Few-layer MoS_2 nanosheet-modified CdS inverse opal heterostructures with enhanced photoelectrochemical hydrogen evolution

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Abstract:

Nowadays, the renewable energy is increasingly needed because of technology advancing, excessive using of fossil fuels, and environment deterioration. However, the energy structure in many countries, for example, the United States, contains only 11% of renewable energy. The clean fuel: hydrogen gas, is one of the most commonly accepted energy sources. The product of hydrogen combustion is water, so the fuel is clean and environmentally friendly, giving it the potential to develop.

There are many ways to produce the hydrogen gas, but the most effective way is by photo-electrochemistry. It is a method that combines the photocatalytic and electrocatalytic water splitting. The efficiency of the photo-electrochemistry is more promising than the other two. Therefore, studies on how to further improve the efficiency of the photo-electrochemistry is an orientation or frontier science that the chemists are exploring on.

Herein, we developed a novel strategy to increase the amount of hydrogen gas made by the photo-electrochemistry. More specifically, we developed a heterostructure based on CdS and MoS_2 for this photo-electrochemical hydrogen evolution with the bond gap of 2.42 eV and 1.8 eV respectively. The CdS as a semiconductor responds to both the natural light and the artificial lights. It has the appropriate conduction bond level to reduce the H^+ to H_2. However, the CdS electrode easily causes recombination and photo-corrosion. Thus, the MoS_2 is used to coat the CdS electrode to improve the performance of the CdS electrode. As a result, the MoS_2 is uniformly coated on CdS inverse opal structure as nanoflakes. Photo-current density of the CdS electrode after coating MoS_2 increases 6 times compared with the pristine CdS at the -0.2V vs. relative hydrogen electrode.

In summary, we have successfully developed a MoS_2 nanosheet coated CdS heterostructure for PEC hydrogen evolution. The hybrid electrode produces the photo-current density of $3mA/cm^2$. This method can be potentially used in other studies, for example, the reduction of carbon dioxide, organic-inorganic hybrid solar cells, and nitrogen reduction.

Key words: clean energy, hydrogen production, semiconductor, photo-electrochemistry

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2. Method

3. Result and discussion

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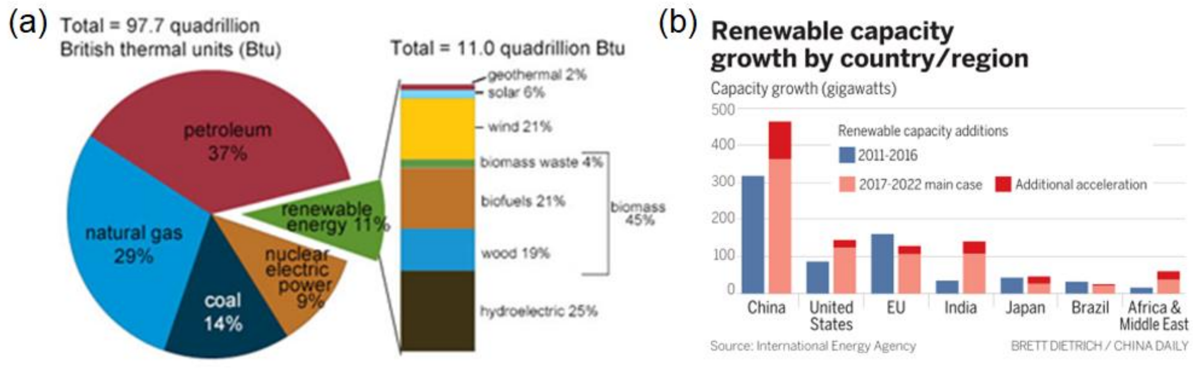
1. Introduction:

1.1 Current energy stage in US and China

Renewable energy is energy that forms from the renewable sources which can be replenished within the human lifetime. The energy source including solar, wind, water, geothermal, etc. Renewable energy is clean energy which does not create greenhouse gas, whereas the traditional fossil fuel (coal, oil, nature gas) produces carbon dioxide during its combustion. In the United States, the total amount of energy using in 2017 was 97.7 quadrillion in British thermal units (Btu) (Figure 1a). The proportions of petroleum, natural gas, coal, nuclear electric power, and renewable energy are 37%, 29%, 14%, 9%, and 11% respectively. The proportions of renewable energy sources are 6% geothermal, 21% wind, 45% biomass, and 25% hydroelectric. Comparing the renewable capacity growth by countries or regions between 2011-2016 and 2017-2022, Figure 1b shows the discrepancy between China, US, Europe, India, Japan, Brazil, and Africa & Middle East. China shows the greatest renewable capacity in 2011-2016, and the greatest additional acceleration; US and India also reflect high renewable capacity in 2017-2022.



Source: International Energy Agency

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Figure 1. (a) The US proportion and amount of total energy usage and proportion of renewable energy in 2017 [1]. (b) Renewable capacity growth by country/region during 2011-2016 and 2017-2022.

1.2 H_2 as an energy carrier

Hydrogen as a clean renewable energy source is ideal to replace fossil fuels. The common fossil fuels like petroleum, coal, and natural gas would produce CO_2 and NO_x, which are known as the greenhouse gas and the one of the elements to form the acid rain, when they are combusted [3]. Hydrogen as one of the most abundant elements on the earth is contained in many compounds. As a fuel, its combustion would only react with oxygen to produce H_2O. Therefore, it is a clean energy source to develop. To produce massive amount of hydrogen gas, there are two methods: water electrolysis and sunlight combustion; and to store it, carbon-fiber- reinforced composite material hydrogen-inert aluminum tanks are available [3, 4].

