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Supplementary Information

Enhanced H_2 Evolution Based on Ultrasound-assisted Piezo-catalysis of Modified MoS_2

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Experimental

Synthesis

Typically, 7 mmol sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) and 35 mmol thiourea (Mo:S ratio =1:5) were dissolved in 40 mL distilled water under vigorous stirring, then the pH was adjusted to less than 1 with 2 M HCl. After stirring for 60 min, the solution was then transferred into a 50 mL Teflon-lined stainless steel autoclave, maintained at 200 ºC for 24 h. After that, the autoclave cooled down to room temperature naturally. The obtained products were collected by centrifugation, washed with distilled water and ethanol for several times, and dried at 60 ºC about 12 h. The further acidized procedure was undertaken by stirring 1 g of as-prepared MoS_2 with 40 mL of 0.5M or 2M HCl for 12 h at room temperature. The Au-MoS_2-2M samples were synthesized through ultrasound and chemical methods(spontaneous redox reaction) in Au-5wt % $HAuCl_4$, separately. The G-SH-decorated MoS_2-2M was

synthesized by adding 0.3g G-SH and 0.3g MoS_2-2M into 30ml distilled water, constantly stirred for 6h. After that, obtained products were collected by centrifugation, washed with distilled water for several times, and dried at 60 ºC about 12 h.

Characterization

The powder X-ray diffraction (XRD) patterns of the synthesized samples were recorded on a D/MAX 2250 diffractmeter (Rigaku, Japan) using monochromatized Cu Kα (λ=0.15418nm) radiation under 40kV and 100mA with the 2θ ranging from 20° to 70°. UV−Vis adsorption spectra of the water-dispersed samples were obtained on an UV−Vis spectrophotometer (Hitachi U-3010). The microstructures and morphologies of the samples were analyzed by Transmission Electron Microscopy (TEM, FEI Tecnai G2 F30). The samples were then analyzed by AFM (Dimension, Bruker, Germany) under electrostatic force microscope pattern (EFM). The samples were added in ethanol solution and disperse uniformly by 15min ultrasound, dip-coated onto the Si (100) substrate and dried under ambient conditions. Raman spectra were recorded on a microscopic confocal Raman spectrometer (Renishaw 1000NR) with an excitationof 514nmexcitation of 514 nm laser light.X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi, ThermoFischer with monochromated aluminum Kα X-rays at 1253.6 eV under ultrahigh-vacuum conditions. The C 1s signal was used to correct the charge effects. The fluorescence spectroscopy was employed to investigate the ·OH radicals. The ·OH scavenger of terephthalic acid was mixed with sodium hydroxide to prepare colorless aqueous solution. 0.05 g of MoS_2-2M was added into the as-prepared solution then ultrasonicated. The peak intensity of FL indicated the concentration of ·OH radicals in the catalytic system. The emission wavelength is 315 nm. And the fluorescence wavelength which represent the generation of ·OH is 425 nm.

Electrochemical measurements

Electrochemical measurements were performed on a CHI660D electrochemical workstation (Shanghai Chenhua, China) using a standard three-electrode cell including a working electrode, the counter electrode platinum wire and a reference electrode saturated calomel electrode (SCE). The working electrodes were prepared by dip-coating: 2mg catalyst was suspended in ethanol solution and ultrasonicated for 15 min to form slurry. 0.1 mL of as-prepared slurry was dip-coated onto a 2.5 cm×1.5 cm fluorine-tin oxide(FTO) glass electrode which was deposited on 2 cm×1.5 cm square. The film was dried under ambient conditions for 12 h. Here, the electrolyte solution was 0.2M KCl. The measurements of impedance potential method was performed under 500Hz to get the Mott-Schottky plots in 0.5M H_2SO_4. After the electrolyte solution was purged by nitrogen, the measurements of electrochemical impedance spectroscopy (EIS) were performed in 10mmol/L potassium ferricyanide. The Zeta potential experiments were performed on Zeta Potential Analyzer(Zetaplus, Brookhaven, USA). In order to avoid the effect of ion concentrations, we sustain the electroconductibility 300μS approximately and use NaOH and HCl to adjust the pH(3-9).

