Photodeposition of metal sulfides on titanium metal–organic frameworks for excellent visible-light-driven photocatalytic Cr(VI) reduction

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1. Experimental
1.1. Materials

All reagents and solvents were of analytical reagent grade and used as received from commercial suppliers. MIL-125(Ti) was synthesized according to the previously reported method.\(^1\) Briefly, a mixture of tetrabutyl titanate (2.4 mL), 1,4-benzenedicarboxylic acid (2.2 g), N’N-dimetylformanide (DMF) (36 mL), and methanol (4.0 mL) was subjected to solvothermal conditions in a Teflon-lined stainless-steel autoclave for 48 h at 150 °C. After reaction, the resultant precipitate was separated by centrifugation, washed with DMF and methanol, and followed by drying for 12 h at 80 °C.

1.2. Photodeposition process of Me\(_{x}\)S\(_{y}\) onto MIL-125(Ti)

Bisource precursor was used to synthesize CdS/MIL-125(Ti), CuS/MIL-125(Ti) and Ag\(_2\)S/MIL-125(Ti) composite. Briefly, metal precursor (CdCl\(_2\)·2.5H\(_2\)O, AgNO\(_3\) and CuCl\(_2\)·2H\(_2\)O) and sulfur powder (S\(_8\)) were added to 250 mL ethanol (CH\(_3\)CN/H\(_2\)O/C\(_2\)H\(_5\)OH = 10:1:1 v/v/v for the preparation of Ag\(_2\)S/MIL-125(Ti)) and then sonication for 10 min until these solids were completely dissolved. Power MIL-125(Ti) was dispersed into the clear solution with vigorous stirring. Meanwhile, nitrogen gas was bubbled into the suspension for 30 min in the dark. And then, the suspension was irradiated under ultraviolet light condition for 2 h. The as-prepared product was centrifuged and washed by ethanol for three times, and then vacuum dried at 80 °C for 12 h. The MoS\(_2\)/MIL-125(Ti) was prepared by using (NH\(_4\))\(_2\)MoS\(_4\) ethanol solution as a single-source precursor under the same conditions.

1.3. Characterization

The transmission electron microscopy (TEM) measurements were conducted using a JEOL JEM-1230. The X-ray diffraction (XRD) patterns were carried out with Bruker AXS D8 Advance diffractometer operating with Cu-K\(_\alpha\) source to investigate the crystal structure of samples. The surface area of samples was determined by Brunauer–Emmett–Teller (BET) measurement (ASAP2020, Micromeritics, USA).
The surface electronic state was analyzed by X-ray photoelectron spectroscopy (Thermo Fisher Scientific, UK). UV–visible diffuse-reflectance spectra (UV-vis DRS) of as-synthesized samples were recorded in the range of 200–800 nm with a Varian Cary 300 spectrometer equipped with an integrating sphere.

**1.4. Photocatalytic Cr(VI) reduction**

The photocatalytic reduction of aqueous Cr(VI) to Cr(III) was carried out in a 100 mL quartz reactor containing 25 mg photocatalyst, 50 mL 48 ppm Cr(VI) aqueous solution and 1 mL anhydrous ethanol. The pH value of reaction solution was about 6. After being stirred for one hour to reach adsorption-desorption equilibrium in dark, the suspensions were irradiated by a 300 W Xe lamp (Beijing China Education Aulight Co. Ltd) with 420 nm cut-off filter. During illumination, 2 mL of suspension was taken from the reactor at a scheduled interval and the photocatalyst was separated. The Cr(VI) concentrations, prior to and after adsorption, were measured using a UV-vis spectrophotometer (UV-2250, SHIMADZU, Japan), which was analyzed by the purple complex of Cr(VI) with 1,5-diphenylcarbazide at 540 nm.
Fig. 1S The XPS spectra of (A) Ag₂S/MIL-125(Ti), (B) CdS/MIL-125(Ti), (C) CuS/MIL-125(Ti) and (D) MoS₂/MIL-125(Ti).
**Fig. 2S** $N_2$ adsorption–desorption isotherms of pure MIL-125(Ti), $Ag_2S$/MIL-125(Ti), CdS/MIL-125(Ti), CuS/MIL-125(Ti) and $MoS_2$/MIL-125(Ti).

**Reference**
