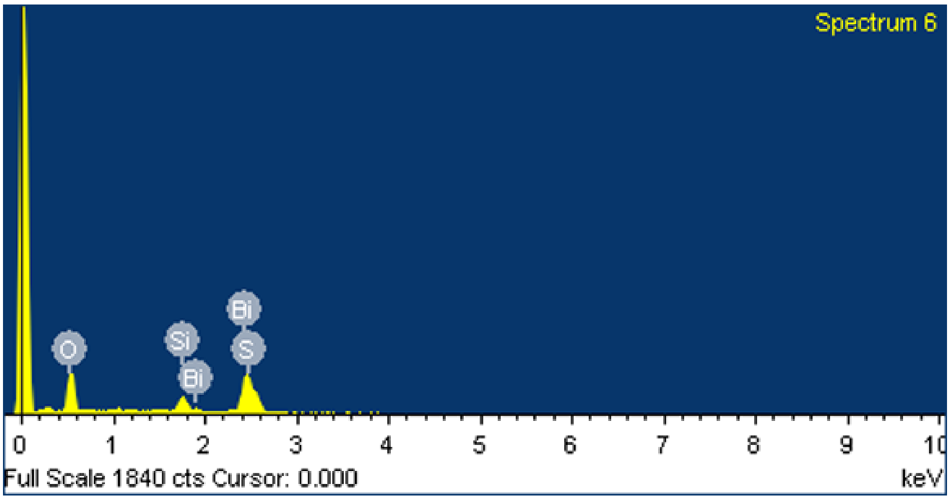
Element	Weight%	Atomic%
O K	19.14	68.89
Si K	4.82	9.88
S K	0.18	0.33
Bi M	75.86	20.90
Totals	100.00	

Fig. S4 EDS spectrum and detailed chemical composition of composite materials of Bi_2S_3/Bi_2SiO_5-15min heterojunction.



Element	Weight%	Atomic%
O K	15.56	64.05
Si K	4.29	10.06
S K	0.36	0.74
Bi M	79.79	25.15
Totals	100.00	

Fig. S5 EDS spectrum and detailed chemical composition of composite materials of Bi_2S_3/Bi_2SiO_5-30min heterojunction.



Element	Weight%	Atomic%
O K	17.69	66.60
Si K	4.63	9.93
S K	0.68	1.28
Bi M	77.01	22.20
Totals	100.00	

Fig. S6 EDS spectrum and detailed chemical composition of composite materials of

Bi_2S_3/Bi_2SiO_5-60min heterojunction.

4. The calculation of the sizes of Bi_2S_3 in Bi_2S_3/Bi_2SiO_5 heterojunctions

When the size of the semiconductor nanoparticles reduce to 1-10 nm, the quantum confinement will appear,[1] the blue shift of the light absorption will happen and the band gap of the semiconductor is adjustable. The different band gap of the products attribute to the quantum confinement. On the basis of the effective mass approximation model, the relationship between ΔE_g and R can be describe by the following equation:[2]

$$\Delta E_g(R) = \frac{h^2}{8m_0R^2}\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right)$$

E_g (R) is the band gap shift, m_0 the electron mass, h the Planck's constant, R the crystal radius, the m_e^* and m_h^* are the effective masses of electrons and holes, respectively. Through the caculation, ΔE_g (R) = $19.4/R^2$, we can get the sizes of Bi_2S_3 in Bi_2S_3/Bi_2SiO_5 heterojunction photocatalysts with different reaction time, 3.41 nm, 3.92 nm and 4.61 nm, respectively. It accord with the conditions of the quantum size.

5. The positions of E_{CB} and E_{VB} of Bi_2SiO_5 and Bi_2S_3/Bi_2SiO_5 heterojunctions

For a semiconductor, the optical absorption near the band edge follows the equation: ahν = $A(h\nu-E_g)^{n/2}$,[3] in the equation, a is the absorption coefficient, ν is light frequency, A is proportionality constant and E_g is band gap, respectively. The value of n depends on the type of the semiconductor, n=1 for direct transition and n=4 for indirect transition.[4] As reported previously, Bi_2SiO_5 and Bi_2S_3 both are direct transition,[5,6] the n values of Bi_2SiO_5 and Bi_2S_3 are 1. From the plot of $(ah\nu)^2$ - hν, we can estimate the band gap of the products, the E_g of Bi_2SiO_5, Bi_2S_3/Bi_2SiO_5-15 min, Bi_2S_3/Bi_2SiO_5-30 min, Bi_2S_3/Bi_2SiO_5-60 min are 3.76 eV, 2.96 eV, 2.56 eV and 2.21 eV, respectively. X_{Bi}=4.885, X_{Si}=4.915, X_O=7.675, X_S=6.385, so the X values for Bi_2SiO_5 and Bi_2S_3 are 6.474eV and 5.276eV. The top of VB of Bi_2SiO_5 is 3.854eV and the bottom of CB is 0.094eV. The values of E_{CB}, E_{VB} and E_g of Bi_2S_3 in Bi_2S_3/Bi_2SiO_5 heterojunctions are listed in Table S1.

Table S1. The values of E_{CB},E_{VB} and E_g of Bi_2S_3 in Bi_2S_3/Bi_2SiO_5 heterojunctions.

Semiconductor	E_{CB} (eV)	E_{VB} (eV)	E_g (eV)
Bi_2S_3 in Bi_2S_3/Bi_2SiO_5-15min	-0.704	2.256	2.96
Bi_2S_3 in Bi_2S_3/Bi_2SiO_5-30min	-0.504	2.056	2.56
Bi_2S_3 in Bi_2S_3/Bi_2SiO_5-60min	-0.329	1.881	2.21

6. The BET surface areas of the samples

Nitrogen adsorption and desorption measurement was used to study the Brunauer–Emmett–Teller (BET) surface areas of the samples, Table S2 shows the BET surface areas of the samples. It shows that the surface areas of the samples are almost the same, because the content of Bi_2S_3 is very low.

Table S2. The BET surface areas of the samples.

sample	Bi_2SiO_5	Bi_2S_3/Bi_2SiO_5-15min	Bi_2S_3/Bi_2SiO_5-30min	Bi_2S_3/Bi_2SiO_5-60min
BET surface area(m^2/g)	22.489	24.606	23.524	24.307

Notes and references

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