

***Electronic Supplementary Information for***

**Well-defined  $\text{Co}_x\text{CeO}_{2+x}\text{-MoS}_2$  Nanotube Hybrids as Novel  
Electrocatalysts for Promising Hydrogen Evolution Reaction**

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## Experimental Section

*Synthesis of MoS<sub>2</sub> nanotubes:* MoS<sub>2</sub> nanotubes were prepared by a solvothermal process. (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> (1.0 mmol, 99.9%, Aldrich) and CH<sub>3</sub>CSNH<sub>2</sub> (2.5 mmol, 99.0%, Aldrich) were dissolved in 30 mL solvent (15 mL absolute ethanol, 99.7%, Sinopharm Chemical Reagent Company and 15 mL hexylamine, 99.0%, TCI Development Company). After continuously stirring for 30 min, the solution was transferred to 50 mL sealed Teflon-lined stainless steel autoclave and heated at 210 °C for 12 h. After the autoclave was cooled down to room temperature, and the powder was centrifuged, washed with absolute ethanol and dried under vacuum at 60 °C overnight.

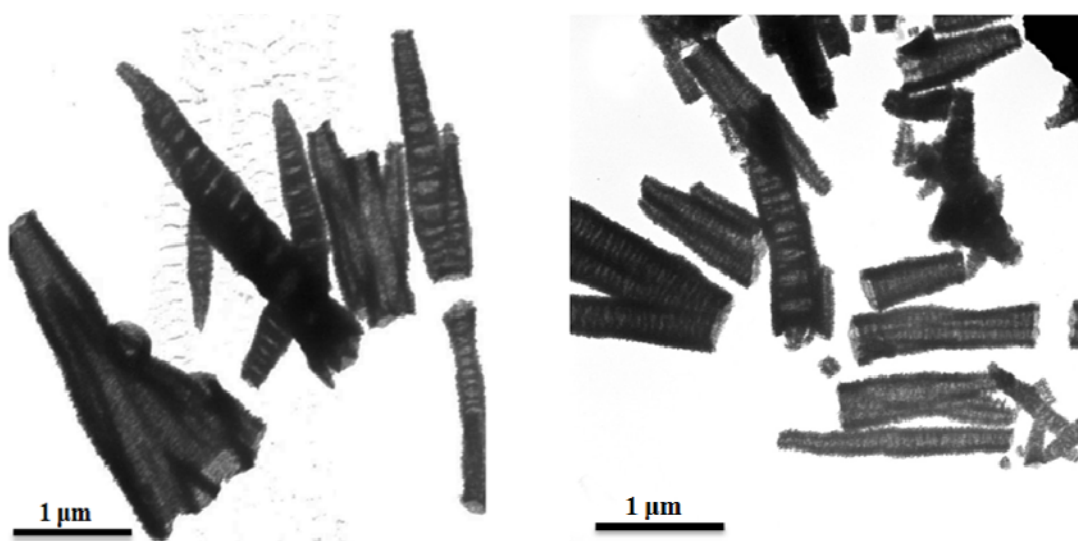
*Synthesis of Co<sub>x</sub>CeO<sub>2+x</sub>-MoS<sub>2</sub> nanocatalysts:* 30 mg MoS<sub>2</sub> was dispersed in 30 mL solution (15 mL absolute ethanol + 15 mL hexylamine) by bath sonication for at least 30 min, specifically, the addition sources of Co and Ce were prescribed for 5 mg. According to the mass concentration, the detailed addition of the reagents can be seen in Table S1. (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 99.9%, Alfa Aesar; hexamethylenetetramine (HMTA), 99.8%, Alfa Aesar and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99.0%, Alfa Aesar). All of the aqueous solutions were slowly added to the corresponding MoS<sub>2</sub> solution. Afterwards, the series of the mixture were vigorously stirred at 90 °C in an oil bath for 6 h. Then the suspensions were transferred to 50 mL sealed Teflon-lined stainless steel autoclave. The reaction was kept at 160 °C for 5 h. A suite of Co<sub>x</sub>CeO<sub>2+x</sub>-MoS<sub>2</sub> nanocatalysts were obtained by centrifuged with absolute ethanol and then

dried under vacuum at 60 °C overnight. Finally, the powders were treated in a tube furnace at 300 °C for 60 min with N<sub>2</sub> flowing.

