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# Supplementary materials

# Carbon quantum dots as a visible light sensitizer to significantly boost the solar water splitting performance of bismuth vanadate photoanodes

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The supplementary materials include:

Calculations

Figure S1 ~ Figure S12

Table S1

Movie S1

Reference list

**Calculations**

The conversion between potentials vs. Ag/AgCl and those vs. RHE is performed using the equation below:

$$E\ (\text{vs. RHE}) = E\ (\text{vs. Ag/AgCl}) + E_{Ag/AgCl}\ (\text{reference}) + 0.0591\ \text{V} \times \text{pH}$$

$$(E_{Ag/AgCl}\ (\text{reference}) = 0.1976\ \text{V vs. NHE at } 25\ ^{o}\text{C})$$ [1]

Incident-photon-to-current conversion efficiency (IPCE) can be expressed as:

$$\text{IPCE} = (1240 \times I) / (\lambda \times J_{light}),$$ [2]

Where $I$ is the photocurrent density, $\lambda$ is the incident light wavelength, and $J_{light}$ is the measured irradiance.

Light harvesting efficiency (LHE) can be expressed as:

$$\text{LHE} = 1 - 10^{-A(\lambda)},$$ [1]

where $A_{(\lambda)}$ is absorbance, λ is wavelength.

The maximum photocurrent density ($J_{max}$):

Firstly, the National Renewable Energy Laboratory (NREL) reference solar spectral irradiance at AM 1.5G (radiation energy ($W \cdot m^{-2} \cdot nm^{-1}$) vs. wavelength (nm))[3]was converted to the solar energy spectrum in terms of number of photons ($s^{-1} \cdot m^{-2} \cdot nm^{-1}$) vs. wavelength (nm). Then, the number of photons above the photo-active range of the $BiVO_4$ shown in this study (300 nm ~ 500 nm) and CQDs/$BiVO_4$ (300 nm ~ 800 nm) was calculated using a trapezoidal integration (in 10 nm increments) of the spectrum and was converted to the current density ($mA \cdot cm^{-2}$). [1]

Photocurrent assuming 100% APCE ($J_{abs}$) can be expressed as：

$$J_{abs} = J_{max} \times \text{LHE}.$$ [1]

The practical water oxidation photocurrent ($J_{PEC}$) can be expressed as:

$$J_{PEC} \approx J_{abs} \times \Phi_{sep} \times \Phi_{OX}.$$ [1, 2, 4]

The electron-hole separation yield ($\Phi_{sep}$) can be expressed as:

$$\Phi_{sep} = J_{HS} / J_{abs},$$ [4]

where $J_{HS}$ is the photocurrent density of sample with $Na_2SO_3$ hole scavenger.

Yield of the surface reaching holes or be named transfer efficiency ($\Phi_{OX}$) can be expressed as:

$$\Phi_{OX} = (J_{PEC}) / (J_{HS}).$$ [1, 4]

Applied bias photo-to-current efficiency (ABPE) can be expressed as:

$$\text{ABPE} = [J_{PEC} \times (1.23 - V_{app})] / P_{light},$$ [1]

Where $J_{PEC}$ is the photocurrent density of samples, $V_{app}$ is the applied external potential vs. RHE and $P_{light}$ is the power density of the illumination ($100 mWcm^2$).