1.3 comparison of photocatalytic, photoelectrochemical, and electro water splitting

As the studies towards the clean energy source hydrogen develop, multiple ways of producing hydrogen gas has been invented. Photocatalysis is a way that can easily use the energy from the natural sunlight or artificial room light. It starts or accelerates the redox reaction of the semiconductors irradiated [5]. When a semiconductor absorbs enough light, the photoelectrochemistry stimulate the electrons shift to a photoelectrode of the semiconductor to reduce water to hydrogen gas, then the holes are transfers to the surface to oxidize the water into oxygen gas [5]. The electro water splitting is another method to decompose the water into hydrogen and oxygen gases by only using electric current about 1.23 volts. In those three massive producing hydrogen techniques, the photocatalytic is relatively weaker and the electro water splitting is stronger, but photoelectrochemical is a combination of the two methods which produce a higher efficiency than the other two. The composition of the PEC system includes photoanode, photocathode, and the cocatalyst.

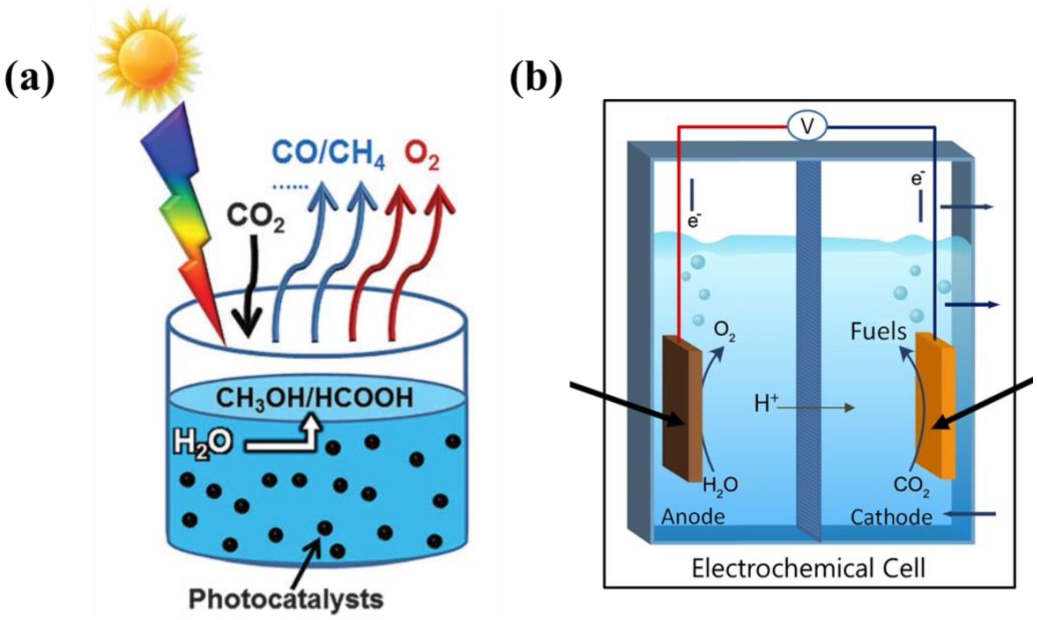


Figure 2. The working mechanism of photocatalysts and electrocatalysts [5].

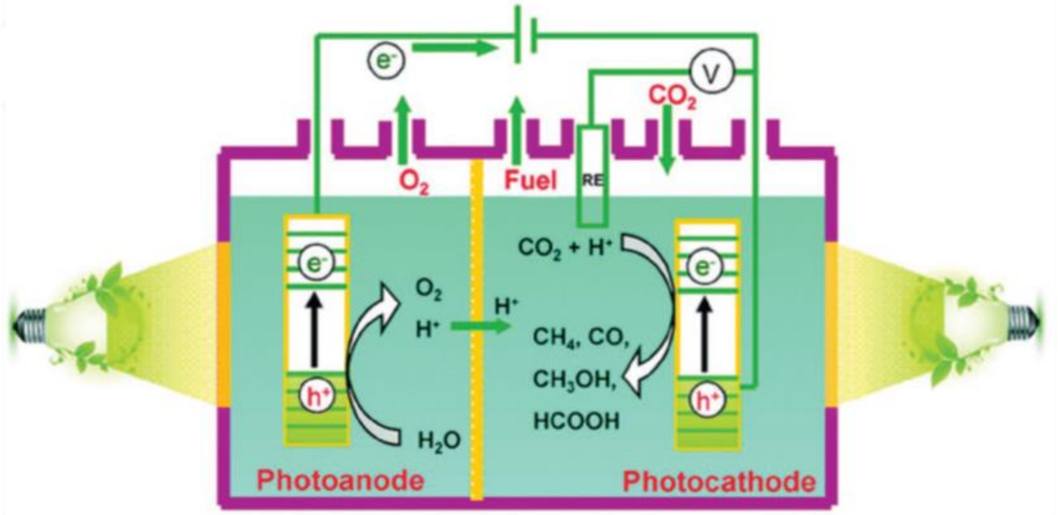


Figure 3. The working mechanism of photoelectrochemical system, including photoanode, photocathode, and reference electrodes [6].

