Supporting Information for

Enhanced performance of $NaTaO_3$ by molecular co-catalyst $[Mo_3S_4]^{4+}$ 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_2CO_3 (High-Purity Chemicals 99%) and Ta_2O_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, $[Mo_3S_4(H2O)_9]Cl_4$ (hereafter $[Mo_3S_4]^{4+}$), was synthesized by reduction of ammonium tetrathiomolybdate with sodium borohydride, as reported in the literature.[1] Solutions of $[Mo_3S_4]^{4+}$ 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 $[Mo_3S_4]^{4+}$ co-catalysts were loaded by impregnating $NaTaO_3$ with an acidic aqueous solution of $[Mo_3S_4]^{4+}$. 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 $[Mo_3S_4]^{4+}$ and $NaTaO_3$ powder were mixed in the acidic aqueous solution under the UV exposure for 2 h. For photo-deposition method, the

$NaTaO_3$ powder (0.1 g) was dispersed in aqueous solution containing $[Mo_3S_4]^{4+}$ 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 $[Mo_3S_4]^{4+}$ cluster was added drop-wise to the surface of $NaTaO_3$ powders. After dropping the cluster solution onto the $NaTaO_3$, the powder was heated to 50 °C to flash off the solvent.[4] For comparison, NiO_x co-catalysts were also deposited onto $NaTaO_3$ by an impregnation method from an aqueous $Ni(NO_3)_2$ solution. In addition, pretreatment of reduction with H_2(5%)/Ar(95%) gas mixture at 500 °C for 2 h and oxidation with O_2 gas at 200 °C for 1 h was carried out for NiO_x loaded $NaTaO_3$ powders.

3. Photocatalytic reactions

The photocatalytic reactions for H_2 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 H_2 and O_2 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

[1] T. F. Jaramillo, J. Bonde, J. Zhang, B. L. Ooi, K. Andersson, J. Ulstrup and I. Chorkendorff, *J. Phys. Chem. C*, 2008, **112**, 17492-17498.

[2] H. Kato and A. Kudo, *J. Phys. Chem. B*, 2001, **105**, 4285-4292.

[3] Shimura, H. Kawai, T. Yoshida and H. Yoshida, *Chem. Commun.*, 2011, **47**, 8958-8960.

[4] Y. Hou, B. L. Abrams, P. C. K. Vesborg, M. E. Björketun, K. Herbst, L. Bech, A. M. Setti, C. D. Damsgaard, T. Pedersen, O. Hansen, J. Rossmeisl, S. Dahl, J. K. Norskov and I. Chorkendorff, *Nat. Mater.*, 2011, **10**, 434-438.