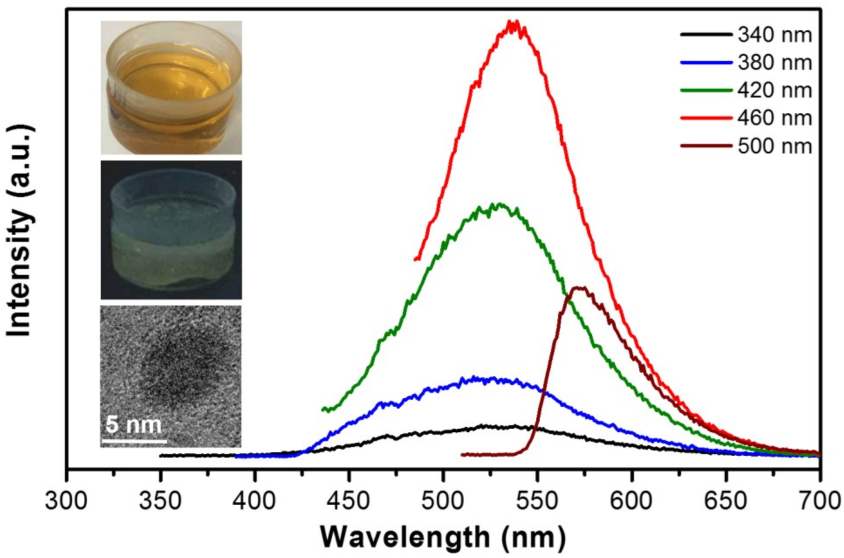



**Figure S1.**TEM, photos and PL emission spectra of CQDs at the excitation wavelength from 340 to 500 nm.

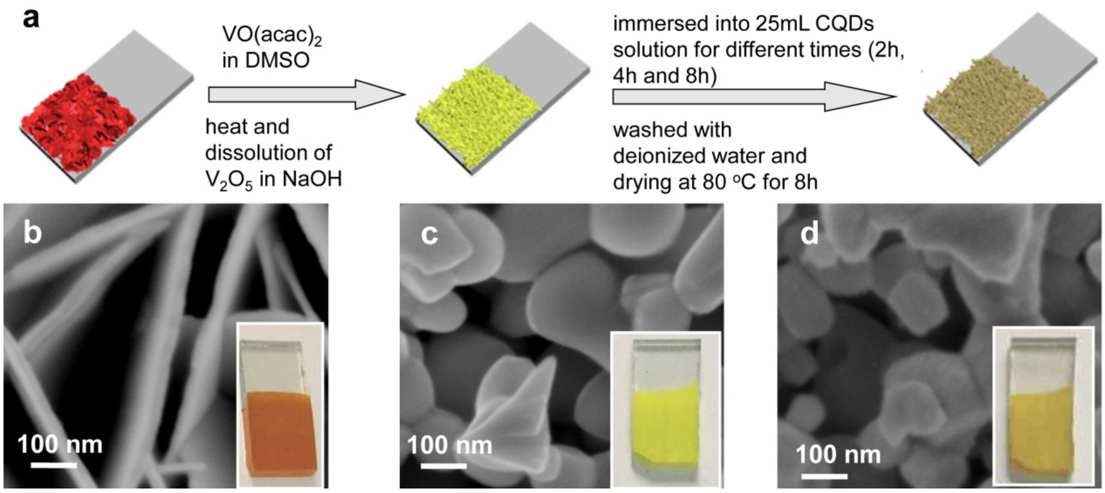



**Figure S2.**Schematic diagrams for the growth process of CQDs/$BiVO_4$ photoanodes, SEM images of (b) BiOI, (c) $BiVO_4$ and (d) CQDs/$BiVO_4$.