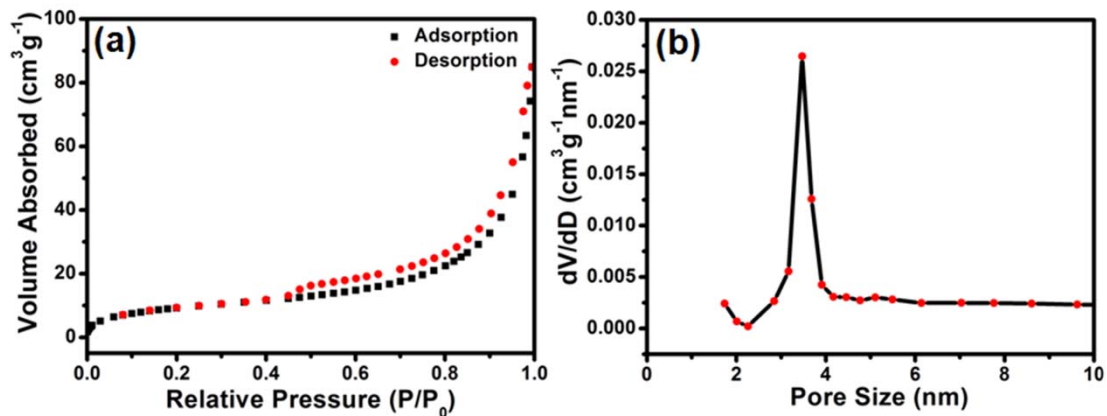
*Electrochemical measurements:* Electrochemical tests were verified in a three-electrode system at an electrochemical station (CHI 660D). A Pt slice acted as counter electrode, and a saturated calomel electrode (SCE) acted as the reference. The fabrication approach for the working electrodes containing HER catalysts is depicted as following. First, 4 mg of given catalyst sample consists of 500 μL absolute ethanol, 450 μL H<sub>2</sub>O, and 50 μL 5% Nafion (5.0%, Aldrich), sonicated for 60 min to form a well-dispersed catalyst ink. Second, 5 μL of the catalyst ink was drop-cast onto a rotating disk electrode made of glassy carbon (3 mm in diameter, loading density ~0.20 mg cm<sup>-2</sup>), which acted as the working electrode. Linear sweep voltammetry starting at 0 V and finishing at -0.4 V (vs. RHE) with a scan rate of 10 mV/s was operated in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Chronoamperometry measurements (i-t curves) were measured under a constant overpotential of -0.5 V (vs. SCE) for catalytic stability test and alternate current (AC) impedance measurements were also carried out in 0.5 M H<sub>2</sub>SO<sub>4</sub> (98.0%, Sinopharm Chemical Reagent Company) from 1 to 10<sup>5</sup> Hz with an AC amplitude of 5 mV. The cyclic voltammetry was measured by the identical standard three-electrode setup ranging from 0.97–0.297 V (vs. RHE) at a scan rate of 40, 60, 80, *etc.* mV s<sup>-1</sup>.

*Characterizations:* The structure and composition of the synthesized samples were characterized by tools including X-ray diffraction (XRD), the

