Performance of recent transition metal cocatalysts under hydrogen evolution reaction

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Abstract. In case clean and renewable energy on earth is urgently needed, converting solar energy into hydrogen is applied. Due to its high efficiency and low cost, photoelectrochemical water splitting (PEC) has become a popular strategy. To achieve this, non-noble metal electrocatalysts as cocatalysts are used to enhance the performance of PEC water splitting. In this review, the recent procedure of the synthesis, performance measurements, and the result of MoSx, TiO_2/NiOx, Pt/TiO_2/InAs NWs, and Co–S are introduced. These materials show a fit onset potential, good current density, and small charge transfer resistance for hydrogen evolution reaction (HER). Compared with TiO_2/NiOx, Pt/TiO_2/InAs NWs, and Co–S, MoSx is the only stable under acidic conditions. Some suggestions for future research on transition metal-based electrocatalysts are also provided.

Keywords: hydrogen evolution reaction (HER), photoelectrochemical water splitting (PEC), non-noble metal electrocatalysts, cocatalysts.

1. Introduction

Replacing fossil fuels with hydrogen has become a noticeable subject in recent years because of its clean and renewable features. There are a couple of methods for producing hydrogen. Instead of using steam methane reforming and coal gasification methods which would produce CO_2 that causes pollution, water electrolysis is the most cost-effective access because water is an abundant and renewable feedstock on earth. The electrolytic process of water involves two parts of half-reactions. One part is hydrogen evolution reaction (HER), the chemical equation could be written as $2H^+(aq) + 2e^- \rightarrow H_2(g)$. Another is called oxygen evolution reaction (OER), giving a chemical equation $2H_2O\ (l) \rightarrow 4e^- + 4H^+(aq) + O_2(g)$. Thus, for HER, H_2 is derived from the water reduction reaction on the cathode. However, the low-yield hydrogen production, in which only 4% is produced, gives a problem on how to improve the yield of hydrogen and reduce the cost of water electrolysis. As a result, some hydrogen evolution catalysts are required to use. Pt-based materials are ideal efficient hydrogen evolution catalysts. However, Pt, as the noble metal, violates the aim of low cost. Therefore, rather than using noble metal Pt as an electrocatalyst, researchers developed some non-noble metal electrocatalysts, which are abundant on earth. These include metal sulfides, metal carbides, metal selenides, metal phosphides, and metal nitrides. Recently, scientists are developing photoelectrochemical water splitting access to meet direct solar-to-hydrogen conversion. There are several advantages. First, solar energy is a sustainable and renewable natural resource. By obtaining energy directly from sunlight, we could minimize the impact on the environment and ensure that we meet our economic goals. H_2, as a good fuel to store solar energy, allows us to harvest and store solar energy simultaneously through photoelectrochemical water splitting. Second, noble metals are not required to be cocatalysts for HER in case using cocatalysts like metal sulfides, metal oxides, and InAs nanowires (NWs) as photocathode gives a higher photocathode efficiency than using noble metals. In this review, these cocatalysts will be discussed based on the synthetic strategies and performance under HER. In the last part, their advantages, limitations, and outlooks for future research are also provided.

2. Synthetic strategies and PEC performance for HER

2.1. MoS_x

Silicon is abundant material on earth. It has a narrow band gap, which makes it a good visible-light absorption material. Besides, its crystal structure, morphology, and conductivity demonstrate that silicon can be used as a photoanode and photocathode because of its diverse crystal structures and flexible morphology [1-2].