Additional Figures

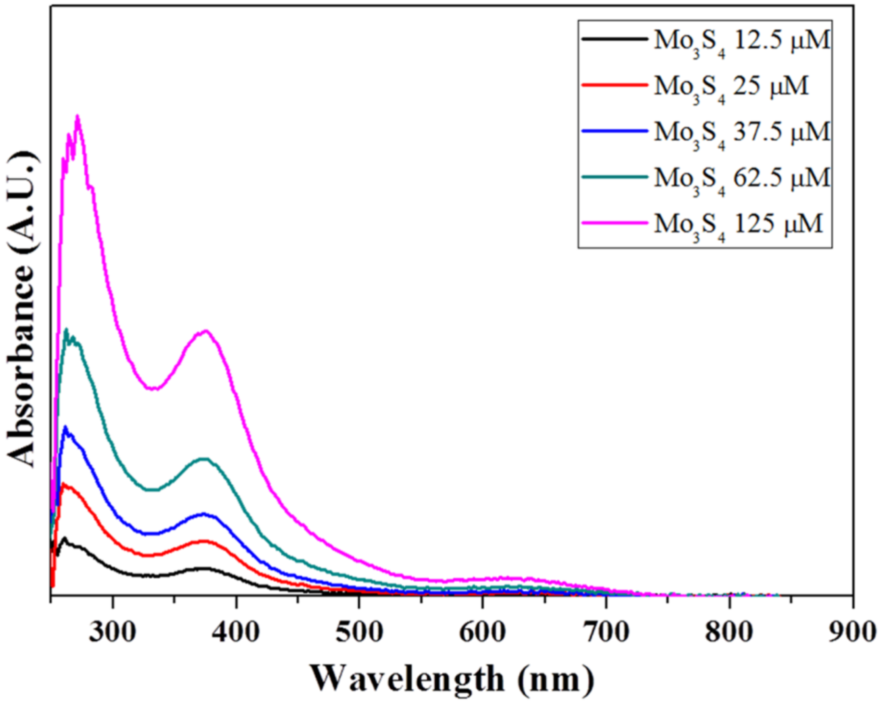

Fig. S1. Absorbance spectra of $[Mo_3S_4]^{4+}$ in HCl solution.

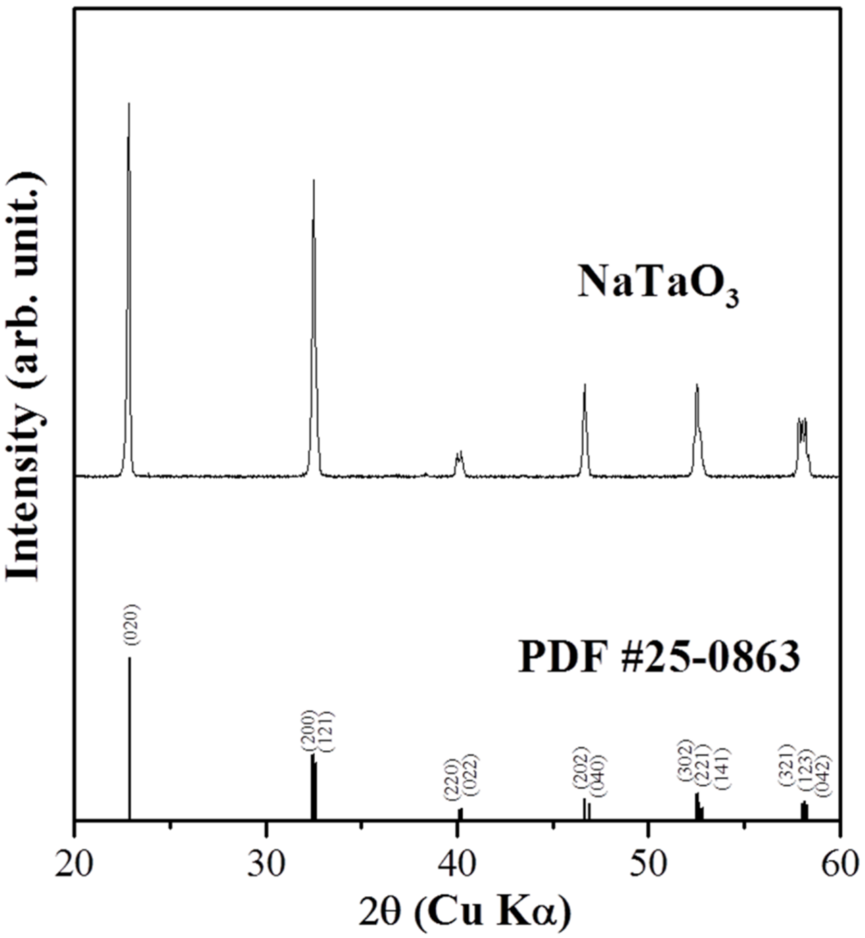

Fig. S2. XRD graph of bulk $NaTaO_3$.