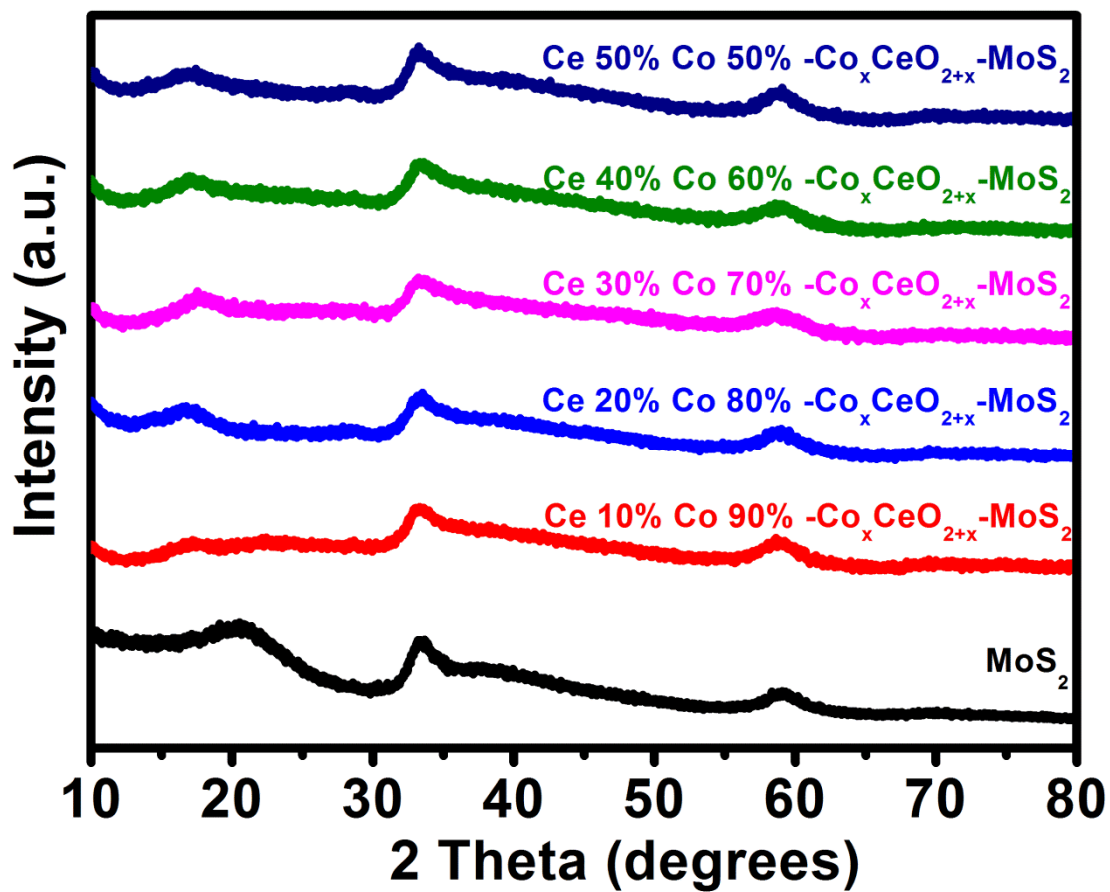
XRD patterns with diffraction intensity versus  $2\theta$  were recorded in a Shimadzu X-ray diffractometer (Model 6000) using Cu K $\alpha$  radiation. And X-ray photoelectron spectroscopy (XPS) were performed on a PHI Quantera SXM analyzer using an Al X-ray source. Morphology analysis was investigated using a JEOL 6700F scanning electron microscope (SEM) at an accelerating voltage of 20 KV. TEM images were acquired from Hitachi HT-7700 transmission electron microscope with an accelerating voltage of 100 kV and HRTEM images were taken with a Philips Tecnai F20 FEG-TEM transmission electron microscope with an accelerating voltage of 200 kV. The specific surface area was verified by the Brunauer-Emmett-Teller (BET) method.



