Supporting Information

Highly efficient photoelectrochemical hydrogen generation using a quantum dot coupled hierarchical ZnO nanowires array

*Heejin Kim and Kijung Yong**

Surface Chemistry Laboratory of Electronic Materials (SCHEMA), Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea

**** To whom correspondence should be addressed, E-mail: kyong@postech.ac.kr***

Solar to hydrogen conversion efficiency

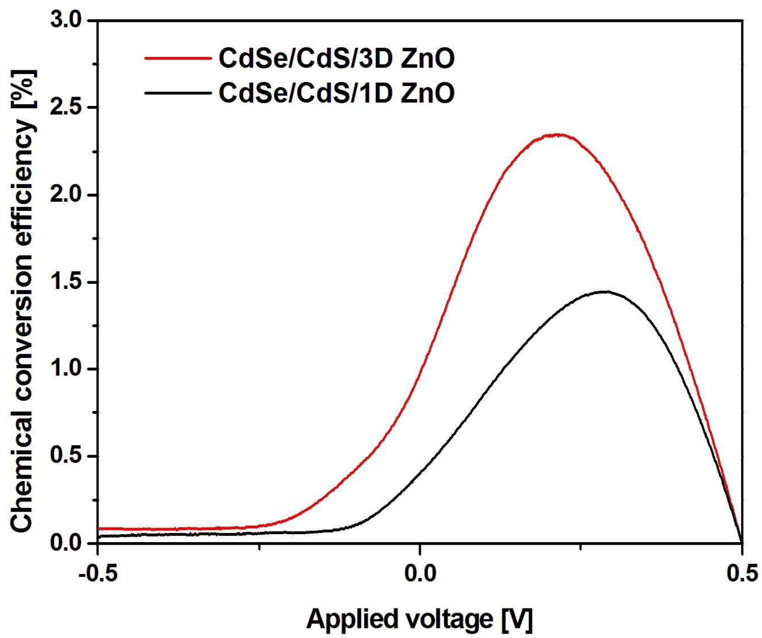

Figure.S1 Calculated chemical conversion efficiency of the CdSe/CdS quantum dot modified ZnO nanostructure photoelectrodes using the obtained photocurrent densities in figure 3.

The solar to hydrogen conversion efficiency can be calculated with following equation as following equation. [Chemical Reviews 2010, 110, 6446-6473” and “Energy Environ. Sci. 2013, 6, 347”] We have measured the real bias system with working electrode as QDs modified ZnO photoelectrode and Pt as counter electrode.

n_c(%) = [(energy converted to chemical reactions – energy supplied by external bias)/energy of incident light] × 100

$$n_c(\%) = \left[\frac{J_p(\Delta G^o{}_{rev} - E_{bias})}{J_0} \right] \times 100$$

where $\Delta G°_{rev}$ is the Gibbs free energy per coulomb of electrons for the redox reactions on electrodes, J_p is the photocurrent density and J_0 is the intensity of the incident light, which is 100 mW cm^{-2}. $\Delta G°_{rev}$ of 1.23 V is generally used for water splitting reaction. However, this value of $\Delta G°_{rev}$ is not adequate in our system due to the sacrificial reagent used in our device. Thus, we have calculated the conversion efficiency using the obtained photocurrent with modified Gibbs free energy corresponding to half reaction in sacrificial reagent (0.5V vs. NHE). The calculated efficiency in figure S1 showed the 2.45% maximum efficiency at 0.2V with the optimized CdSe/CdS/3D ZnO nanostructure photoelectrode. In addition, the 3D photoelectrode showed the solar to hydrogen conversion efficiency of 0.98 % at zero bias.