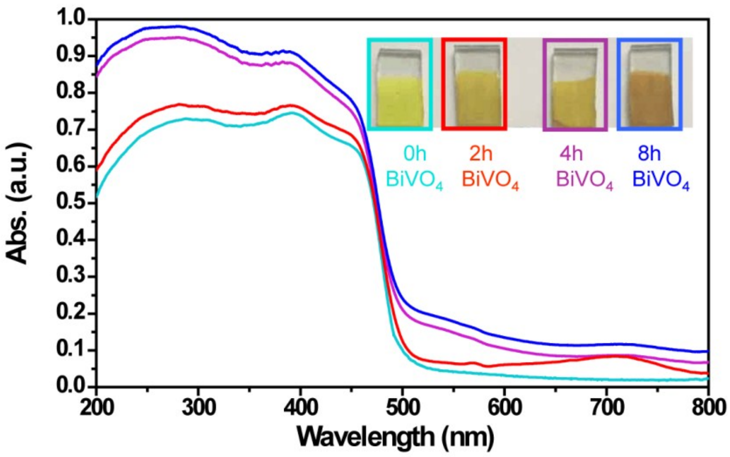



**Figure S3.** UV-vis diffuse absorption spectra of different samples increased with longer adsorption CQDs time.

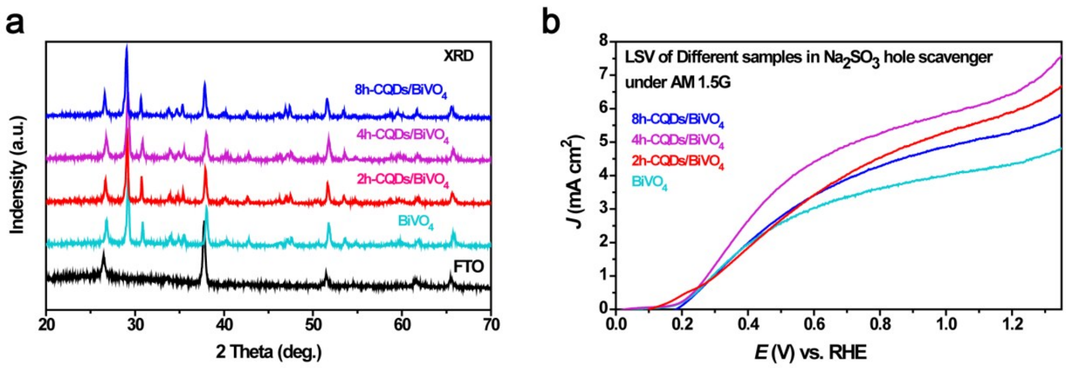



**Figure S4.** (a)XRD patterns of FTO, $BiVO_4$, 2h-CQDs/$BiVO_4$, 4h-CQDs/$BiVO_4$ and

8h-CQDs/$BiVO_4$; (b) *J–V* curves of$BiVO_4$, 2h-CQDs/$BiVO_4$, 4h-CQDs/$BiVO_4$ and 8h-CQDs/$BiVO_4$recorded at a scan rate of 25mVs$^{-1}$under AM 1.5G irradiation in potassium phosphate solution with $Na_2SO_3$ as hole scavenger (pH 7).

