Supporting Information for

Enhanced performance of NaTaO$_3$ by molecular co-catalyst [Mo$_3$S$_4$]$^{4+}$ for water splitting into H$_2$ and O$_2$

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Experimental Section

1. Preparation of Catalysts

NaTaO$_3$ bulk was prepared by a conventional solid-state reaction method. Na$_2$CO$_3$ (High-Purity Chemicals 99%) and Ta$_2$O$_5$ (High-Purity Chemicals 99.9%) were used as raw materials. Stoichiometric mixtures of starting materials were ball-milled with ethanol and zirconia media for 24 h. The mixtures were dried in an oven (100 °C), and calcined at 1100 °C for 6 h in an Air atmosphere.

2. Preparation of Cocatalysts

Molybdenum sulfur, [Mo$_3$S$_4$(H$_2$O)$_9$]Cl$_4$ (hereafter [Mo$_3$S$_4$]$^{4+}$), was synthesized by reduction of ammonium tetrathiomolybdate with sodium borohydride, as reported in the literature.[1] Solutions of [Mo$_3$S$_4$]$^{4+}$ in HCl were obtained by repeated cation-exchange chromatography (Dowex 50W-X2, 400 mesh) and checked by UV-vis spectroscopy (Hewlett-Packard 8453). For loading co-catalysts onto NaTaO$_3$, facile and early reported impregnation method was adopted.[2] The [Mo$_3$S$_4$]$^{4+}$ co-catalysts were loaded by impregnating NaTaO$_3$ with an acidic aqueous solution of [Mo$_3$S$_4$]$^{4+}$. To investigate the effects of co-catalysts loading method, simple mixing, photo-deposition and drop-casting method are also employed. For simple mixing method, a little solution of [Mo$_3$S$_4$]$^{4+}$ and NaTaO$_3$ powder were mixed in the acidic aqueous solution under the UV exposure for 2 h. For photo-deposition method, the
NaTaO₃ powder (0.1 g) was dispersed in aqueous solution containing [Mo₅S₄]⁴⁺ clusters, followed by photoirradiation for 2 h using a UV lamp with stirring under Ar bubbling.[3] In case of drop-casting method, the solution of [Mo₅S₄]⁴⁺ cluster was added drop-wise to the surface of NaTaO₃ powders. After dropping the cluster solution onto the NaTaO₃, the powder was heated to 50 °C to flash off the solvent.[4] For comparison, NiOₓ co-catalysts were also deposited onto NaTaO₃ by an impregnation method from an aqueous Ni(NO₃)₂ solution. In addition, pretreatment of reduction with H₂(5%)/Ar(95%) gas mixture at 500 °C for 2 h and oxidation with O₂ gas at 200 °C for 1 h was carried out for NiOₓ loaded NaTaO₃ powders.

3. Photocatalytic reactions

The photocatalytic reactions for H₂ evolution were conducted at room temperature, in an outer-irradiation-type quartz reactor (200 mL) with a closed circulating gas system. A 450 W high-pressure mercury lamp was employed as the UV light source. It was laid down inside a cylindrical vessel, surrounded by a circulating cooling water jacket. The distance between the reactor and the Hg lamp was 15 cm. The photocatalyst powder (0.1 g) was dispersed in deionized water (120 mL), by magnetic stirring (10 min) and sonication (30 min). The closed gas circulation system and the reactor inside were well evacuated with high-purity Ar gas (99.999%), before irradiation. The amount of evolved H₂ and O₂ was detected via gas chromatography (Donam, DS6200).

4. Characterization

The crystal structures of the synthesized powders were determined using an X-ray powder diffractometer (XRD; D8-Advance, Bruker Miller Co). The morphologies and micro-structures were investigated using a field emission scanning electron microscopes (FESEM; JEOL, JSM-6330F) and a high-resolution transmission electron microscopy (HRTEM; JEOL, JEM-3000F). The elemental
analysis was studied using Energy dispersive spectrometer (EDS; JEOL, JSM-6360). The UV-Vis absorbance spectra were obtained using a UV-VIS spectrophotometer (UV-Vis spectroscopy; U-3501m, Hitachi). X-ray photoelectron spectroscopy (XPS) spectra were collected using an ESCA spectrometer (Al KR X-ray source, Sigma Probe).

References


Additional Figures

Fig. S1. Absorbance spectra of $[\text{Mo}_3\text{S}_4]^{4+}$ in HCl solution.
Fig. S2. XRD graph of bulk NaTaO$_3$. 
**Fig. S3.** UV-vis spectra of NaTaO$_3$ bulk (a) without and (b) with [Mo$_3$S$_4$]$^{4+}$ clusters.
Fig. S4. EDS mapping of [Mo$_3$S$_4$]$^{4+}$ molecular clusters loaded on NaTaO$_3$. 
**Fig. S5.** HRTEM image of (a) bare NaTaO$_3$ powder and (b) [Mo$_3$S$_4$]$^{4+}$ loaded NaTaO$_3$ powder.
Fig. S6. Energy diagrams of various photocatalysts and cocatalysts.