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Electronic Supplementary Information

Sn^{4+} Self-doped Hollow Cubic SnS as Efficient Visible-Light Photocatalyst for Cr(VI) Reduction and Detoxification of Cyanide

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Introduction of photocatalytic detoxification of cyanide

The highly toxic cyanides are present in effluent waters of several industries especially in chemical and mineral processing industry. Therefore, cyanide must be destroyed or removed from wastewater prior to discharge.[1-3] The normal treatment processes of cyanides are: alkaline chlorination, wet air oxidation, electrolytic oxidation, ozonation, and ion exchange, of which the alkaline chlorination is the best available proven technique.[4-6] However, it results in formation of highly toxic cyanogen chloride gas. Many efforts show that semiconductor photocatalysis can utilize solar energy for photocatalytic oxidation of cyanide, such as TiO_2 and ZnO materials.[7-11] Unfortunately, the wide band gap of these materials limits its light absorption only to the UV-light range and thus most investigations are focused on photocatalytic cyanide oxidation with ultraviolet (UV) light of wavelengths of 300-400 nm, while reports on visible light photocatalytic mineralization of cyanide are quite few. The difficulty can be attributed to such reasons. The process must be stable in a highly alkaline basic medium with the value of pH ca. over 9.3 to avoid volatilization of free CN^{-1}. The carbon in the CN^{-1} is more strongly bound to nitrogen than with atoms in dye molecules. The adsorption of the CN^{-1} on the photocatalytic surface becomes more difficulty with the increase of negative charge. So, photocatalytic removal of cyanide under visible light is still a great challenge.

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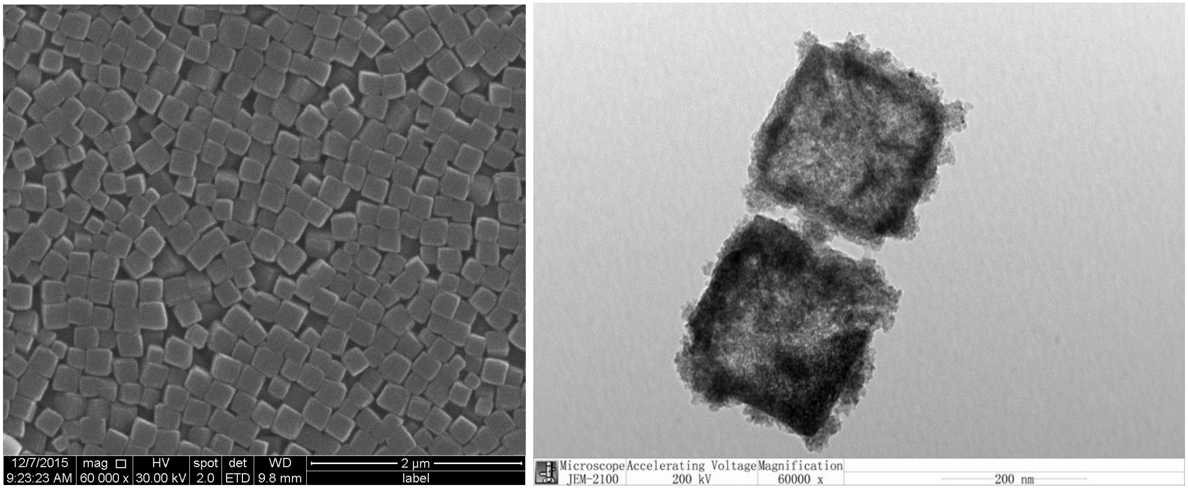

Figure S1. SEM and TEM image of hollow CoS nanoboxes.

