

Cu₂O Quantum Dots (QDs) Sensitized Cu/p-CuI Photo-electrode for H₂ Generation through Efficient Water Splitting

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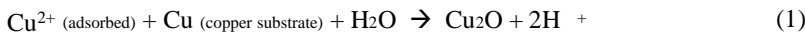
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Introduction

Water splitting by sunlight to generate hydrogen and oxygen is a fascinating way of energy production. Metal oxides such as Cu₂O, TiO₂, ZnO and WO₃ with various morphologies have been investigated for water splitting (Fujishima & Honda, 1972). However, most of these metal oxides have large band gaps, which limit the light absorption in the visible region and hence the overall efficiency of the process. To achieve a better photoelectrochemical response with these materials, an extensive research has been done on adding nanostructures (Feng et al., 2008; Wu & Yu, 2004). One possibility is the use of semiconductor nanocrystals (3D nanostructure), known as quantum dots (QDs), as an alternative to this problem (Adachi et al., 2004). In this research study, H₂ generation at QDs is presented for the first time efficiently. Energy level positions were used to confirm the QD sensitization process associated at Cu/p-CuI/QD electrolyte interface.

Methodology

Cu/p-CuI photoelectrodes were immersed in CuSO₄ (10⁻³M) solution and boiled until the formation of Cu₂O QDs on p-CuI nano-particles at Cu/p-CuI. Variation in boiling time produce various sizes of Cu₂O QD on Cu/p-CuI electrode and colour variation according to the boiling time is shown in Fig.1 (b-f). Table 1 shows the variation of the extent of Cu₂O QD produced on the Cu/CuI photoelectrode by weight with boiling time in CuSO₄ solution. The mechanism of the formation of QDs on the p-CuI particles may be presented from the following reaction.



The amount of produced H₂ gas was estimated from gas chromatography (Shimadzu GC-2014).

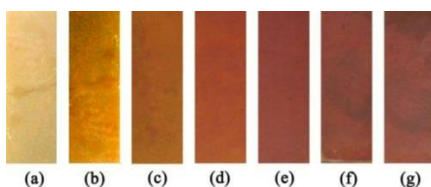


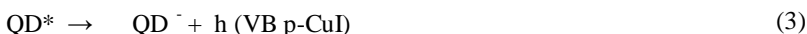
Figure 1: (a) Cu/p-CuI cell- 5min immersing time in KI/CuSO₄ solution. Figure (b), (c), (d), (e), (f) and (g) are shown in Table 1.

Table 1: Cu₂O QD amount formed by boiling Cu/CuI samples in a CuSO₄ solution.

Electrode	Boiling Time (min)	Cu ₂ O Weight (μg)
(b)	5	0.4
(c)	10	2.2
(d)	15	3.1
(e)	20	3.9
(f)	30	8.2
(g)	45	9.6

Results and Discussion

Fig.3 shows the variation of H₂ evolution GC profiles with time for samples exhibited in Fig.1(b)-(g) in the presence of 0.025M Na₂SO₄ electrolyte buffered at a pH of 5.2 under visible light irradiation. It should be mentioned that Cu/p-CuI photoelectrodes did not produce any considerable amounts of H₂ under visible light irradiation. The highest H₂ generation exhibited for the samples prepared by boiling Cu/p-CuI photoelectrodes in CuSO₄ (10⁻²M) solution for 20min (sample-(e)). After the saturation of H₂ evolution, H₂ bubbles were accumulated on Cu/p-CuI/QD photoelectrode without showing any photo degradation of the photoelectrodes. During the H₂ evolution process a remarkable photocurrent was observed under the illumination confirming that the H₂ generation caused only from the photogenerated electrons. The mechanism of the H₂ generation can be explained from the following reactions.



The CB position of the QD may be more negative according the onset potentials obtained from the V-I characteristics curve and the energy level diagram as shown in Fig.2. So that QD⁻ produced photogenerated electrons can transfer to H⁺/H₂ redox level efficiently to generate H₂ under visible light.

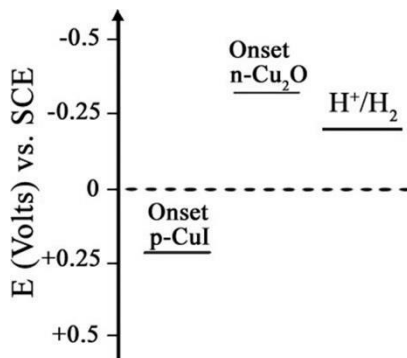


Figure 2: Estimated band positions of p-CuI, n-Cu₂O and H⁺/H₂ redox levels with respect to Ag/AgCl.

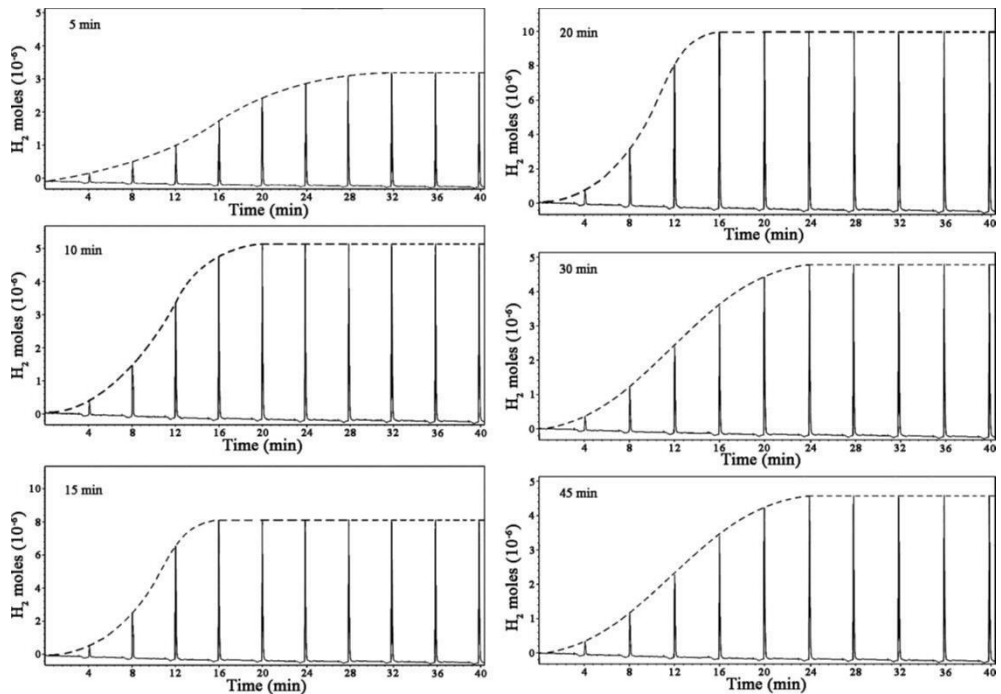


Figure 3: The variation of H₂ production with time measured by gas chromatography for various samples at maximum H₂ production voltage vs. Ag/AgCl in the presence of 0.025M Na₂SO₄.

Conclusions

p-CuI was sensitized by Cu₂O quantum dots for the first time in a photoelectrochemical cell at low cost and easy fabrication processes on a well cleaned commercially available copper sheets. When the size of the QD increased, a photocurrent quantum efficiency enhancement was observed. Any chemical dissolution of p-CuI or Cu₂O QDs not significant after long time irradiation profiles. H₂ generation was presented with the different sizes of the QDs from photogenerated carriers at Cu/pCuI/QD-electrolyte interface.

Acknowledgement

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References

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