Electronic Supplementary Information

CdSe Sensitized Branched CdS Hierarchical Nanostructures for Efficient Photoelectrochemical Solar Hydrogen Generation

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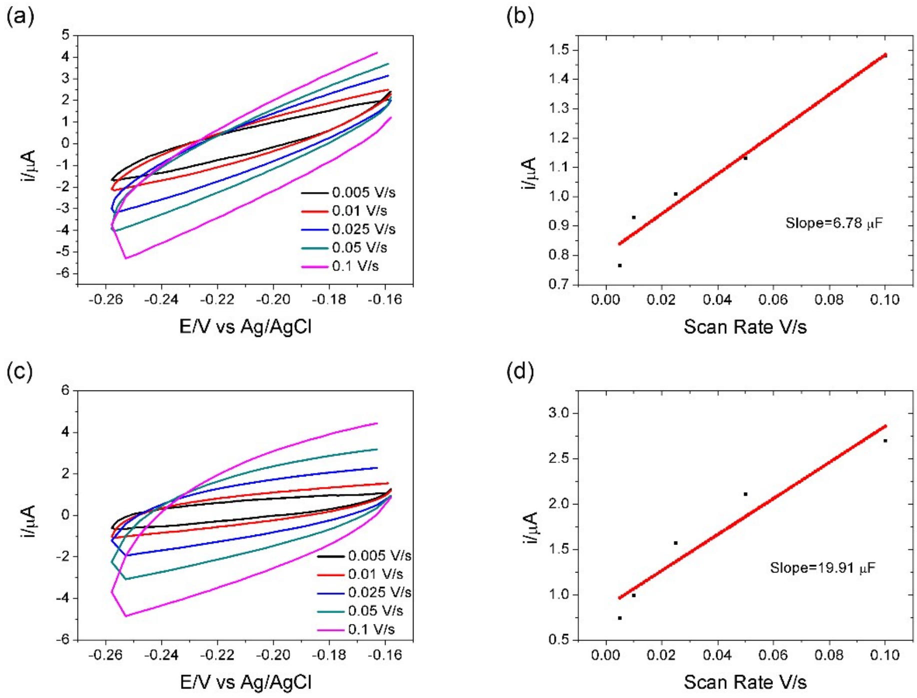

Figure S1. (a) Cyclic voltammograms of rod-like CdS/CdSe-80, which is measured in the 0.1 V potential range at the scan rates of: 0.005, 0.01, 0.025, 0.05 and 0.1 V/s. (b) Anodic charging currents of rod-like CdS/CdSe-80 measured at -0.208 V vs. Ag/AgCl plotted as a function of scan rate. The electrochemical capacitance of rod-like CdS/CdSe-80 is taken as the slope of the least squares fitting line. (c) Cyclic voltammograms of branched CdS/CdSe-80. (d) Anodic charging currents of branched CdS/CdSe-80 measured at -0.208 V vs. Ag/AgCl plotted as a function of scan rate.

Electrochemical active surface area (ECSA) was measured for both CdSe sensitized rod-like and branched CdS nanorod arrays, in which the ECSA were estimated by determining the double layer capacitance from cyclic voltammograms (CV)[1]. Firstly, a non-Faradaic potential range was identified from CV in quiescent solution. This non-Faradaic region is typically a 0.1 V window about open circuit potential (OCP), and all measured currents in this region are assumed to be double-layer charging. According to this assumption, the charging current, i, is equal to the product of the electrochemical capacitance, C_E, and the scan rate, v, as shown below[2, 3]:

$$i = \upsilon g C_E \qquad \text{* MERGEFORMAT (1)}$$

Plotting i as a function of v yields a straight line with slope equal to C_E. The ECSA of the catalyst can be calculated by dividing C_E by the specific capacitance (C_S) of the sample as shown in equation* MERGEFORMAT (2).[1]

$$ECSA = \frac{C_E}{C_S} \qquad \text{* MERGEFORMAT (2)}$$

We applied this measurement in rod-like CdS/CdSe-80 and branched CdS/CdSe-80 films. CV measurements were carried out in a convenient three electrodes cell containing aqueous solution of Na_2SO_3 (0.5 M) as the electrolyte. The obtained CdS/CdSe-A films as working electrodes were mounted onto a special designed electrode holder. The surface areas exposed to electrolyte were fixed at 0.785 cm^2. An Ag/AgCl electrode was used as a reference electrode and a large area platinum plate was used as a counter electrode.

OCP was measured in the dark condition, and then 0.1 V window centered at OCP was utilized as the potential range in subsequent CV measurements (Figure S1a and S1c). For the present system, the measured OCP was -0.208 V. Therefore, the potential range for CV measurement was determined from -0.158 V to -0.258 V. Scan rates of 0.005, 0.01, 0.025, 0.05 and 0.1 V/s were conducted, and the anodic charging currents measured at -0.208 V *vs.* Ag/AgCl were plotted as a function of scan rate (Figure S1b and S1d). As described in equation (1), the slopes in Figure S1b and S1d equal to the electrochemical capacitances of CdS/CdSe-80 and branched CdS/CdSe-80, which were 6.78 μF and 19.91 μF, respectively. Moreover, the specific capacitance, C_S, is usually a constant for a specific system[4], therefore the ECSA is proportional to C_E, suggesting the ECSA of branched CdS/CdSe-80 is nearly 3 times than that of rod-like CdS/CdSe-80.