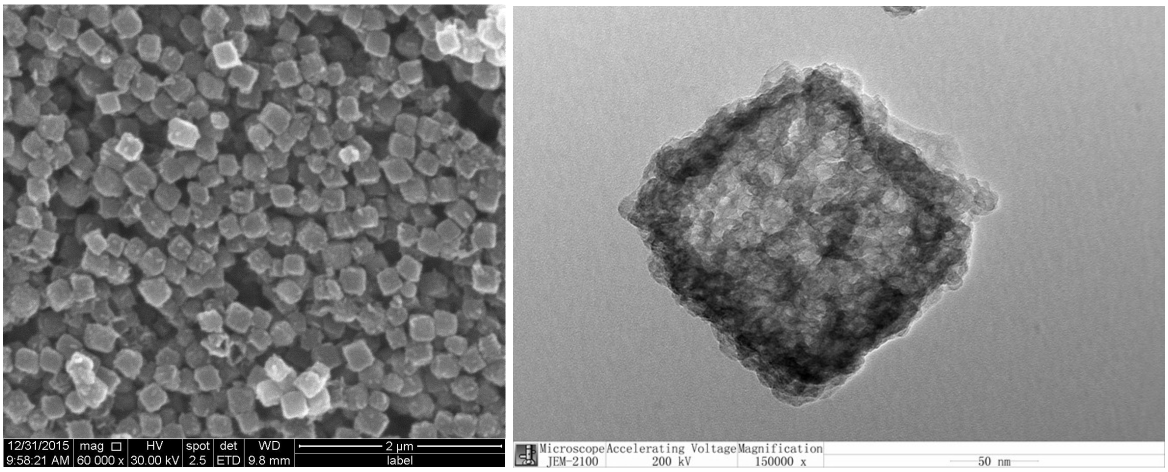

Figure S2. SEM and image of hollow MoS_2 nanoboxes.

Considering the stability of sulfide-based photocatalysts has always been a concern, it is obliged to examine the stability and reusability of catalysts in photocatalytic reduction of aqueous Cr(VI). Therefore, in this study, SnS_x was recycled for five times in the same photocatalytic reactions as shown in Figure S2. After each cycle photocatalytic use which lasted 60 min, the photocatalyst was separated from aqueous suspension by centrifugation, washed with 1 mol/L HNO_3 aqueous solution and deionized water, and dried in vacuum at 100 °C for 12 h.

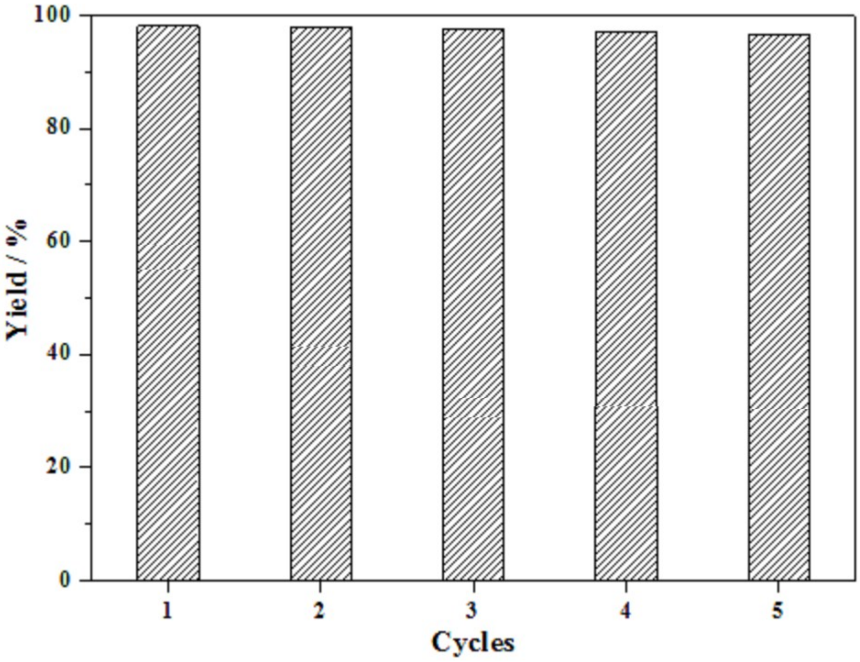

Figure S3. Recyclability experiments of hollow Sn^{4+} self-doped SnS catalysts for photocatalytic reduction of Cr(VI) for five cycles. The yield is calculated based on the same amount of catalysts and the same amount of reactants for all the five experiments.

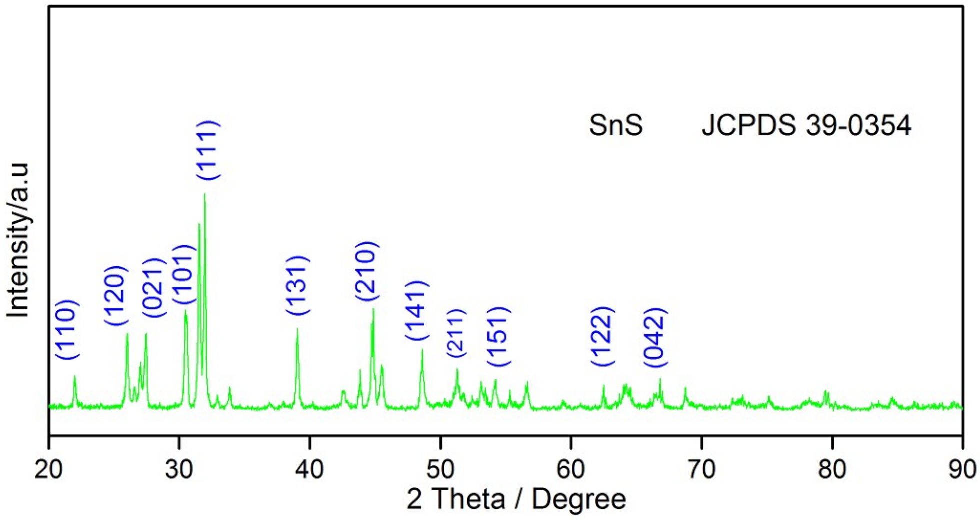

Figure S4. XRD of Sn^{4+} self-doped SnS after the 5th photocatalytic reduction of Cr(VI).