To replace Pt, MoS_x has been investigated as cocatalysts on a Si electrode. One-dimensional nanostructures have been demonstrated to be highly effective at both light absorption and photocurrent collection in recent years. Si nanowires (SiNWs) are one type of material that could satisfy solar energy conversion. However, p-Si photocathode has limitations on negative open circuit potential and slow intrinsic hydrogen evolution reaction, which deviate from the requirements of photoelectrochemical water splitting cell-the large positive open circuit potential and large photocurrent at positive potential. This can be enhanced by the process of a buried metallurgical n+p junction to p-SiMWs. MoS_x has then been investigated as a replacing photocatalysts material for noble metal Pt. When it combines with Si electrode, an effective enhancement shows in catalytic activity [1]. There are multiple pathways to fabricate these two types of materials. Chi et al. introduced one method which is called SiNWs at MoS_3. It is achieved by the two-step synthesis. First is the fabrication of SiNWs. P-type (100) Si wafer was degreased and boiled in a solution that is consist of H_2O_2, $NH_3{\cdot}H_2O$, and H_2O. The degreased Si is followed by metal-assisted chemical etching. The second step is to drop $(NH_4)_2MoS_4$/methanal dispersion on fabricated SiNWs sample by a fast spin-coating. Strong adhesion between MoS_3 and SiNWs has been confirmed by Transmission electron microscopy in Figure 1, which means good durability for photoelectrochemical hydrogen production. The result in Figure 2 shows that SiNWs@MoS_3 has an open circuit potential at +0.36 V, which is similar to SiNWs. However, a 24.9 mA cm^{-2} photocurrent density (Jsc) under 100 mW cm^{-2} illuminations has been shown by SiNWs@MoS_3, which is 50 times bigger than that of SiNWs. Even using noble metal Pt as a cocatalyst, SiNWs@MoS_3 has a 50% larger Jsc than SiNWs@PtNPs. There are two aspects explain this improved electrochemical performance of SiNWs@MoS3. First, the charge transfer resistance of SiNWs@MoS_3 is 61 Ω tested by Electrochemical impedance spectroscopy (EIS) spectra shown in Figure 3, which is far smaller than pure SiNWs. Second, the larger solid–liquid interface of SiNWs@PtNPs, which is proportional to CPEdp, is experimentally proved to be correlated with HER activity. The stability test by photocurrent density–time (*J–t*) measurement shows that degradation happens after 30 mins because SiNWs is oxidized. An HF treatment could resolve this problem, as shown in Figure 4 [3]. Song et al. suggest another method for combining Si and MoSx. The synthesized compound called 1T-MoS_2/Si. Researchers in his group found that a thin film of 1T-MoS_2 covered Si fabricated by chemically exfoliating MoS_2 nanoflakes synthesis with moderate 2H-MoS_2, temperature and reaction time, following with chemical vapor deposition (CVD), could optimize the photoelectrochemical (PEC) performance of compound. The enhancement can be shown by multiple results. A +0.25 V *vs* RHE onset potential for photocurrent measurement and a 17.5 mA/cm^2 current density at 0 V *vs* RHE, was given by 1T- MoS_2/Si which was measured in 0.5 M H_2SO_4. Compared with Si in Figure 5a, which is -0.14 V vs RHE, we can find a remarkable improvement. The charge-transfer resistances measured by EIS in Figures 5b, c, and d show a 24.1 Ω cm^2 from Si to MoS_2 (Rct, Si) and a 49.2 Ω cm^2 impeded charge transfer resistance (Rct, MoS_2) was also shown, which presenting the smallest resistance among 2H-MoS_2/ Si and Si. Moreover, Figure 6 shows that the charge separation is fast and charge recombination is slow across the MoS_2/Si interface, which is measured by time-resolved surface photoresponse (SPR) spectroscopy, implying that 1T- MoS_2/Si has an efficient PEC performance. The stability of 1T- MoS_2/Si test by chronoamperometry shows that current density decreases by 23% after 3h. This oxidized p-Si could also be treated by a buffered HF etch, resulting in no decrease on current density at 0 V vs RHE over 70 days [4]. Besides MoS_x, WS_3 has also been investigated as a cocatalyst that could enhance the HER performances. Since W and Mo are in the same group, they are expected to have similar chemical properties. Also, bridging S_2^{2-} or apical S^{2-} is the active site in MoS_x, and amorphous WS_3 is another compound that has these sites. As a result, WS_3 was deduced to be a proper cocatalyst for photoelectrochemical water splitting when it combines with Si. The synthesis process of SiNWs/WS_3 introduced by Chi et al. is similar to SiNWs@MoS_3, which is fabricated by pyrolysis and drop coating. In polarization experiments, the photocurrent density relations of SiNWs/WS_3 are compared with SiNWs and SiNWs/WS_2 in Figure 7. It turns out SiNWs/WS_3 has the biggest Jsc, which is 19.0 mA/cm2, and the largest Voc (0.40 V). The EIS spectra in Figure 8 show that the charge transfer resistance (Rct, dl) of SiNWs/WS_3 is 98.12 Ω, which is smaller than both SiNWs/WS_2 and SiNWs which is 136 and 1323 Ω, respectively. The result of potentiostatic electrolysis experiments in Figure 9 introduces the stability of SiNWs/WS_3. The current density decreases initially but then remains unchanged in the following 2 hrs [5].