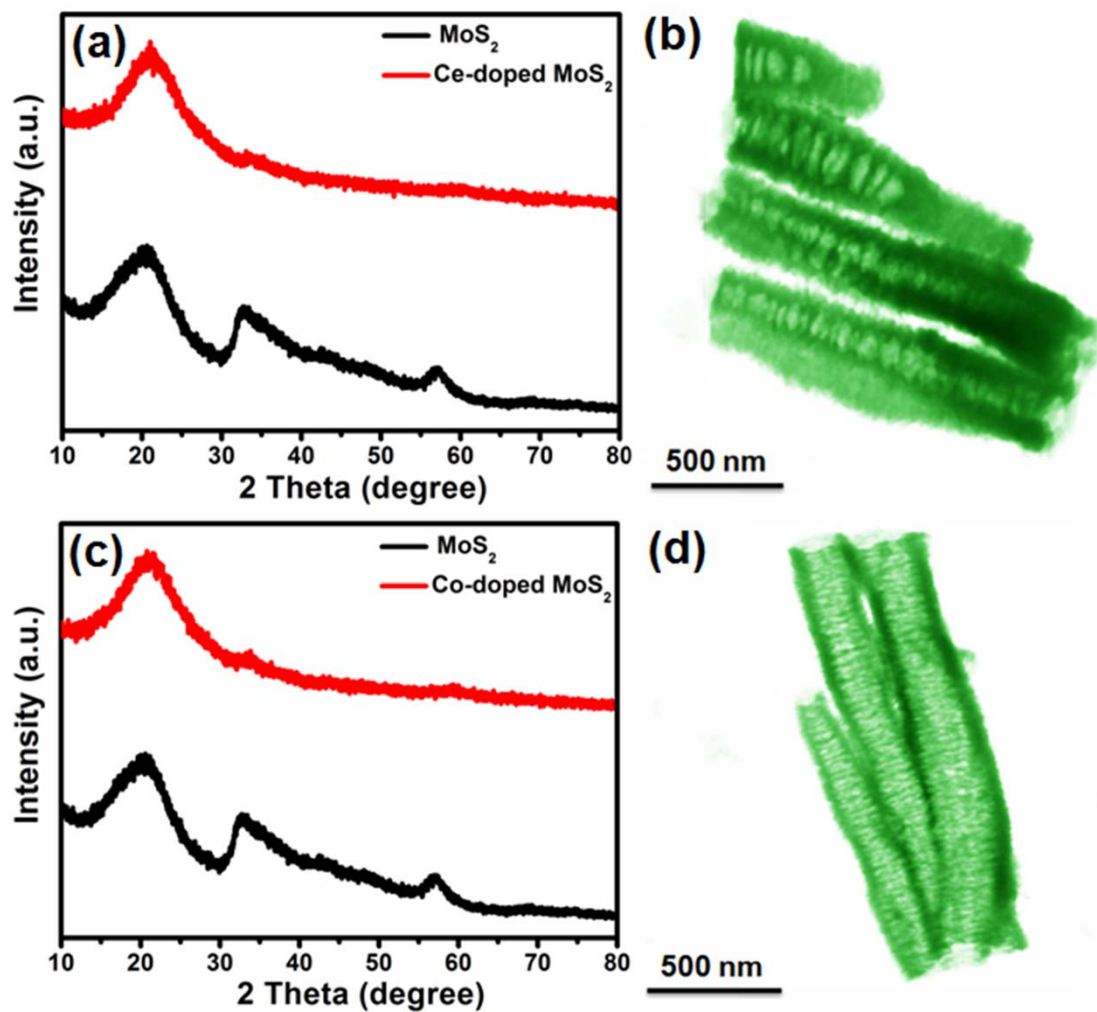
**Fig. S1** TEM images of MoS<sub>2</sub> nanotubes.



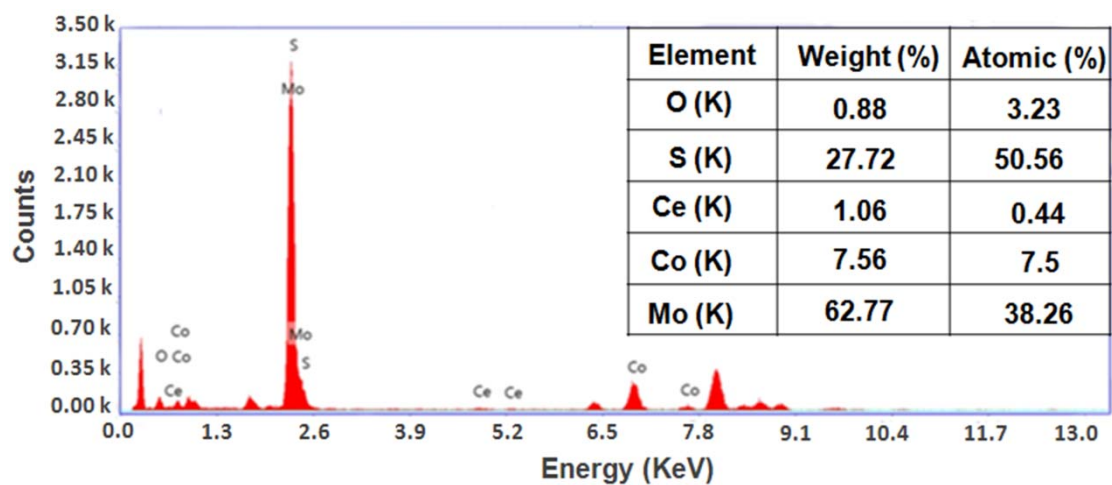
**Fig. S2** (a) The typical nitrogen adsorption-desorption isotherm of MoS<sub>2</sub> nanotubes. (b) Pore size distribution of MoS<sub>2</sub> nanotubes.