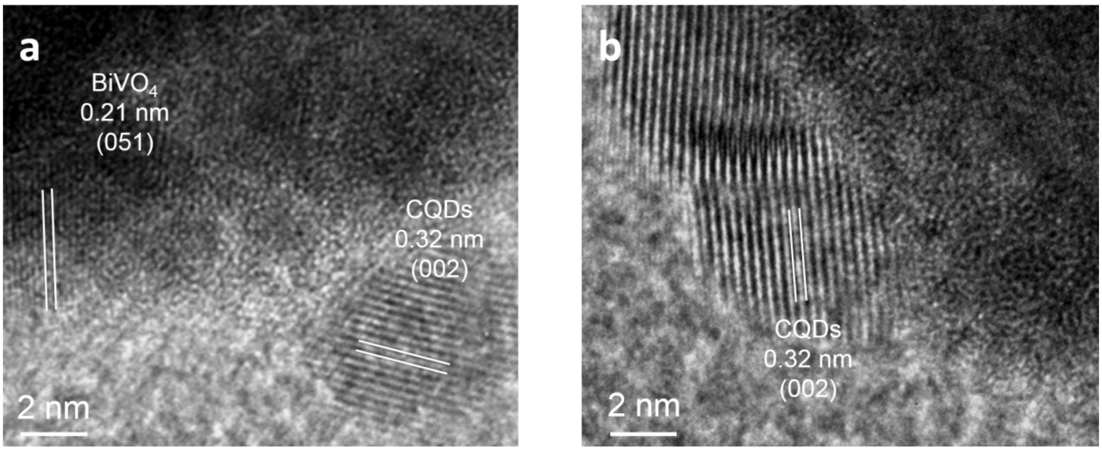



**Figure S5.** HRTEM images of the 4h-CQDs/$BiVO_4$ and 8h-CQDs/$BiVO_4$.

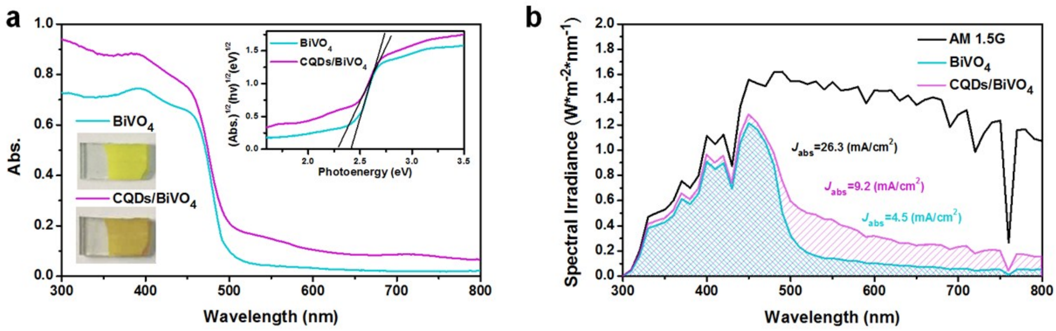



**Figure S6.** Optical characterizations. (a) UV–vis absorption spectra(derived from diffuse reflectance spectra), photographs (bottom left inset) and Tauc plots (top right inset) of the $BiVO_4$ and CQDs/$BiVO_4$ photoanodes; (b) Spectra of the solar irradiance of AM 1.5G (ASTM G173-03) and those weighted by the LHE spectra of the $BiVO_4$ and CQDs/$BiVO_4$ photoanodes (300~800 nm). The photocurrent $J_{abs}$ given for each curve was calculated from integration of the corresponding spectrum.