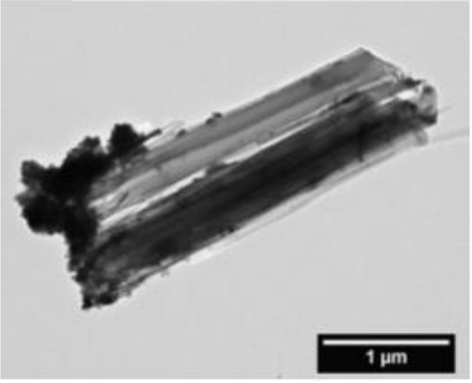

Figure 1. TEM image of SiNWs@MoS_3 [3].

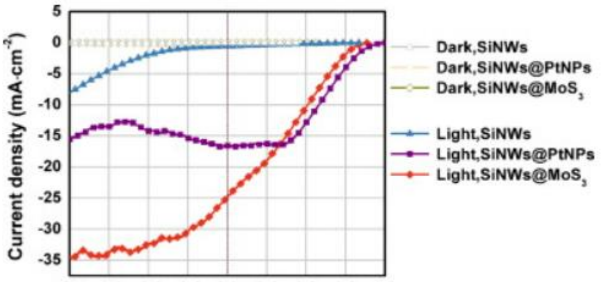

Figure 2. The current density of SiNWs, SiNWs@PtNPs and SiNWs@MoS_3. Grey, yellow and green lines correspond to SiNWs, SiNWs@PtNPs and SiNWs@MoS_3 are measured in the dark. Blue, purple and red lines correspond to SiNWs, SiNWs@PtNPs and SiNWs@MoS_3 are measured with illumination. [3].

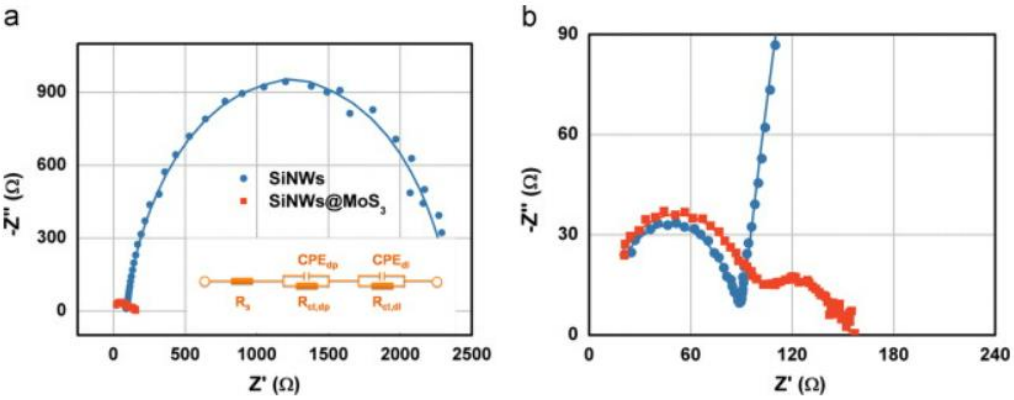

Figure 3. EISspectra of SiNWs@MoS_3 and SiNWs. (a)Nyquist plotmeasured at$V$=0V vs.RHE with light (100 mW/cm^2). (b) Plot (a) is zoomed in [3].

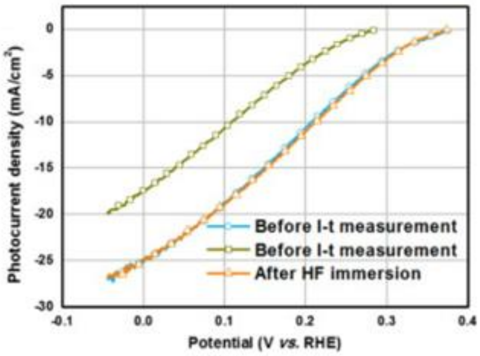

Figure 4. The current density-potential relation was measured for performance stability of SiNWs@MoS_3. Blue line is the initial J–t measurement. Green line is J–t measurement after 30 min. Orange line is J–$t$measurement after HF treatment [3].