Hydrogen evolution catalytic test

With a water cooling jacket outside the reactor, the piezo-catalytic reaction was performed in a hermetic gas circulation under 25±0.5 °C and the ultrasound resource was from a KuDos ultrasound cleaner(SK6200 LHC, 280W). Then 0.05 g of catalyst was added in 200 mL aqueous solution in a Pyrex reaction cell. In order to degas the air in the system, the solution was purged by nitrogen for 20 min before irradiation. The production of H_2 was measured by an online gas chromatograph (Tianmei, GC-7890, TCD, N_2 or Ar carrier). The reaction was continued 2.5h for H_2 evolution. Fe^{2+} has been used as inorganic oxidizable sacrificial agent

for the trap of holes to explore effect of holes.

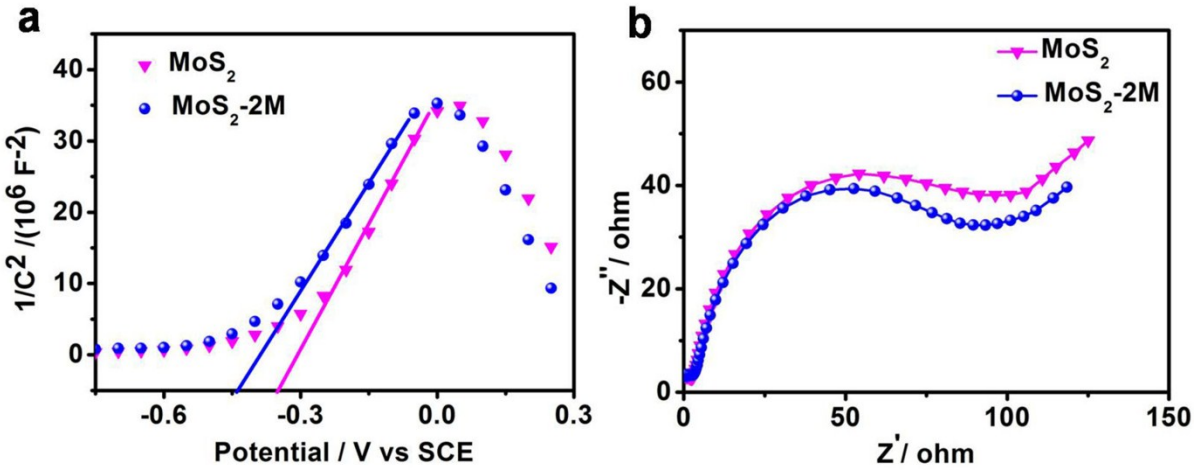

Figure S1. (a) Mott-Schottky (MS) plots of MoS_2 and acidized MoS_2 (MoS_2-2M), (b) Electrochemical Impedance Spectroscopy (EIS) of MoS_2 and acidized MoS_2.

Mott−Schottky curves indicated the HER activity of the as-prepared MoS_2 and the MoS_2-2M (shown in Figure. S1a). The MoS_2-2M gave more negative potential (-0.206 V vs NHE) than that of MoS_2 (-0.109V vs NHE) which is not acidized.

