Energy of the Future – Hydrogen

A highly promising and stable photocathode for the production of solar hydrogen is a Cu_2O/CuO heterostructure modified with CuS.

Global warming, caused by greenhouse gases, has been discussed for years; it has shown its power to affect climate change on our planet, especially in recent years. An agreement by more than one hundred countries to decrease greenhouse gas was made in the Paris Climate Conference 2015. The consumption of conventional fossil fuels such as natural gas, coal and petroleum must decrease. Although nuclear power is a powerful energy supply of one type that does not release greenhouse gas, the danger of using nuclear power is still of concern after the Fukushima Daiichi nuclear disaster. For green energy (so-called renewable energy) such as solar, wind, landfill gas, biomass and hydroelectric power, time is of the essence.

Hydrogen is considered to be one type of next-generation energy carrier.[1] To generate gaseous hydrogen in a green way, photoelectro-chemical (PEC) water splitting might be one possible and attractive method because it requires only semiconductor electrodes, water and sunlight.[2] The performance of such a device depends on how much visible light the semiconductors can harvest. This amount is determined by the optical and electronic properties – appropriate band gap for sunlight absorption, suitable band positions for water reduction or oxidation, and stability under the required conditions.[3]

Cu_2O is a material for solar-driven hydrogen production more promising and attractive than TiO_2, $SrTiO_3$, WO_3, CdS *etc.* because of its highly effective harvest of visible light and sufficiently negative conduction band edge.[4-5] Furthermore, copper is inexpensive and naturally abundant, which makes it cost-competitive. In recent literature, Bing-Joe Hwang and his co-workers proposed a Cu_2O/CuO heterostructure modified with CuS (as a cocatalyst) as a highly prom-