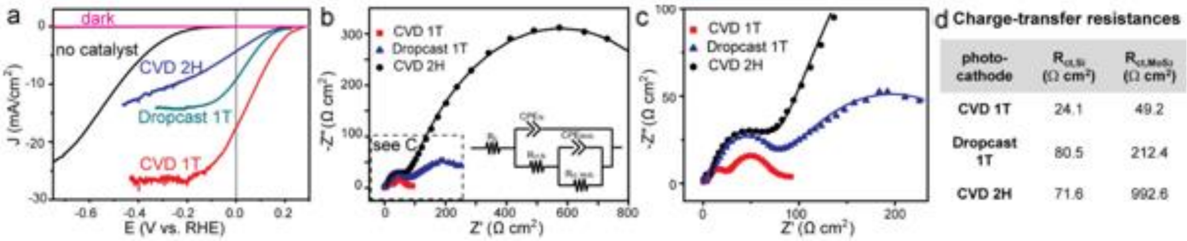

photo-cathode	$R_{ct,Si}$ (Ω cm^2)	R_{ct,MoS_3} (Ω cm^2)
CVD 1T	24.1	49.2
Dropcast 1T	80.5	212.4
CVD 2H	71.6	992.6

Figure 5. (a)curves of J–E measurement. Blue, cyan and red lines correspond to CVD 2H, drop cast 1T and CVD 1T. (b) Nyquist plot. (c) A detailed plot of (b). (d) the fitted charge-transfer resistance values of a CVD 2H, drop cast 1T and CVD 1T measured in 0.5 M H_2SO_4 under simulated 1 sun irradiation [4].

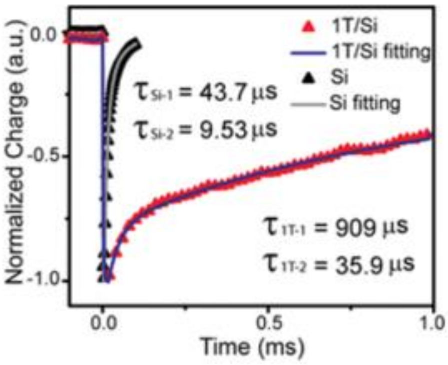

Figure 6. TR-SPR spectra is integrated and biexponential fittings are shown. Red line is 1T-MoS_2/Si and blue is its fitting. Black line is Si and gray is its fitting [4].

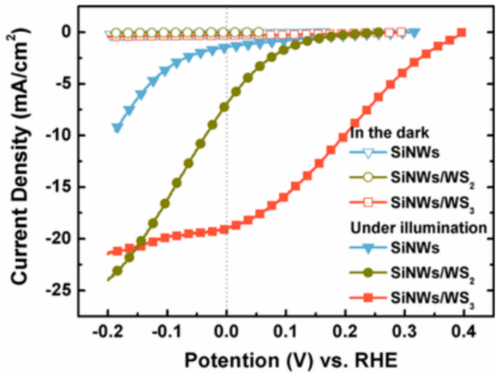

Figure 7. *J–V* relation of SiNWs, SiNWs/WS_2, and SiNWs/WS_3. Blue, green and red lines with hollow dots means SiNWs, SiNWs/WS_2, and SiNWs/WS_3 are measured with light (100 mW/cm^2). Blue, green and red lines with solid dots means SiNWs, SiNWs/WS_2, and SiNWs/WS_3 are measured in the dark [5].

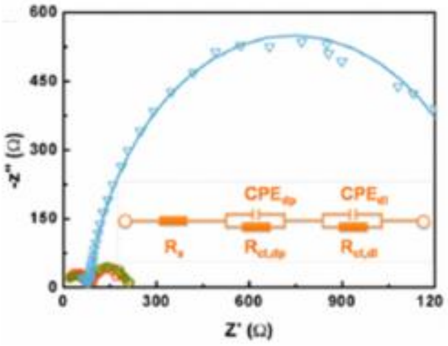

Figure 8. EIS spectra (Nyquist plot) of SiNWs(blue), SiNWs/WS_2(green) and SiNWs/WS_3(orange) at 0 V vs RHE under illumination (100 mW/cm^2) [5].