1.4 Materials for photoelectrochemical hydrogen evolution

1.4.1 Cadmium sulfide (CdS)

Cadmium sulfide (CdS) is an inorganic compound used as a semiconductor in the photoelectrochemical (PEC) water splitting experiment to produce hydrogen gas. It responses to visible lights including natural light and artificial lights. CdS has been verified as a crucial photoanode material for PEC water splitting because its distinguishing light absorption ability, band gap of 2.42eV. Moreover, to reduce the H^+ to H_2, CdS has the appropriate conduction bond level for it [6]. Above all, its nanopores structure has higher efficiency than the nanostructures of other semiconductors. However, CdS photoelectrode can easily cause carrier recombination and photocorrosion [6].

1.4.2 Cu_2O

Cuprous oxide (Cu_2O) is a p-type semiconductor with direct bond gap of 2.137 eV and is below the theoretical photocurrent density of -14.7 mA/cm^2. The properties of Cu_2O guarantees its use in generating H_2 from water. Moreover, the abundance of copper in nature offer inexpensive material for the use of PEC [7]. However, the Cu_2O has high electron-hold recombination rate and poor photostability prevent it from highly effective as a potential material for PEC [8]. Methods to improve photocorrosion inhibition and photostability of Cu_2O are coating Pt, RuO_x, and MoS2+x on CuO heterostructure, and preparing with thermal oxidation Cu sheet [7, 9].

1.4.3 TiO_2

Titanium dioxide (TiO_2) is a p-type semiconductor with properties of inexpensive, non-toxic, high stability. However, as a photocatalyst for PEC, it has a relatively wide bond gap of 3.05 eV, thus its reaction to visible light is poor [10]. Moreover, the TiO_2 is hard to decompose large amount of pollutants and refractory chemicals [11].

1.4.4 Si

Silicon (Si) is a commercial productive PEC semiconductor material. Compared with other materials, Si has a relatively narrow band gap of 1.17eV, excellent crystallinity, and industrial maturity. Porous structure of Si, known as the black Si, can minimize the light reflection by increasing the surface area [12]. The Si has been used as a photoelectrode in PEC CO_2 reduction and as a photocathode in PEC to improve H_2 production [13, 14].

1.4.5 Molybdenum disulfide (MoS_2)

Molybdenum disulfide (MoS_2) has an indirect band gap about 1.2 eV, and a direct band gap of 1.8 eV [15]. As a catalyst in this experiment, MoS_2 has the advantage of smaller bond gap, thus capturing more light than the CdS. Moreover, it has other benefits of inexpensive, available, and these superities make the MoS_2 an improving material of electrodes [16].

1.5 Research goals for this project

Since the demand for clean energy is increasing, the development of the photoelectrochemical hydrogen evolution is essential to promote the reusable energy. Other than producing hydrogen, the techniques in photoelectrochemistry can also be applied to the removal of organic or inorganic species from gas or aqueous stage [17].

2. Method

2.1 CdS IO synthesis

The polystyrene (PS) spheres is a kind of carbon hydrogen compound that disappear when it is heated in hot water. It has a diameter of 200 nm. It is used in the experiment so the CdS can form an inverse opal (IO) structure film on the glass base and thus form an electrode layer. The CdS quantum dots that has a diameter of 2-3 nm and the PS spheres should be added into the beaker forming a homogeneous solution. Then the fluorine-doped tin oxide (FTO) conducting glass-like base is vertically inserted into the solution, so the CdS solution can attach on the glass. The film is heated in air at 300˚C for 1 hour, and then keep heating it at 400˚C for another 30 minutes, therefore the solution forms a uniform film on the FTO, and this is the electrode layer. The purpose of annealing the film is that the structure easily collapse if it is heated at 400˚C at first, but the PS spheres melt only at 400˚C, so the film need to be warmed at 300˚C and then calcined at higher temperature.

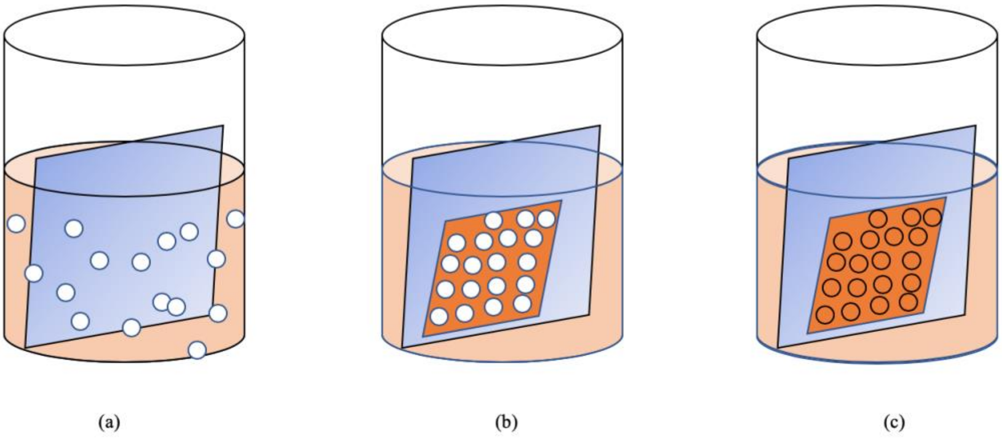


Figure 4. The synthesis of CdS inverse opal structure.