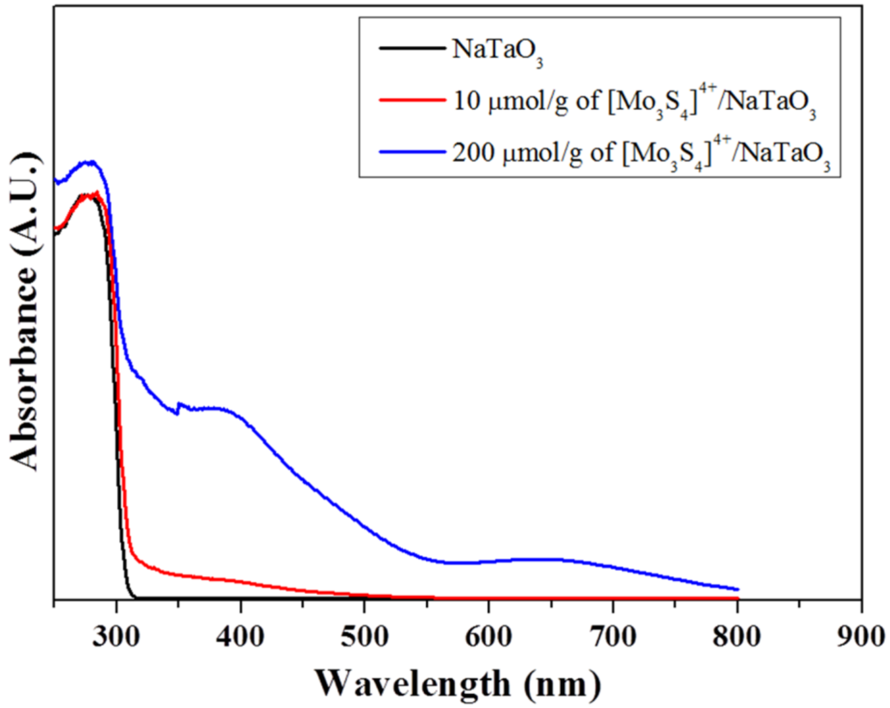

Fig. S3. UV-vis spectra of $NaTaO_3$ bulk (a) without and (b) with $[Mo_3S_4]^{4+}$ clusters.

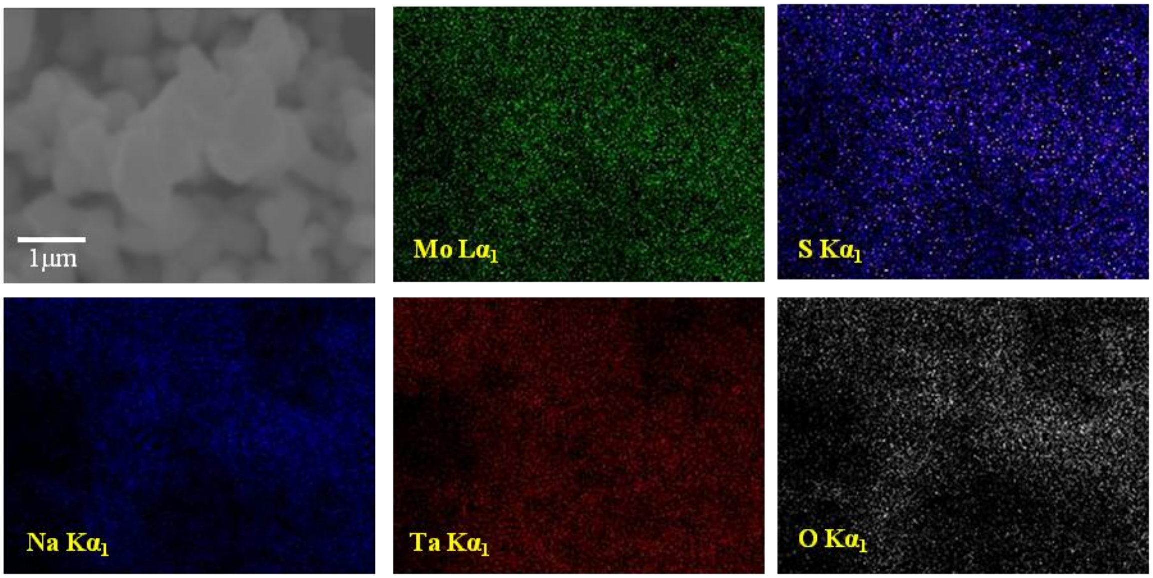

Fig. S4. EDS mapping of $[Mo_3S_4]^{4+}$ molecular clusters loaded on $NaTaO_3$.