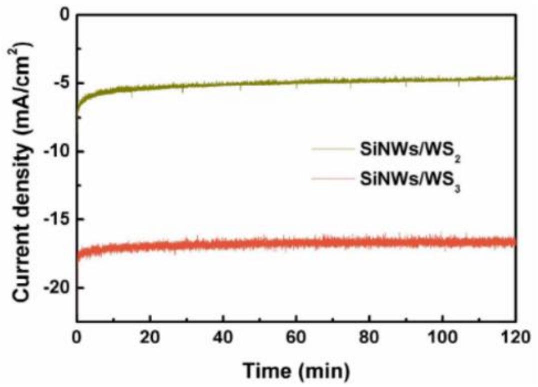

Figure 9. Photocurrent density of SiNWs/WS$_3$(green) and SiNWs/WS$_2$(red) at 0 V vs RHE in potentiostatic electrolysis experiments [5].

2.2. *TiO$_2$/NiO$_x$, Pt/TiO$_2$/InAs NWs, and Co–S*

By observing the above three types of cocatalysts, all MoS$_x$-related compounds require an acidic condition to maintain their stability. However, to minimize environmental impact and to improve their biocompatibility, ideal non-Pt HER photo electrocatalysts should avoid using strong acids or bases. Researchers have recently found some cocatalysts with high catalytic activity at neutral PH conditions. One is called p-Si/TiO$_2$/NiO$_x$. There are two interesting facts about this cocatalyst. First, by coating a thin TiO$_2$ film, Si could be stable without using strongly acidic and alkaline solutions to protect. Second, previous research has not studied NiO$_x$ as HER co-catalyst at neutral PH. Rather, it has mostly been studied as an oxygen evolution reaction (OER) catalyst. As a result, it would be an innovation if NiO$_x$ has a good PEC performance. p-Si/TiO$_2$/NiO$_x$ is fabricated by a wet-etching and spin-coating of TiO$_2$ and NiO$_x$. According to Messinger et al., the V$_{onset}$ of p-Si/TiO$_2$/NiO$_x$ at neutral PH is +0.42 V vs. RHE at a photocurrent density of -0.1 mA·cm^{-2}, which is higher than p-Si/NiCoSe$_x$ nanopillars that obtains a +0.25 V vs. RHE in 0.5 M H_2SO_4. The simultaneously recorded photocurrent density was shown in Figure 10, measured at a stable value at -1.48 mA/cm^2 at 0V and 1 sun illumination over 5 hours with a 96% Faradaic efficiency. The charge transfer resistance measured by EIS under 1 sun illumination is shown in Figure 11, showing p-Si/TiO$_2$/NiO$_x$ has the most efficient charge transfer capability, compared to p-Si/TiO$_2$/CoO$_x$ and p-Si/TiO$_2$ [6]. Another TiO$_2$-related photocathode is called Pt/TiO$_2$/InAs NWs/*p*-Si. InAs semiconductor has two advantages as potential heterojunction with silicon. It has both a narrow band gap and high electron mobility. Jang et al. introduced one access to fabricate InAs NWs with silicon, called “The growth of the catalyst-free InAs NWs” using a horizontal reactor metal-organic chemical vapor deposition (MOCVD) system. After that, the TiO$_2$ passivation layer and Pt were deposited by plasma-enhanced atomic layer deposition (PEALD) and photo-assisted electrodeposition. The scheme is shown in Figure 12. The PEC performance was measured in phosphate buffered solution, which has a pH of 7.0. The J-V curves in Figure 13(a) show a photocurrent density of Pt/TiO$_2$/InAs NWs (5 μm)/p-Si photocathode, which is 8.6 mA/cm^2 at 0 V (vs. RHE), compared to a photocurrent density of 7.4 mA/cm^2 in 0.5 M H_2SO_4 (PH~0) and -6.683 mA/cm2 in 1 M NaOH (PH~14) in Figure 13(b), showing that Pt/TiO$_2$/InAs NWs (5 μm)/*p*-Si photocathode at neutral has the highest catalytic activity for HER. Furthermore, the charge transfer resistance measured by EIS in Figure 13(c) shows that Pt/TiO$_2$/InAs NWs (5 μm)/p-Si photocathode has the lowest resistance, compared to bare *p*-Si, InAs (5 μm)/*p*-Si, and TiO$_2$/InAs (5 μm)/*p*-Si. Chronoamperometric measurements were also performed for stability tests. Figure 14 shows the Pt/TiO$_2$/InAs NWs/*p*-Si photocathode maintained 80% photocurrent over 20 h, which has the best performance among the three heterostructure photocathodes [7]. Cobalt-sulfide (Co–S) film has been regarded as another efficient HER catalyst in PH 7 aqueous. It could be easily coated on silicon and perform a photoelectrochemical hydrogen evolution under a water-compatible system. Chang et al. shows the annealed Co–S film on fluorine-doped tin oxide (FTO) was measured, giving a 43 mV onset overpotential at $\eta = 287$ mV for 3 h and 50 mA/cm^2 catalytic current densities at $\eta = 397$ mV, which is far higher than an elegant Janus cobalt catalyst shown in Figure 15.