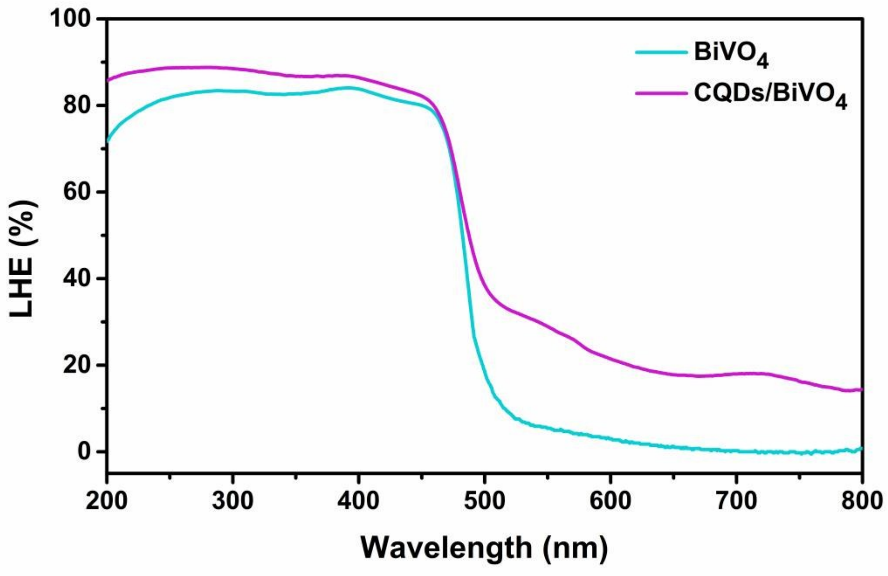



**Figure S7.** LHE of $BiVO_4$ and CQDs/$BiVO_4$ photoanodes.

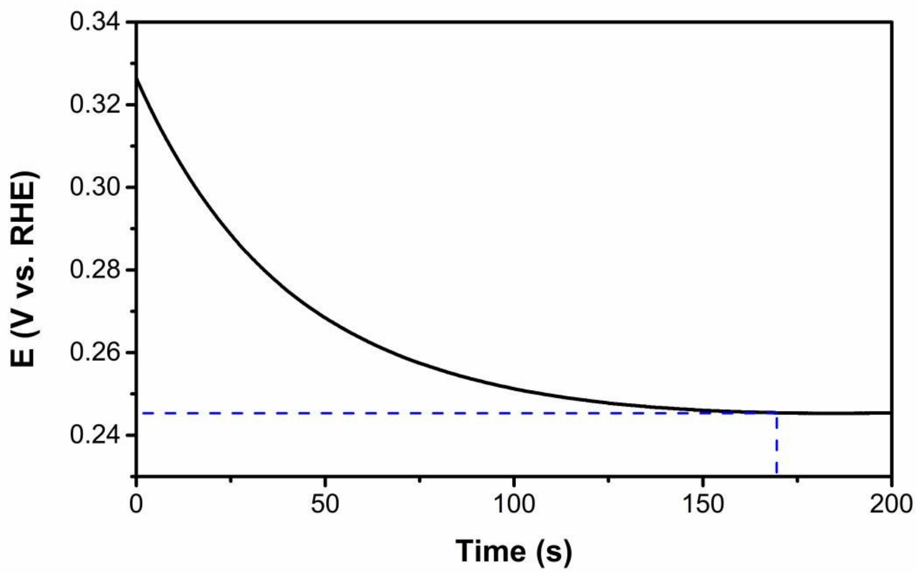



**Figure S8.** Open-circuit voltage curves of sample after photoelectrodeposited OEC layer under AM 1.5G irradiation in potassium phosphate solution without hole scavenger (pH 7).