2.2 MoS_2 coating CdS

The certain amount of $(NH_4)6Mo_7O_{24}\bullet4H_2O$ and L-cysteine (0.50 g) are added together in 35mL deionized water stirring at room temperature for 60 minutes forming a precursor. Then the liquid is transferred to a 50mL Teflon-lined stainless-steel autoclave, and the FTO with CdS on it is vertically inserted in the container. The Teflon-lined stainless-steel autoclave is heated at 200˚C for 20hrs, then cooled at room temperature. After the FTO is cooled, the product is washed with deionized water and ethanol for several times. While washing the FTO, it should be treated carefully so the film formed on the FTO would not be also washed down. The moist FTO is then dried at 60˚C for 12 h and annealed in a tubular furnace at 800˚C for 2h in H_2/Ar flow at heating rate of 1.0˚C min^{-1}. At this time, the MoS_2 is successfully coated on CdS IO structure, and after the MoS_2 coating on CdS IO structure, the yellow CdS layer changes to greenish-brown.

2.3 PEC Measurement of CdS

The coated electrode layer needs 1*1 cm^2 space for the experiment to make the result measurable. The nail polish is coated on top of the electrode layer, because the light does not go through the nail polish, and the efficiency of the electrode is not affected.

When measuring the CdS electrode layer, there are three electrodes: reference electrode, counter (Pt) electrode, and working electrode.

2.4 Characterization

The scanning electron microscope (SEM) is an electron microscope that image the two-dimensional surface morphology of a sample by using a focused beam of electrons to interact with the atoms in the sample. The signals made by interaction pictures the image of the surface of the sample. The transmission electron microscopy (TEM) is a microscope technique. It forms and magnifies by the interaction between the electrons and the sample. The sample is better seen if it is ultrathin (less than 100nm thick). Ultraviolet-visible absorption spectroscopy (UV-Vis absorption spectroscopy) is a measurement of the recession of a beam of light after it penetrates or reflects from a sample. Photoluminescence (PL) is the process when a molecule absorbs a photon, and excites an electron in the molecule, then radiates a photon as the electron returning to the ground state. The linear sweep voltammetry measures the currents of the photoelectrode, and the potential between the photoelectrode and reference electrode is swept in linear timeline. The measurements were measured by a Versastat 3 potentiostats electrochemistry workstation at a scan rate of 0.05 V s^{-1}. One sun illumination (100 mW cm^{-2}) was produced by a 300 W Xe lamp and a standard Si solar cell.

3. Result and discussion

3.1 Morphology of CdS inverse opal

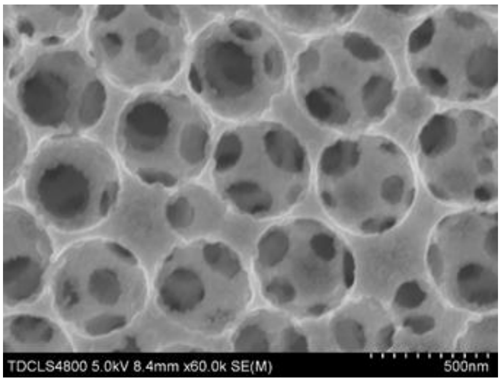


Figure 5. High magnification of scanning electron microscopy (SEM) image of CdS inverse opal under scale of 500 nm.

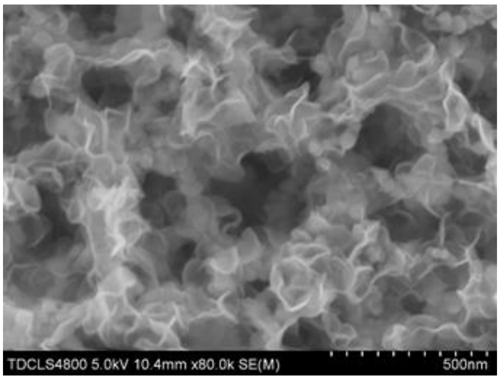


Figure 6. High magnification of SEM image of CdS with coating of MoS_2 under scale of 500nm.

Figure 2 shows the pristine CdS IO. The pore diameter in this figure is around 450 nm, and the size is uniform. Figure 3 shows the CdS after coating the MoS_2. The MoS_2 nanosheets disperse on the pores of CdS forming a flower-like structure. The two figures illustrate the difference of the roughness after the coating process: CdS IO without coating is relatively smooth, but with the MoS_2 the material becomes rougher and irregular.

3.2 Interfaces of CdS and MoS_2

Crystal structure is the arrangement of atoms, ions, and molecules in a crystalline material. The ordered structure is a symmetrical three-dimensional matter.