Compared to amorphous MoS2 films prepared by a similar potentiodynamic deposition, a 7 mA/cm^2 current density was given under the same overpotential and PH condition. Besides, Co–S film was also measured under acidic and alkaline conditions. A Tafel slope of 56 mV/dec at -0.05 V vs. RHE in 0.5 M H_2SO_4 was shown in Figure 16. An onset potential of η = 100 mV and a linear charge accumulation during a 25 h controlled potential electrolysis in 1.0 M KOH was shown in Figure 17. Both prove that Co–S catalyst could also be efficient under a wide range of pH values. Finally, the durability test depicted in Figure 18 shows a linear charge with no substantial loss in the catalytic activity of Co–S in PH 7 buffer [8].

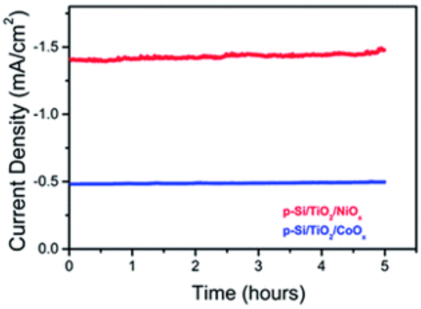

Figure 10. The current density of p-Si/TiO_2/NiO_x which has a red line and p-Si/TiO_2/CoO_x which has a blue line at 0.0 V vs RHE, under 1 sun illumination [6].

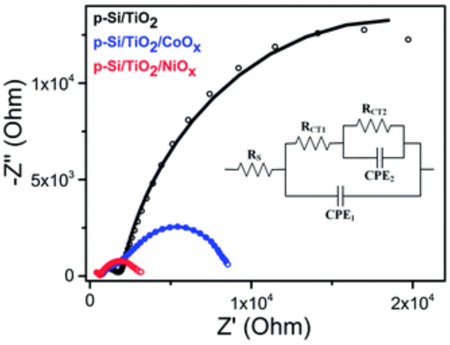

Figure 11. Nyquist plots of p-Si/TiO_2 which has a black line, p-Si/TiO_2/CoO_x which has a blue line, and p-Si/TiO_2/NiO_2 which has a red line. They are measured at 0.0 V vs RHE, under 1 sun illumination [7].

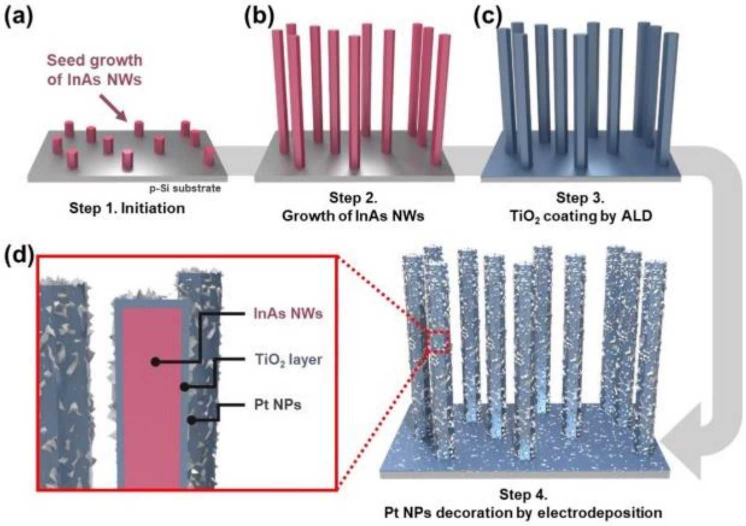

Figure 12. Schematic diagrams of synthesis of Pt/TiO_2/InAs NWs/p-Si [7].