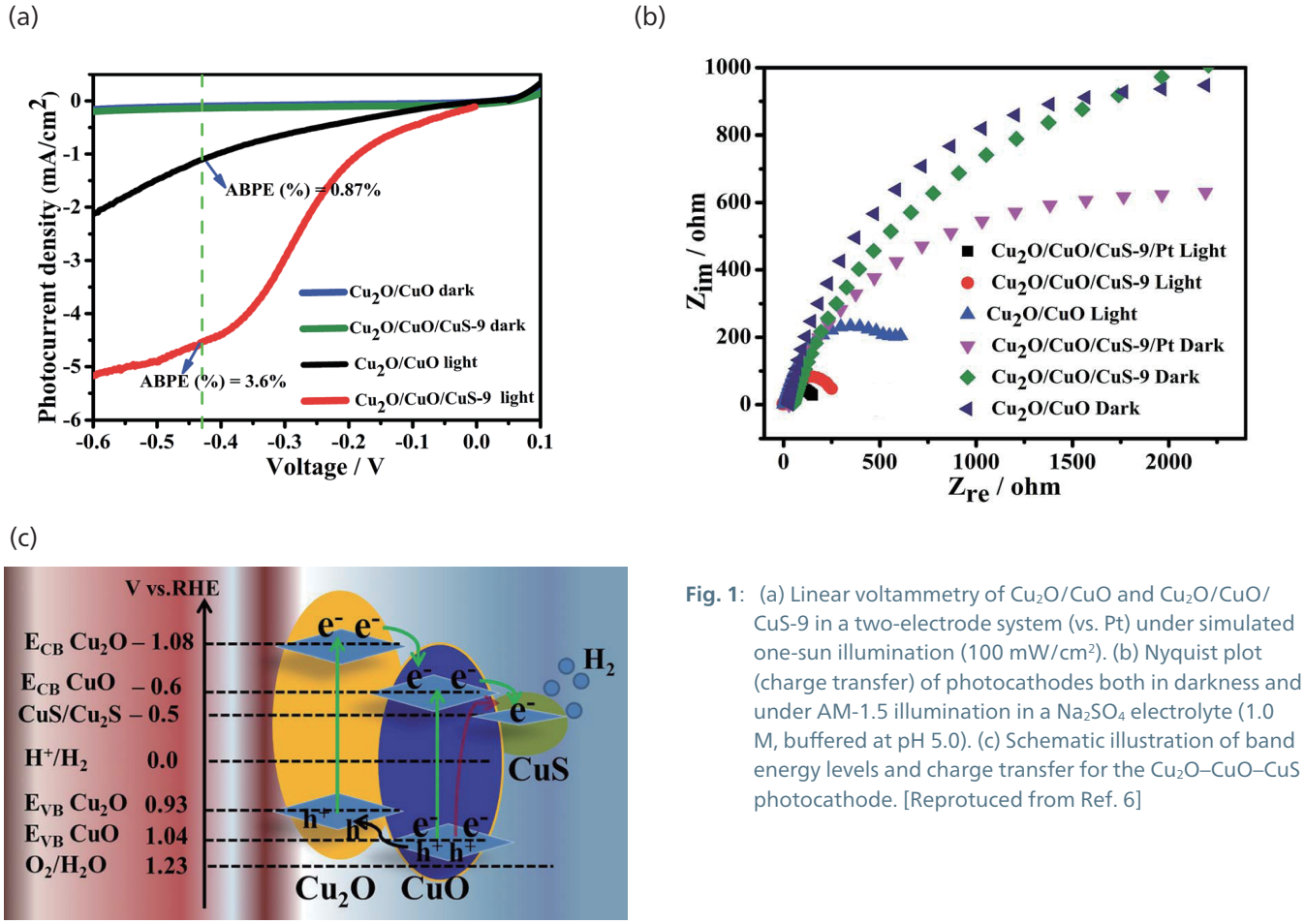

Fig. 1: (a) Linear voltammetry of Cu_2O/CuO and Cu_2O/CuO/CuS-9 in a two-electrode system (vs. Pt) under simulated one-sun illumination (100 mW/cm²). (b) Nyquist plot (charge transfer) of photocathodes both in darkness and under AM-1.5 illumination in a Na_2SO_4 electrolyte (1.0 M, buffered at pH 5.0). (c) Schematic illustration of band energy levels and charge transfer for the Cu_2O–CuO–CuS photocathode. [Reprotuced from Ref. 6]

ising and stable photocathode for the production of solar hydrogen. This photocathode is produced with successive ion-layer adsorption and reaction (SILAR) and deposits with Pt nanoparticles with a sputtering technique. It is characterized using XRD, SEM, DRS, UV-vis, Raman, XPS and XANES/EXAFS techniques. XPS and XANES/ EXAFS were recorded at **TLS 24A** and **TLS 17C**.

Both CuS and the Pt-modified photoelectrodes show significantly stable photocurrent density, 92% within 1 h. The amounts of evolved H_2 gas for Cu_2O/CuO and CuS-modified photocathodes are 0.0035 and 0.0126 mmol, giving Faradaic efficiencies 56% and 87%, respectively. The applied bias efficiency of photons to current (ABPE) with and without light are shown in **Fig. 1(a)**. The results[6] exhibit that the CuS-modified electrode attains approximately 3.6% at applied bias -0.43 V, whereas Cu_2O/CuO attains 0.87% at the same voltage.

The Nyquist plot of the charge-transfer resistance of the photocathodes, **Fig. 1(b)**, indicates that the CuS-modified photocathode has a smaller charge-transfer resistance and greater conductivity than bare Cu_2O/CuO both in darkness and under illumination.

The mechanism (**Fig. 1(c)**) of the enhancement of the photocurrent density and the stability of the Cu_2O/CuO photoelectrode modified with CuS is suggested to result from two conditions: (1) deposited CuS aids transfer of accumulated photogenerated electrons from the Cu_2O/CuO surface to the solution for hydrogen production; (2) electron-hole recombination is suppressed through interfacial charge transfer (IFCT). When electrons transfer from CuO to CuS under visible illumination, these reactions occur:

$2\ CuS + 2\ e^- \rightarrow Cu_2S + S^{2-}$

$Cu_2S + S^{2-} + 2\ H^+ \rightarrow 2\ CuS + H_2$

CuS not only helps charge separation but also decreases electron-hole recombination.

A remarkable material with enhanced efficiency of solar conversion and stability involves use of a heterostructure Cu_2O/CuO modified with CuS. This work makes great progress on an energy material and in the development of hydrogen as an energy carrier. (Reported by Yu-Chun Chuang)

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TLS 24A1 BM – (WR-SGM) XPS, UPS
TLS 17C1 W200 – EXAFS

- XPS
- Materials Science, Chemistry, Condensed-matter Physics, Soft Matter, Environmental and Earth Science, Surface, Interface and Thin Films, Chemical Engineering

| References |

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