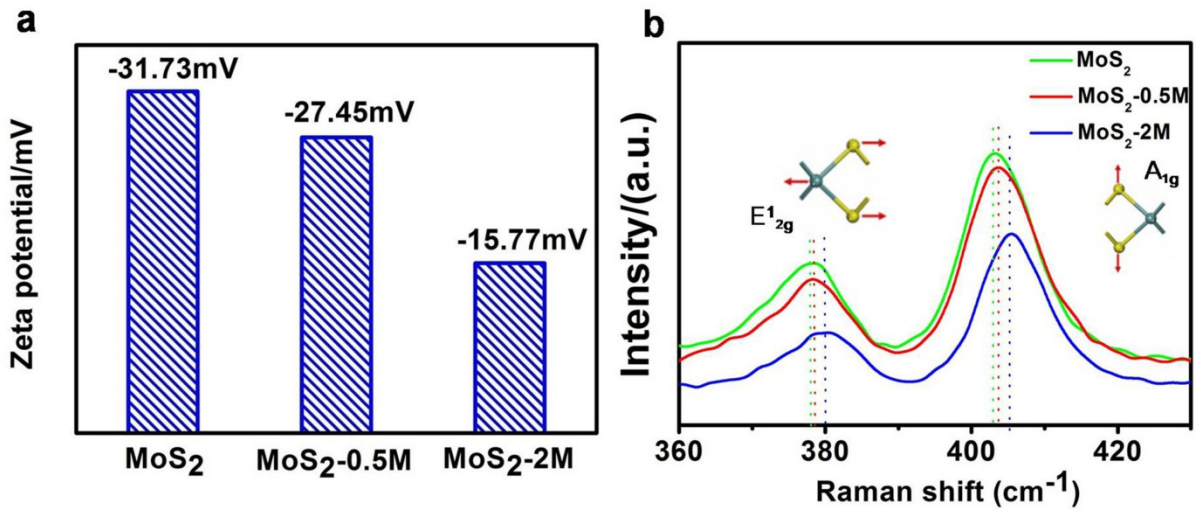

Figure S2. (a) Zeta potential of different acidized samples, (b) Raman spectra of different acidized samples.

Figure. S2a are the zeta potential of three as-fabricated MoS_2 samples. According to the test outcome, MoS_2-2M gave a more positive potential (-15.77 mV) as the result of high acidification. Acidification procedure obviously altered the surface electrical property due to the enhancement of the H^+ adsorption. To be specific, the abundant proton absorbed around the active edge sites that drived the surface charge positive[1]. Raman spectrum was also applied in characterize the acidification shown in Figure. S2b. The Raman peaks at 378 cm^{-1} and 404 cm^{-1} are attributed to E^1_{2g} and A_{1g} vibrations, which could be ascribed to interlayer and intralayer vibration of MoS_2[2, 3], respectively.

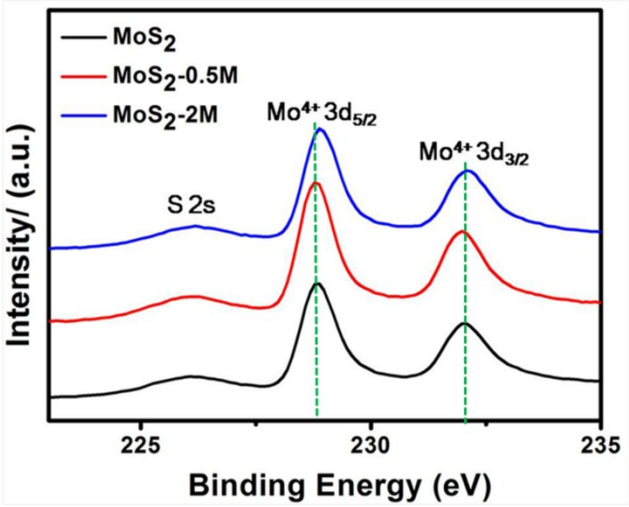

Figure S3. XPS spectra of Mo 3d and S 2s.