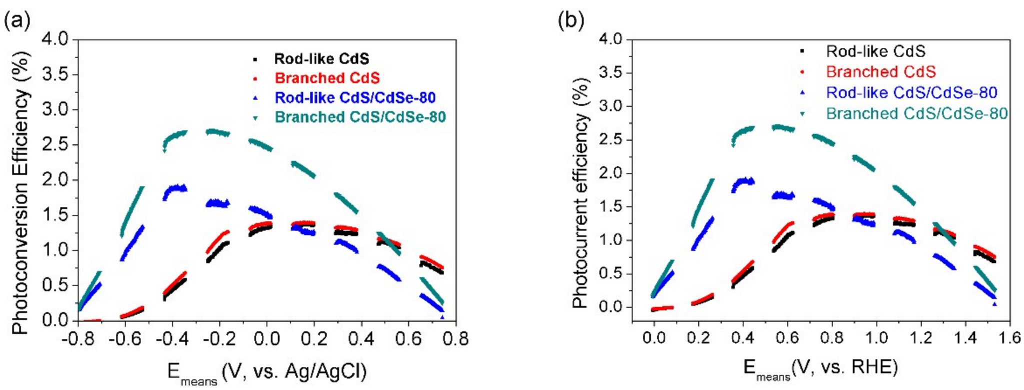

Figure S2. (a) Photo-conversion efficiencies of rod-like CdS, branched CdS, rod-like CdS/CdSe-80 and branched CdS/CdSe-80 films based on the reference potential of Ag/AgCl. (b) Photo-conversion efficiencies of rod-like CdS, branched CdS, rod-like CdS/CdSe-80 and branched CdS/CdSe-80 films based on the reference potential of RHE.

Table S1. The calculated values of E_{app}, E_{means}, E_{aoc}, Currents and Efficiencies of selected samples.

Samples	E_{means}/V	E_{aoc}/V	E_{app}/V	$Current/mA{\cdot}cm^{-2}$	*Efficiency*
Rod-like CdS	-0.75	-0.186	-0.564	-0.0279	-0.01858
	-0.55		-0.364	0.1386	0.12003
	-0.35		-0.164	0.54076	0.57645
	-0.245		-0.059	0.74917	0.87728
	-0.05		0.136	1.16076	1.26988
	0.15		0.336	1.52866	1.36662
	0.35		0.536	1.79108	1.24301
	0.55		0.736	2.13758	1.05596
	0.74		0.926	2.23567	0.67964
Branched CdS	-0.75	-0.186	-0.564	-0.0214	-0.01425
	-0.55		-0.364	0.17045	0.14761
	-0.35		-0.164	0.62624	0.66757
	-0.245		-0.059	0.8665	1.01467
	-0.05		0.136	1.2293	1.34485
	0.15		0.336	1.55669	1.39168
	0.35		0.536	1.89299	1.31374
	0.55		0.736	2.22166	1.0975
	0.74		0.926	2.48917	0.75671
Rod-like CdS/CdSe-80	-0.75	-0.429	-0.32111	0.40395	0.36715
	-0.55		-0.12111	1.11083	1.23179
	-0.35		0.07889	1.63057	1.87697
	-0.245		0.18389	1.58981	1.66312
	-0.05		0.37889	1.83949	1.56561
	0.15		0.57889	1.9414	1.26407
	0.35		0.77889	2.3414	1.05623
	0.55		0.97889	2.43567	0.61162
	0.74		1.16889	2.48408	0.1518
Branched CdS/CdSe-80	-0.75	-0.429	-0.32111	0.49287	0.44796
	-0.55		-0.12111	1.56561	1.73608
	-0.35		0.07889	2.32611	2.67761
	-0.245		0.18389	2.58726	2.70656
	-0.05		0.37889	2.97452	2.53165
	0.15		0.57889	3.32611	2.16567
	0.35		0.77889	3.63439	1.63951
	0.55		0.97889	3.92484	0.98557
	0.74		1.16889	4.27006	0.26094

Reference:

1. C. C. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters and T. F. Jaramillo, *Journal of the American Chemical Society*, 2015, **137**, 4347-4357.
2. S. Trasatti and O. Petrii, *Pure and Applied Chemistry*, 1991, **63**, 711-734.
3. J. M. Bockris and S. Srinivasan, *Journal of Electroanalytical Chemistry*, 1966, **11**, 350-389.
4. C. C. McCrory, S. Jung, J. C. Peters and T. F. Jaramillo, *Journal of the American Chemical Society*, 2013, **135**, 16977-16987.