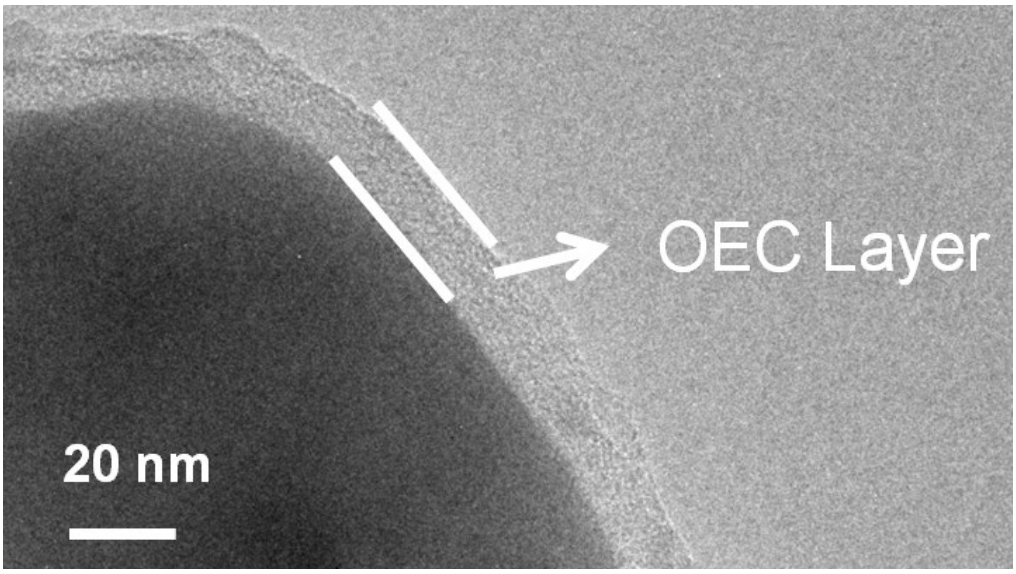



**Figure S9.** TEM images of OEC layer and CQDs/$BiVO_4$.

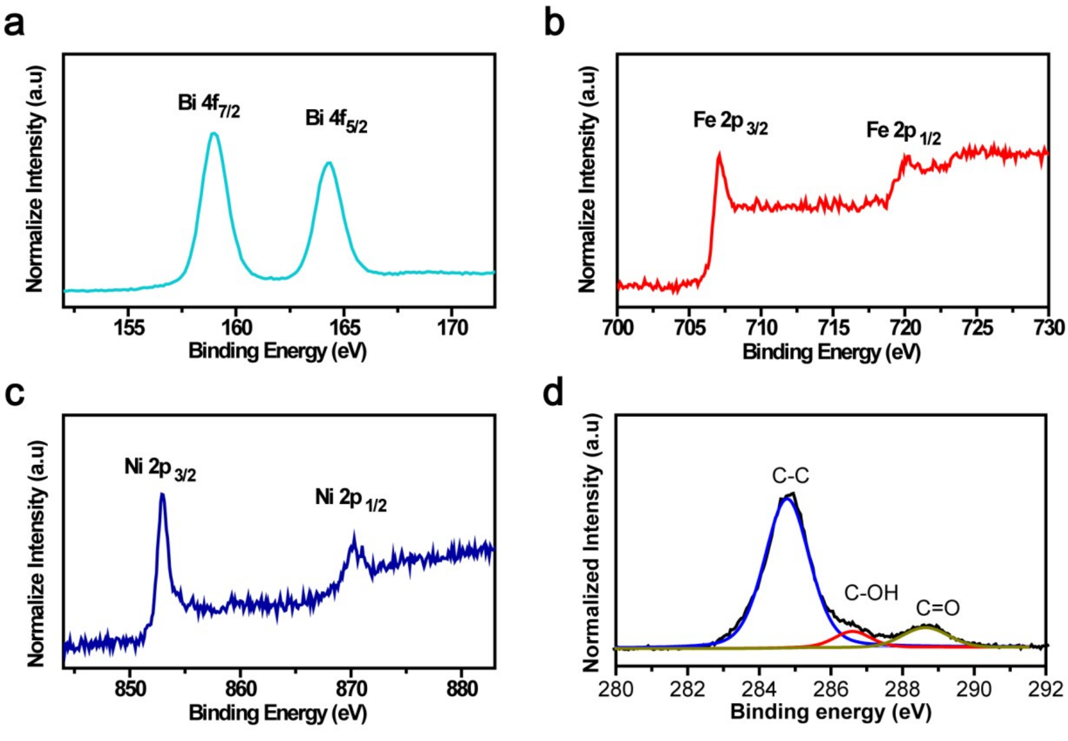



**Figure S10.** High-resolution XPS spectra of $Bi_{4f}$, $Fe_{2p}$, $Ni_{2p}$ and $C_{1s}$.

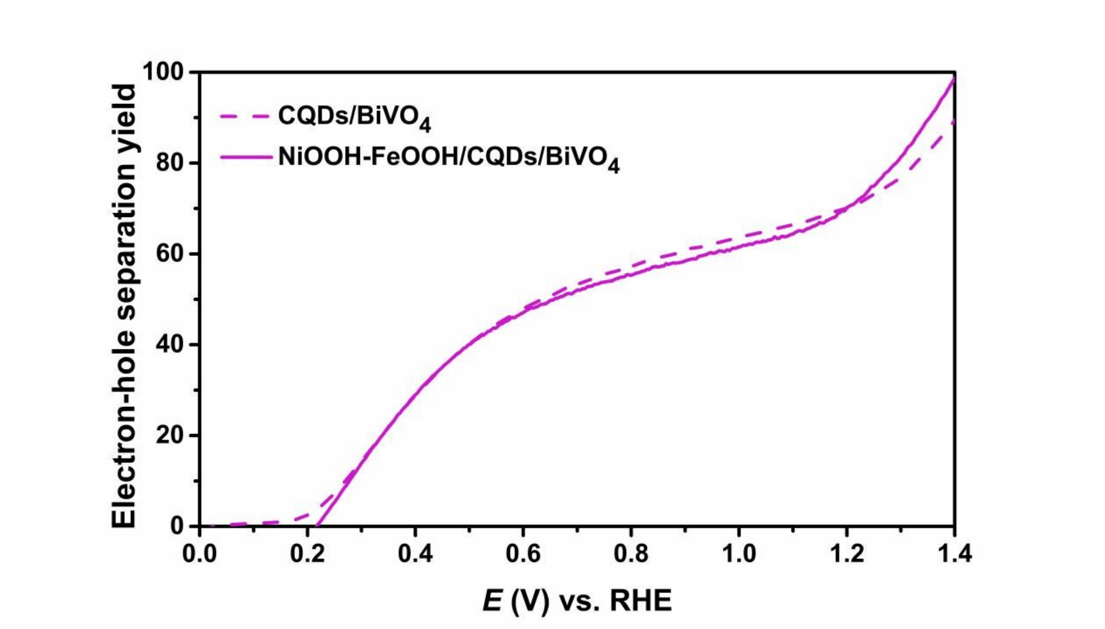