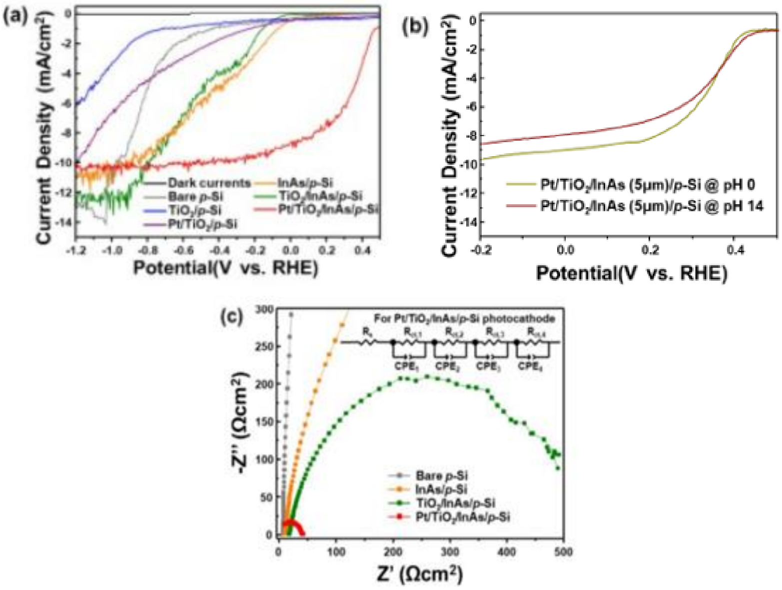

Figure 13. Photoelectrochemical (PEC) performance of heterostructure photocathodes. (a) J-V curves of all photocathodes. (b) J-V curves of Pt/TiO_2/InAs NWs (5 μm)/p-Si in 0.5 M H_2SO_4 and 1 M NaOH. (c) EIS spectra for p-Si, InAs (5 μm)/p-Si, Pt/TiO_2/InAs NWs (5 μm)/p-Si and TiO_2/InAs (5 μm)/p-Si [7].

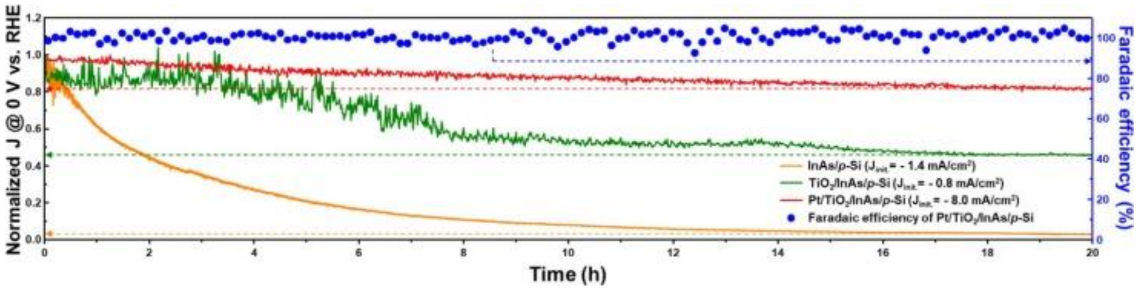

Figure 14. Stability tests for the InAs NWs, TiO_2/InAs, and Pt/TiO_2/InAs NWs combined p-Si photocathodes [7].

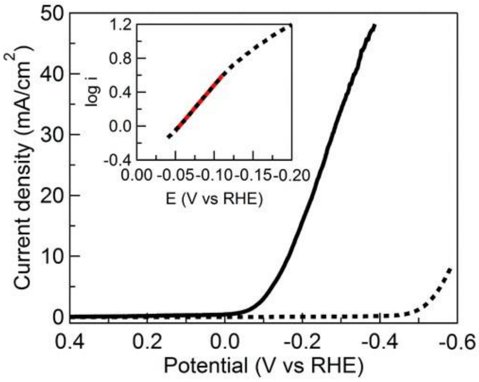

Figure 15. The plot of current density versus potential. The solid line is the annealed Co–S/FTO which is measured under electrolysis at η = 287 mV for 3 h. The dotted line is the plot of blank FTO. They are measured in 1.0 M potassium phosphate buffered solution with a pH of 7.0 with a scan rate of 5 mV/s [8].