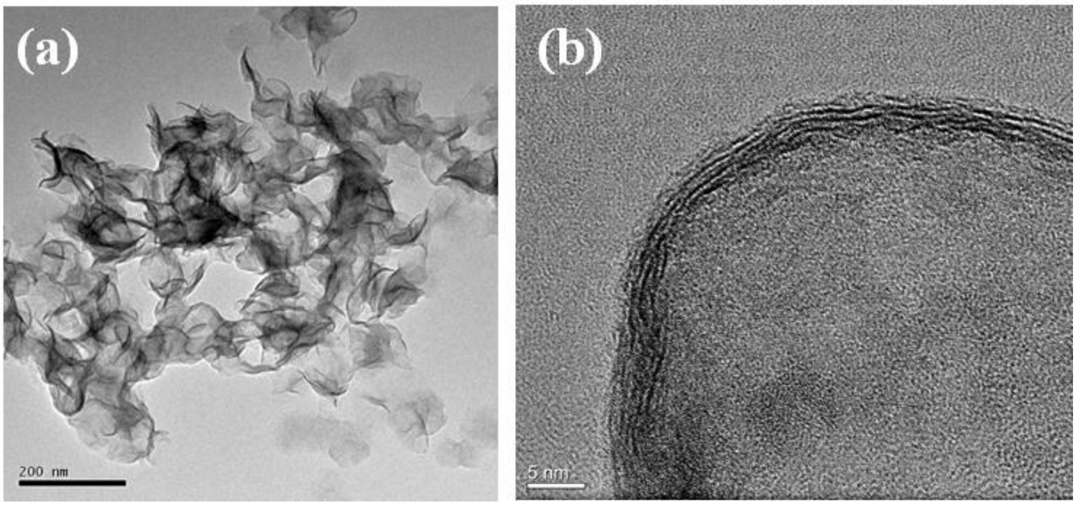


Figure 7. (a) Low-resolution TEM image of the pure MoS_2 nanosheets. (b) HRTEM image of one MoS_2 nanosheet.

The magnified images of MoS_2 are shown by Figure 7a, b. The MoS_2 nanosheets under low-resolution TEM showed in Figure 7a crinkly hold together. Different darkness in Figure 7a shows the degree of overlapping of the MoS_2 nanosheets, darker the image is, more nano sheets overlapping on each other in that area. Figure 7b is seen under high resolution TEM (HRTEM) and is the horizontal section of the signal MoS_2 nanosheet. Each nanosheet only contains 3-5 layers, therefore, it is called few-layer MoS_2 nanosheet.

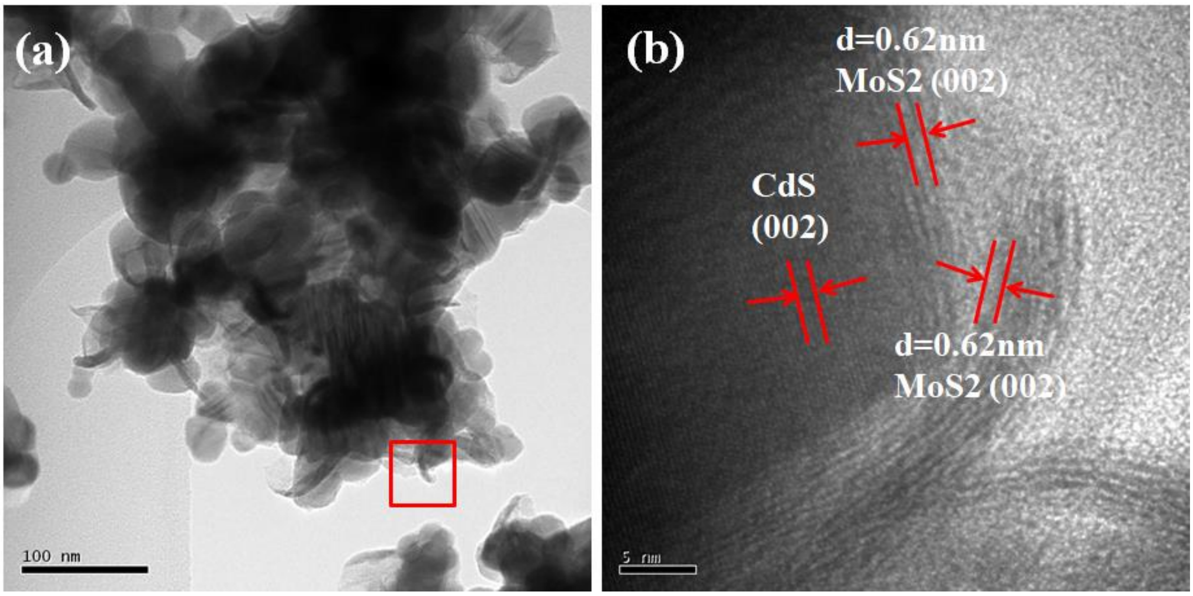


Figure 8 (a) Low-resolution TEM image of MoS_2 nanosheets coated on CdS IO heterostructure. (b) HRTEM image of the region framed by the red square from Figure 8a.

Both of the figures are seen under TEM scope, and the figures showed MoS_2 nanosheets coated on CdS inverse opal heterostructure. In Figure 8a, each extended tail of the heterostructure is the MoS_2 nanosheet on the CdS IO structure. Figure 8b exhibits the HRTEM image of the heterostructure (framed by the red square from Figure 8a), presenting the stripe plane (002) MoS_2 crystal with a space of 0.62nm. The texture of the plane (002) of the cubic-phase CdS crystal is smoother and denser than the MoS_2 crystal. Moreover, outside of each CdS IO structure, coated with 10-12 layers of MoS_2.