**Figure S11.** The electron-hole separation yield of $CQDs/BiVO_4$ and NFCB photoanodes.

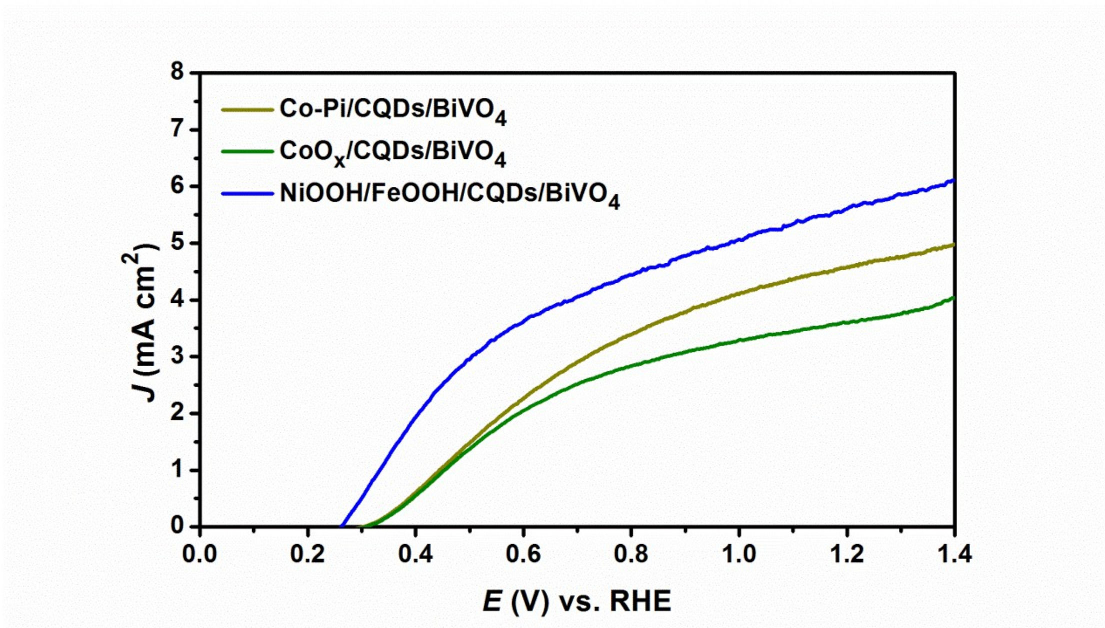



**Figure S12.** *J–V* curves of the NFCB sample, Co-Pi/CQDs/$BiVO_4$ sample, and $CoO_x$/CQDs/$BiVO_4$ sample recorded at a scan rate of $25 mVs^{-1}$ under AM 1.5G irradiation in potassium phosphate electrolyte with no hole scavenger (pH 7)