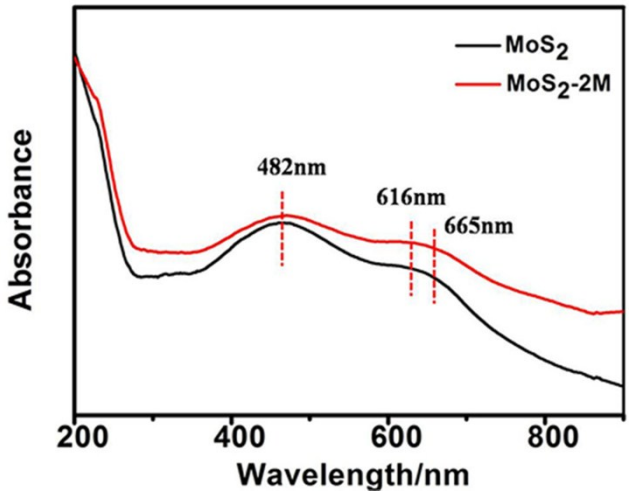

Figure S4. UV−vis absorption spectra of the as-prepared MoS_2 samples dispersed in pure water.

The UV–vis absorption spectrum was also studied to investigate the MoS_2 characteristics of layer structure (shown in Figure S4). The typical A and B excitonic[4, 5] absorption bands at 665 nm (1.86 eV) and 616 nm (2.01 eV) have been observed in the water-dispersed samples after ultrasound dispersion. These two absorption bands have been well established to be the direct excitonic transitions at the K point of the Brillouin zone in monolayer and few-layers MoS_2[3]. Apart from the above observations, an intense absorption band centered at 434 nm (2.85 eV), which is a feature absorption that is universal to monolayer transition metal dichalcogenides, was also clearly founded. All of the results demonstrated that monolayer and few-layers MoS_2 widely distributed in the as-prepared samples which play the main role of generating the piezo-electric field.

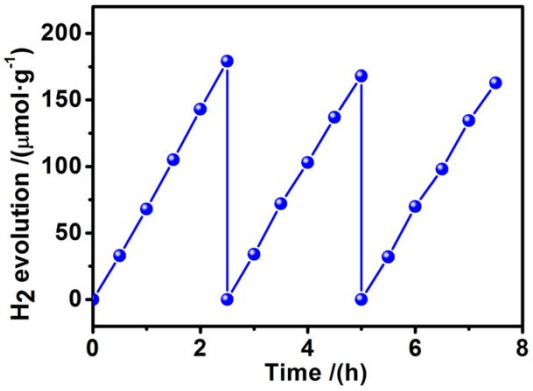

Figure S5. The cycle experiments of MoS_2-2M.

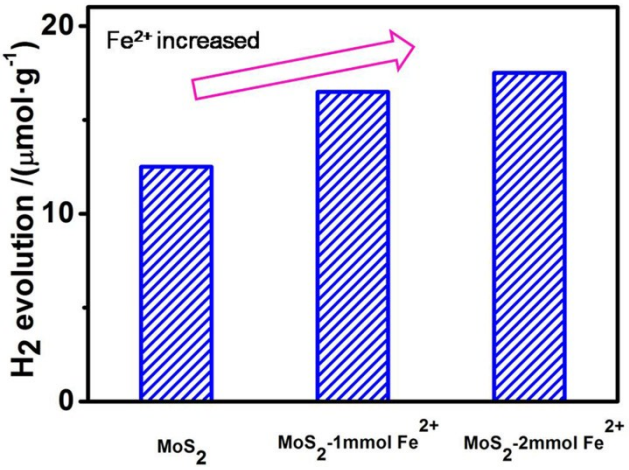

Figure S6. The H_2 evolution of MoS_2(no addition and Fe^{2+} added into the system，reaction time 0.5h)

We have carried out the experiments using inorganic oxidizable sacrificial agent(Fe^{2+}) for the trap of holes to explore effect of holes. As the amount of Fe^{2+} increased, the H_2 evolution gave an increase. Definite increase of H_2 evolution demonstrated that the separation of carriers in MoS_2 was promoted by the consumption of holes for oxidizing Fe^{2+} to Fe^{3+}. If holes can be consumed by sacrificial agent, the separation of carriers can be enhanced further thus increased the H_2 evolution.

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