3.3 Light absorption and charge separation of MoS_2 coated CdS heterostructure

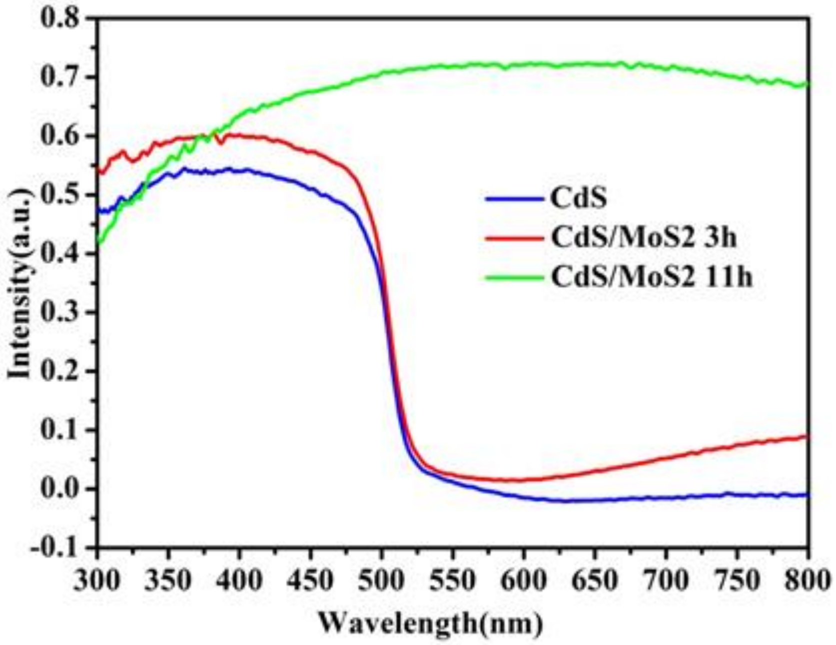


Figure 9 UV-vis absorption spectra of CdS, CdS/MoS_2 3 h, and CdS/MoS_2 11 h structures.

Figure 9 presents the UV-vis absorption spectra of the CdS crystal and CdS/MoS_2 heterostructure. The pure CdS IO structure shows an obvious absorption decline around 540nm. Though the CdS/MoS_2 heterostructure does not show a striking difference when experimenting in 3 hours, its PEC activity improved apparently starting from 400nm. Moreover, it is also noted that the CdS/MoS_2 heterostructure shows an increase along with increasing of time.

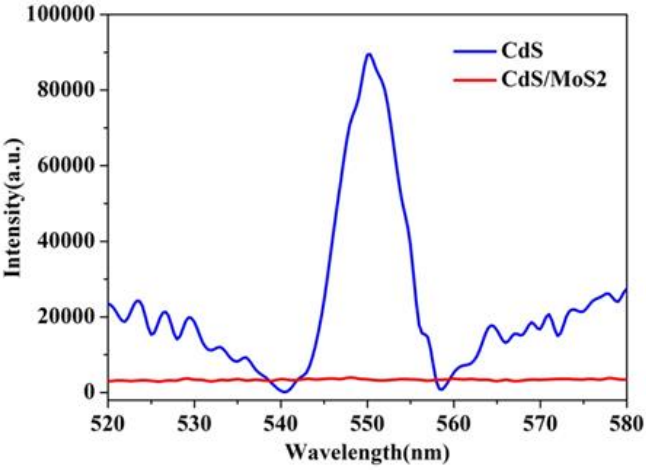
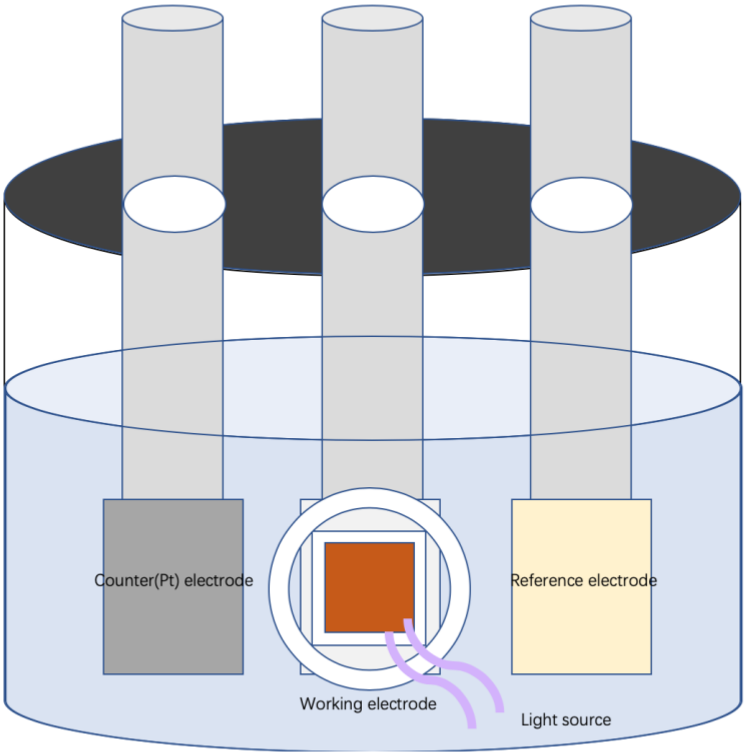