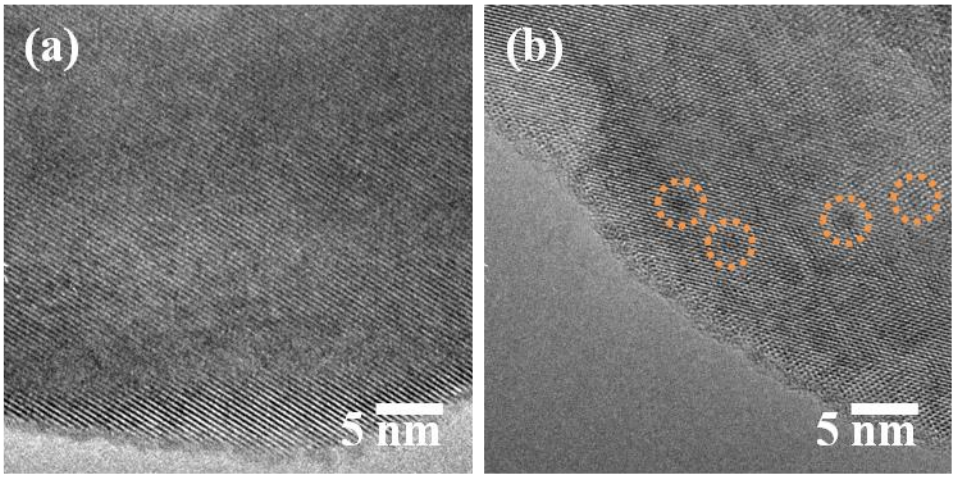

Fig. S5. HRTEM image of (a) bare $NaTaO_3$ powder and (b) $[Mo_3S_4]^{4+}$ loaded $NaTaO_3$ powder.

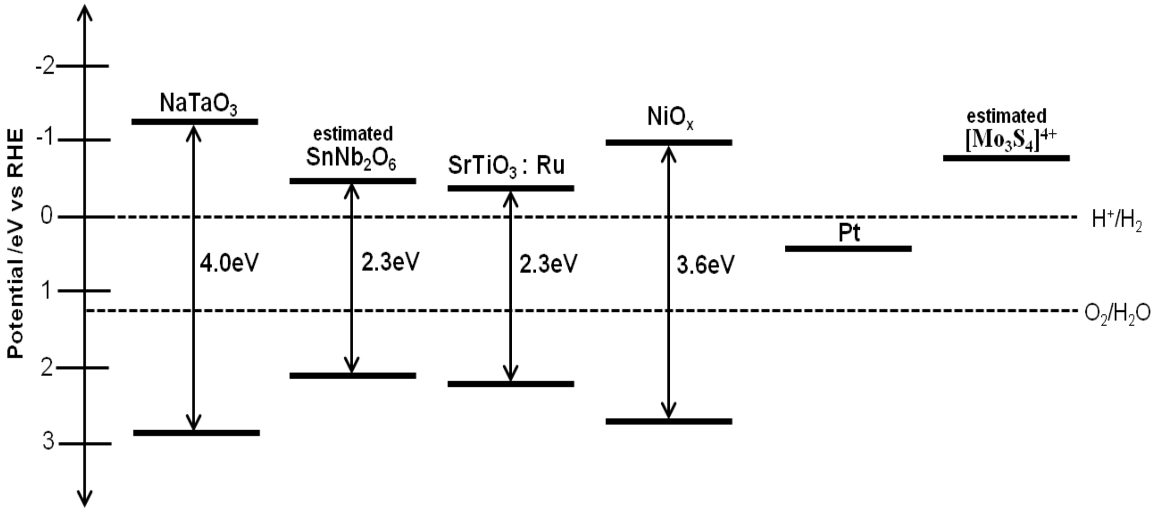

Fig. S6. Energy diagrams of various photocatalysts and cocatalysts.