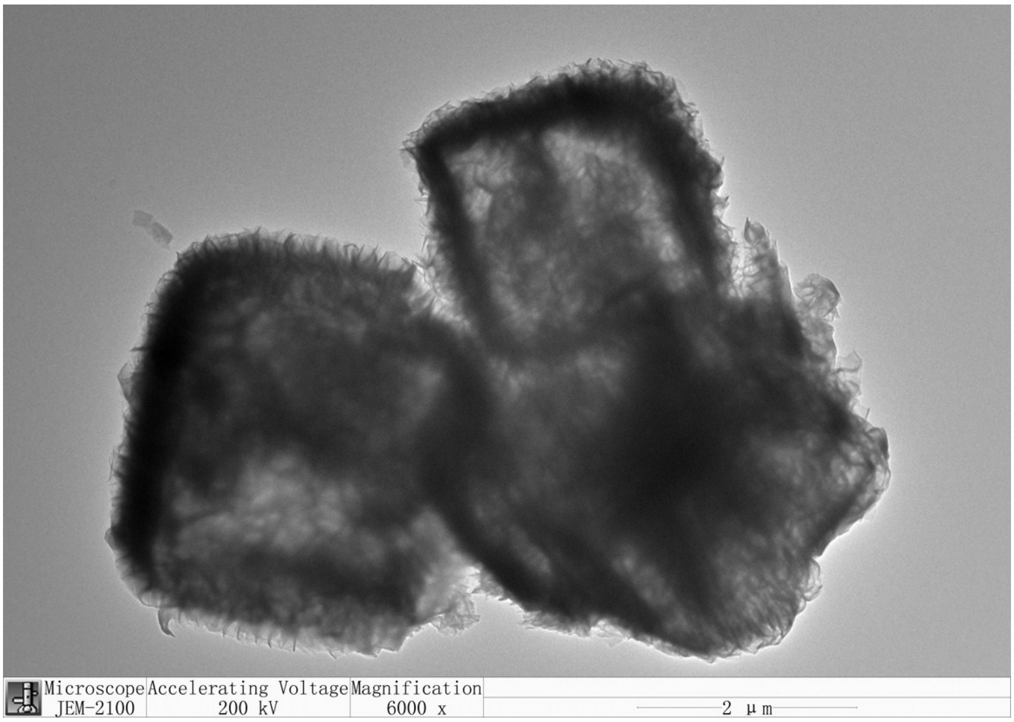

Figure S5. TEM of Sn^{4+} self-doped SnS after the 5th photocatalytic reduction of Cr(VI).

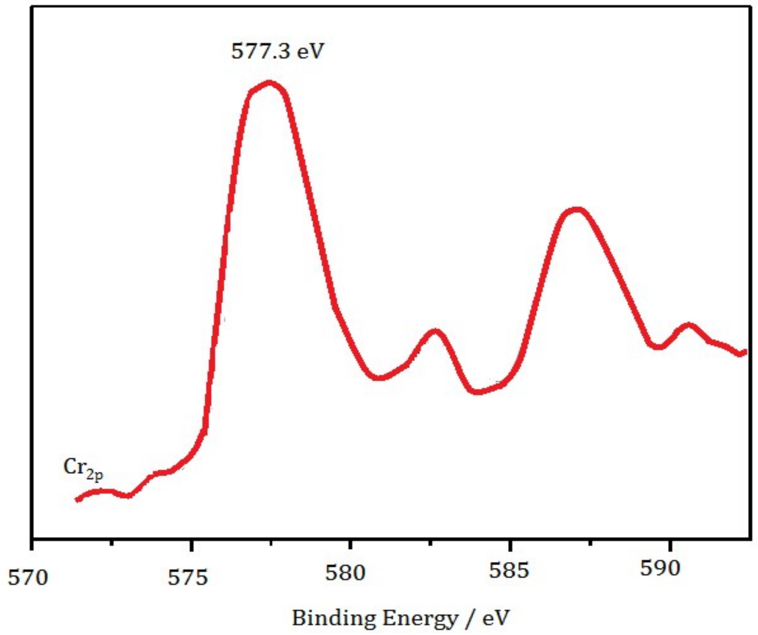

Figure S6. XPS spectrum of the surface of Sn^{4+} self-doped SnS after photocatalytic reduction of Cr(VI).