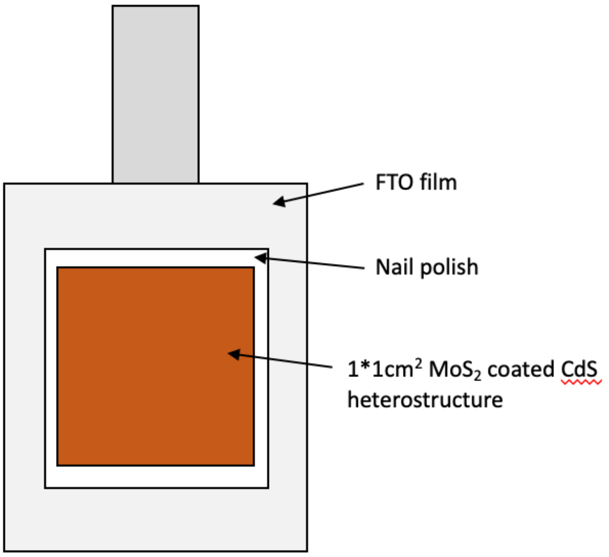
Figure 10. Photoluminescence of pristine CdS and CdS/MoS_2 heterostructure.

Photoluminescence is used to measure the charge separation. Figure 10 shows the photoluminescence of CdS presented by the blue line. The excitation of pristine CdS occurs around 550 nm, which is the same as the past results [18]. However, the intensity of PL significantly decreases when the MoS_2 coats with the CdS (shown by the red line), meaning that applying the MoS_2 can allow electron transfer and the charge is separated, so the electron hole pairs can recombine [19].

3.4 Photo-electrochemical hydrogen evolution performance of MoS_2 coated CdS heterostructure



(a)



(b)

Figure 11, (a) Composition of the PEC system. (b) Magnified working electrode shown in (a).

Figure 11 presents the device of this experiment. This device is a three-electrode system. Three electrodes are in this transparent sealed bottle: reference electrode, photoelectrode (working electrode), and counter (Pt) electrode. The orange color material on the photoelectrode in Figure 11 (b) is the film of MoS_2 coating CdS IO heterostructure. The electrode area of the working electrode is 1cm^2, and it is the only electrode being illuminated.

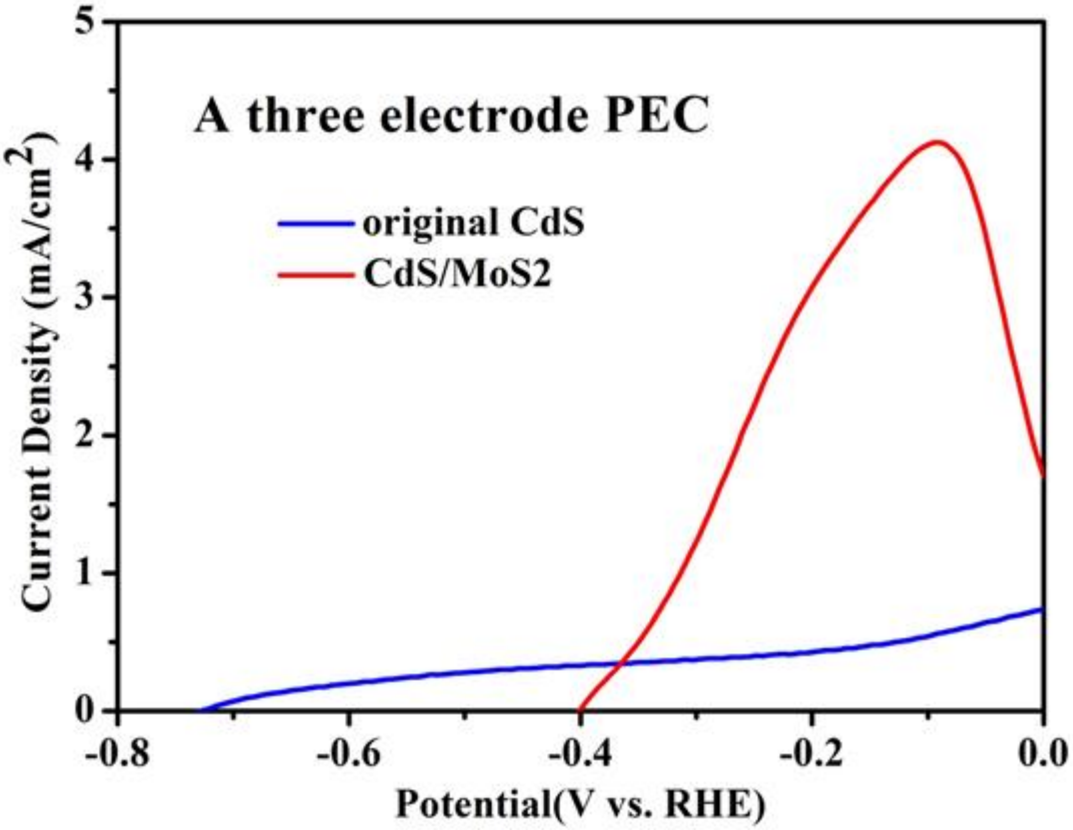


Figure 12. Linear sweep voltammetry result of efficiency of the pristine CdS photoelectrode and the MoS_2 coated CdS photoelectrode.