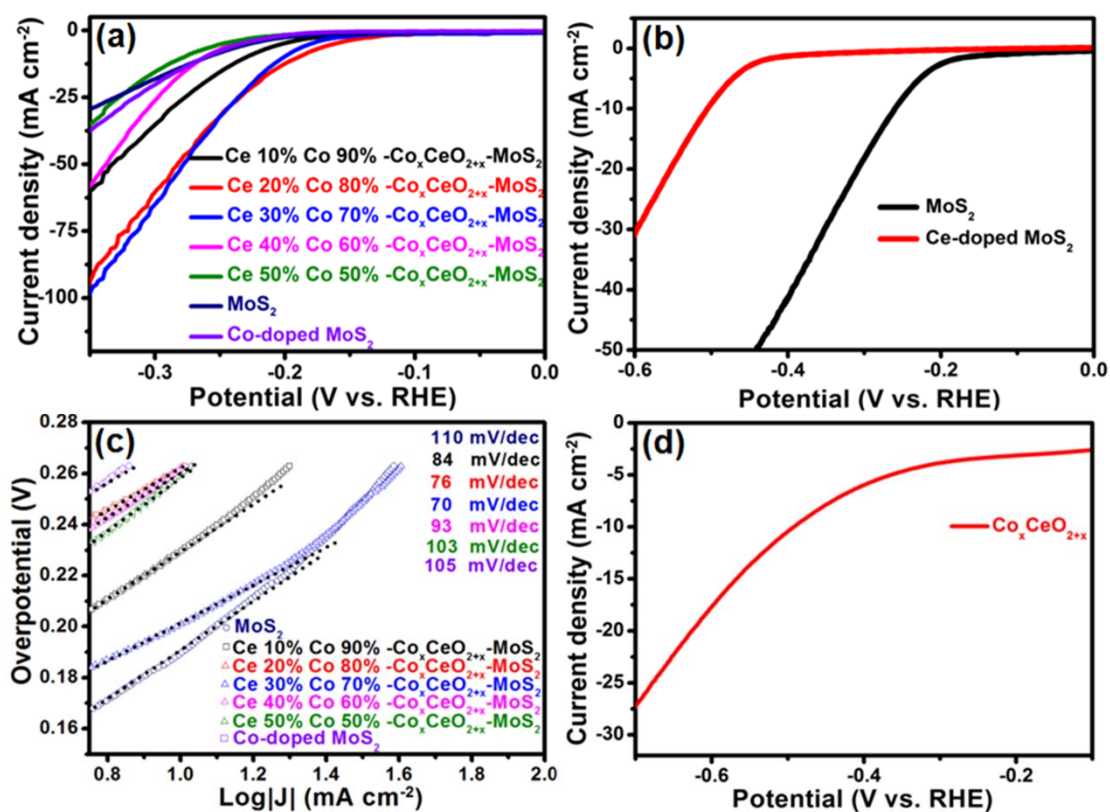
**Fig. S3** XRD patterns of MoS<sub>2</sub> and Co<sub>x</sub>CeO<sub>2+x</sub>-MoS<sub>2</sub> with different Ce/Co mass ratios.