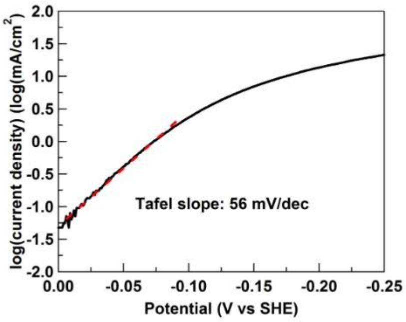

Figure 16. Tafel plot of annealed Co–S/FTO in 0.5 M H_2SO_4 with a scan rate of 5 mV/s [8].

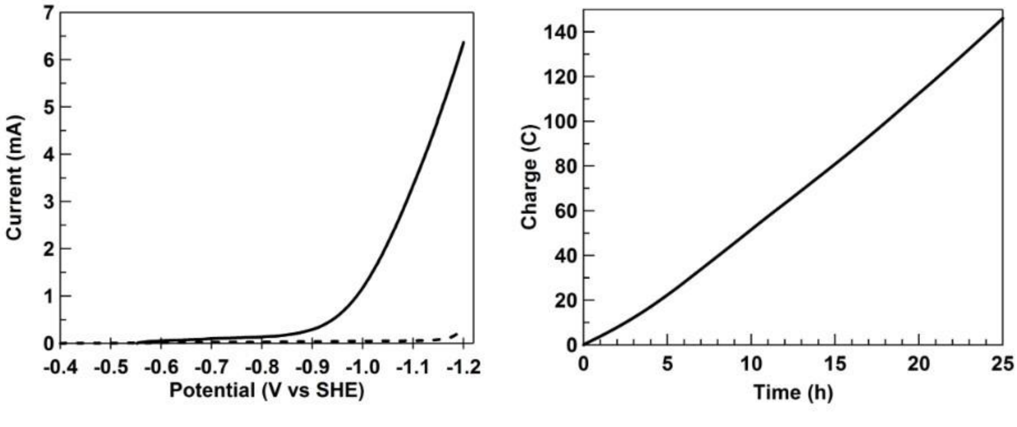

Figure 17. The left one is a plot of Current versus potential for annealed Co–S/FTO which has a solid line and blank FTO which has a dotted line. They are measured with a scan rate of 5 mV/s. The right one is the controlled potential electrolysis of annealed Co–S/FTO at η = 274 mV in 1.0 M KOH [8].

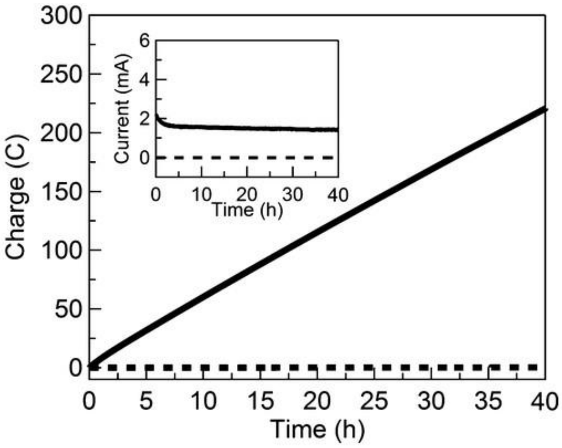

Figure 18. Accumulated charge versus time for annealed Co–S/FTO that has a solid line and a blank FTO that has a dotted line are measured in 1.0 M potassium phosphate buffered solution at η = 187 mV. The current density is also shown on the top-left corner [8].

3. Conclusion

This paper has summarized several cocatalysts deposited on the Si nanowire electrode to enhance hydrogen evolution reaction (HER). The performance and stability of these photoelectrochemical (PEC) electrodes were generally promoted. MoS_x, TiO_2/NiO_x, $Pt/TiO_2/InAs$ NWs, and Co–S all turn out to have a fit onset potential, good current density, and small charge transfer resistance. However, the applications of these HER cocatalysts for boosting PEC performance are still limited. The storage of MoS_x under acid conditions is problematic due to environmental and biocompatible reasons. TiO_2/NiO_x, $Pt/TiO_2/InAs$ NWs, and Co–S don't have as good durability as MoS_x. An ideal non-Pt HER electrocatalyst should have both good durability over several years and high catalytic stability over a wide pH range [1]. Therefore, nothing is more important than exploring new electrocatalysts in the future. One possible direction to approach is to investigate the cocatalysts that have good durability under seawater, which could effectively minimize the environmental impact.

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