The result of three electrodes is shown in Figure 11 using the method of linear sweep voltammetry, presenting the relationship of the photocurrent density versus potential. The pristine CdS has the photocurrent density of 0.5 mA/cm^2 at -0.2 V vs. RHE. The CdS/MoS_2 has photocurrent density of 3.2 mA/cm^2 at -0.2 V vs. RHE, which is more than 6 times higher than the result of the pristine CdS. However, the photocurrent density of CdS/MoS_2 has a drop when the potential is higher than -0.1 V vs. RHE, implying that the interface of the CdS and the MoS_2 needs to be further optimized.

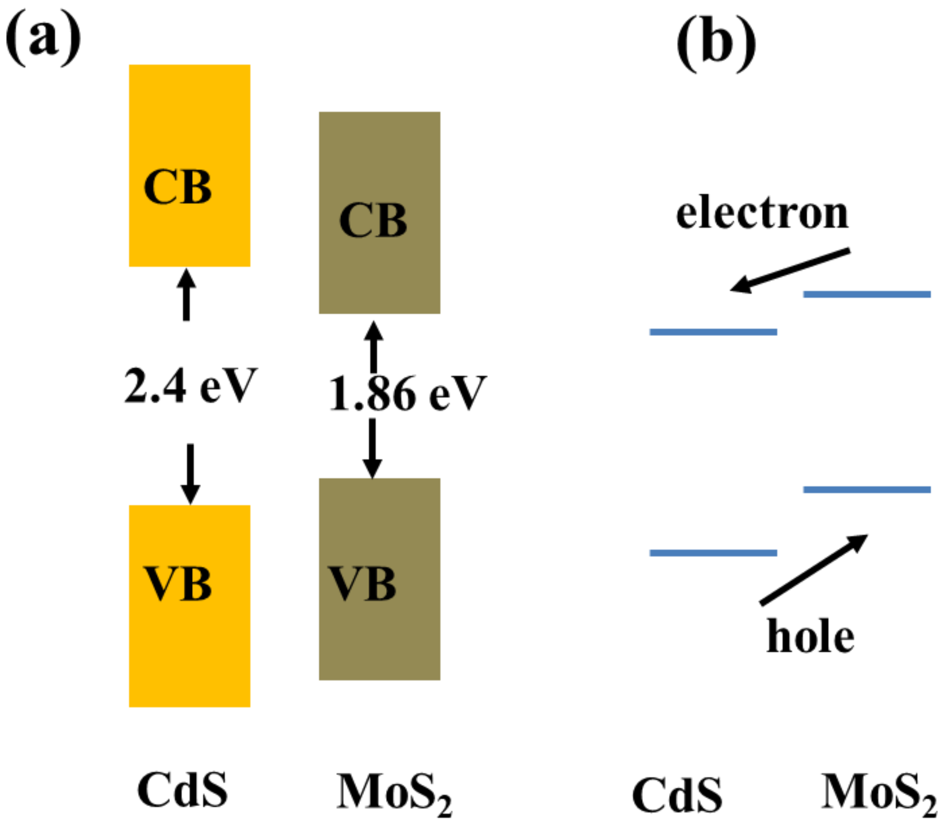


Figure 13. Band structure of CdS and MoS_2 (a); Electron and hole transport in the CdS and MoS_2 heterostructure (b).

The band structure of CdS and MoS_2 are shown in Figure 13a. Figure 13b further illustrated the electron and hole transport in the CdS and MoS_2 heterostructure. Moreover, we summarized and compared our work with some reported photoelectrochemical hydrogen evolution systems (Table 1).

Table 1. Comparison of MoS_2 nanosheets coated CdS with reported photoelectrochemical hydrogen evolution systems.

Materials	Electrolytes	Photocurrent density at -	References

		0.2(V vs. RHE)	
CdS/MoS$_2$	Na$_2$S/Na$_2$SO$_3$	3.2	This work
Nafion coated CdS	Na$_2$S/Na$_2$SO$_3$	1.9	Adv. Mater. 2016 [20]
ZnO:N nanowire	0.5 M NaClO$_4$	0.1 (-0.2V vs. Ag/AgCl)	Nano Letters 2009 [21]
Cu$_2$O nanowire	0.5 M Na$_2$SO$_4$ and 0.1 M KH$_2$PO$_4$	-7.5	Nano Letters 2016 [10]
m-TiO$_2$ nanoparticles under visible light	0.2M Na$_2$SO$_4$	0.008 (-0.2V vs. Ag/AgCl)	J. Mater. Chem. A 2014 [12]

4. Conclusion

The MoS$_2$ has been successfully combined with the CdS IO structure to form a few-layer MoS$_2$ nanosheet-modified CdS IO heterostructure. As a photocatalyst, the MoS$_2$ coated CdS heterostructure has shown significant improvement for a PEC water-splitting device compared with the pristine CdS photocatalyst, presenting by the results of UV-vis spectra, photoluminescence, and the linear sweep voltammetry. The intensity value of the UV-vis spectra of the MoS$_2$ coated CdS started to increase from 400 nm, whereas the pristine CdS electrode started to decrease from the same point. The intensity value of MoS$_2$ coated CdS structure is also better than the pure CdS electrode at any wavelength. Moreover, the linear sweep voltammetry value of the heterostructure is 6 times higher than the non-coated structure when the photocurrent density is at -0.2 vs. RHE. This work presents a promising enhanced photoelectrode in PEC water-splitting.

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