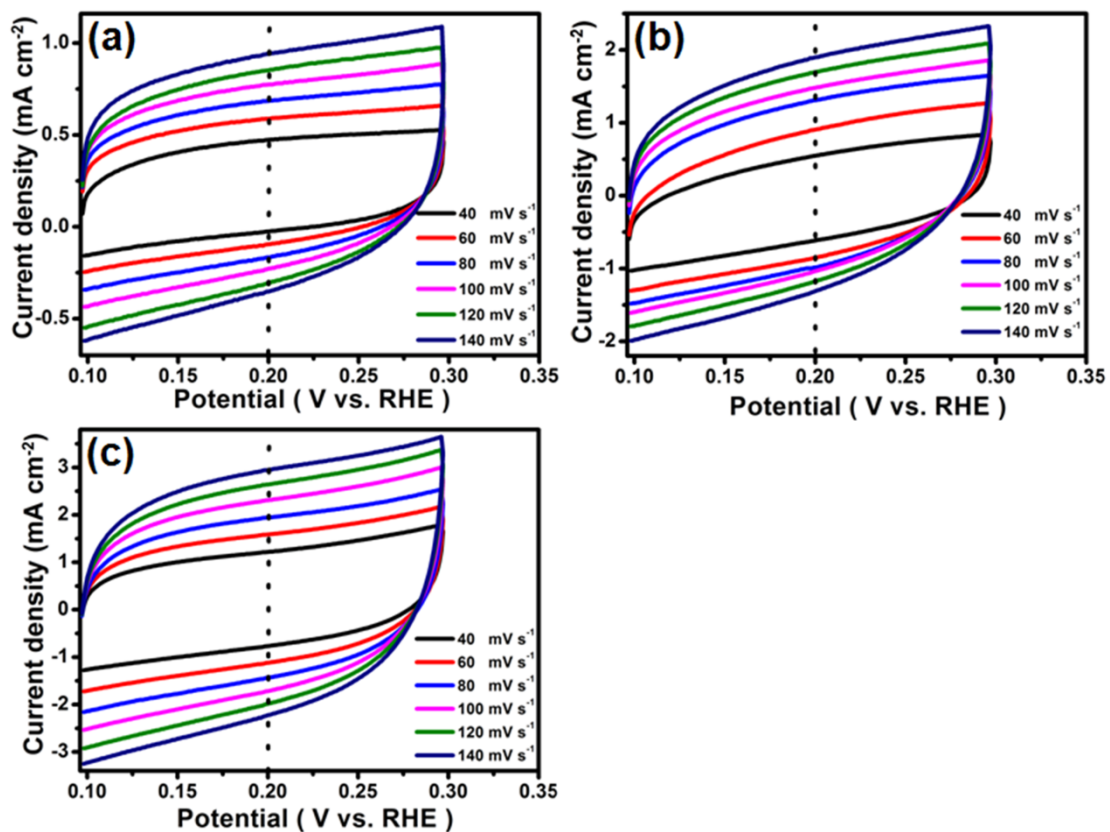
**Fig. S4** (a) XRD patterns of MoS<sub>2</sub> and Ce-doped MoS<sub>2</sub> electrocatalysts. (b) TEM image of Ce-doped MoS<sub>2</sub> electrocatalyst. (c) XRD patterns of MoS<sub>2</sub> and Co-doped MoS<sub>2</sub> electrocatalysts. (d) TEM image of Co-doped MoS<sub>2</sub> electrocatalyst.



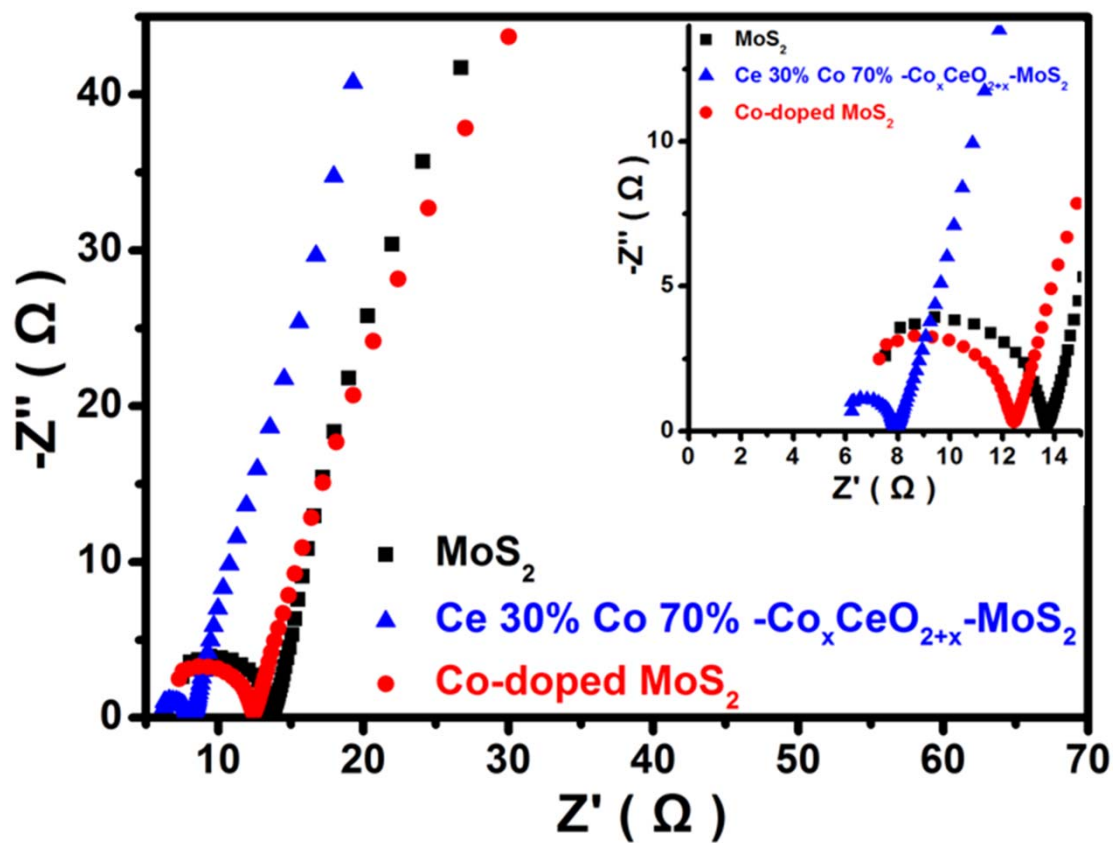
**Fig. S5** TEM-EDS spectrum of the Ce<sub>0.3</sub>Co<sub>0.7</sub>O<sub>x</sub>-MoS<sub>2</sub>.



**Fig. S6** (a) Polarization curves of pure MoS<sub>2</sub>, Co-doped MoS<sub>2</sub> and different Ce/Co mass ratio of Co<sub>x</sub>CeO<sub>2+x</sub>-MoS<sub>2</sub>. (b) Polarization curves of pure MoS<sub>2</sub> and Ce-doped MoS<sub>2</sub>. (c) Corresponding Tafel plots obtained from the polarization curves of pure MoS<sub>2</sub>, Co-doped MoS<sub>2</sub> and different Ce/Co mass ratio of Co<sub>x</sub>CeO<sub>2+x</sub>-MoS<sub>2</sub>. (d) Polarization curve of Co<sub>x</sub>CeO<sub>2+x</sub> nanocrystals.



**Fig. S7** Voltammograms of the (a) pure MoS<sub>2</sub>, (b) Co-doped MoS<sub>2</sub> and (c) Ce<sub>0.3</sub>Co<sub>0.7</sub>O<sub>x</sub>-MoS<sub>2</sub> electrocatalysts at various scan rates (40-140 mV s<sup>-1</sup>).





**Fig. S8** EIS curves measured in the frequency ranging from 1 Hz to  $10^5$  Hz at the open circuit voltage with an alternate current amplitude of 5 mV for pure MoS<sub>2</sub>, Ce<sub>0.3</sub>Co<sub>0.7</sub>O<sub>x</sub>-MoS<sub>2</sub> and Co-doped MoS<sub>2</sub>.

**Table. S1** The detailed addition of the reagents for Ce-doped MoS<sub>2</sub>, Co-doped MoS<sub>2</sub> and different mass ratio Co<sub>x</sub>CeO<sub>2+x</sub>-MoS<sub>2</sub> electrocatalyst.

	0.2 M Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O (μL)	0.2 M Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (μL)	0.2 M C <sub>6</sub> H <sub>16</sub> N <sub>4</sub> (μL)
Ce10% Co90%- Co <sub>x</sub> CeO <sub>2+x</sub> -MoS <sub>2</sub>	5.8	77.3	23.0
Ce20% Co80%- Co <sub>x</sub> CeO <sub>2+x</sub> -MoS <sub>2</sub>	11.5	68.0	46.0
Ce30% Co70%- Co <sub>x</sub> CeO <sub>2+x</sub> -MoS <sub>2</sub>	17.3	60.0	69.0
Ce40% Co60%- Co <sub>x</sub> CeO <sub>2+x</sub> -MoS <sub>2</sub>	23.0	51.5	92.0
Ce50% Co50%- Co <sub>x</sub> CeO <sub>2+x</sub> -MoS <sub>2</sub>	28.8	43.0	115.0
Ce-doped MoS <sub>2</sub>	57.6	0	230.4
Co-doped MoS <sub>2</sub>	0	86.0	5.0