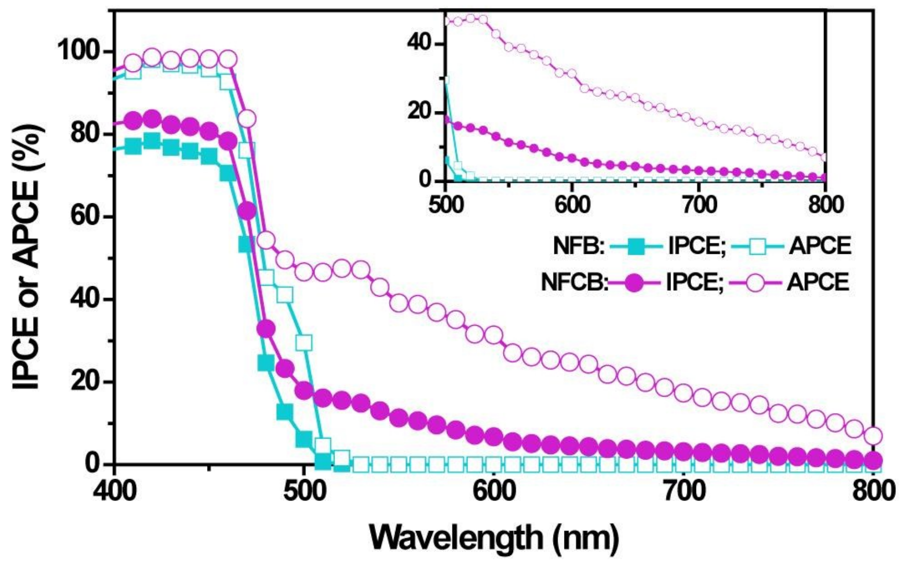



**Figure S13.** APCE and IPCE spectra collected at the incident wavelength range from 400 to 800nm at 1.23V vs. RHE in potassium phosphate electrolyte without hole scavenger (pH 7)

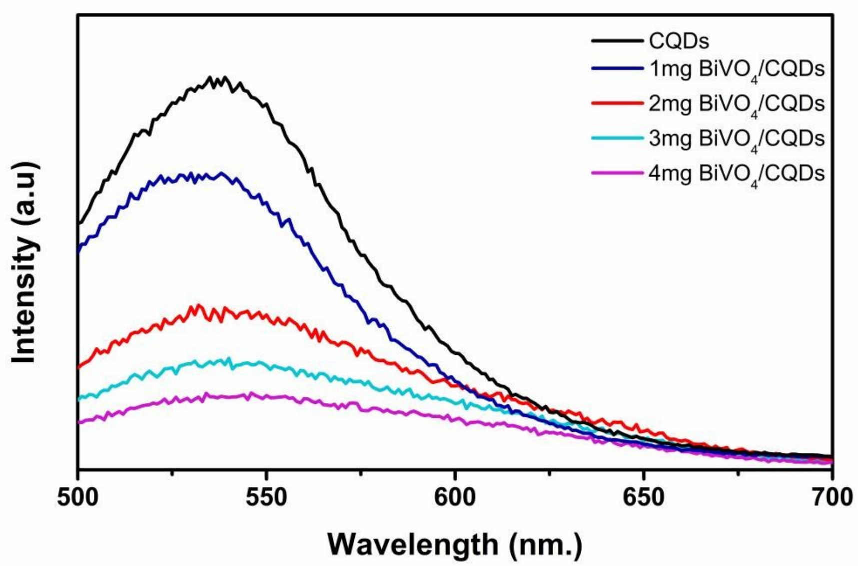



**Figure S14.** Fluorescence quenching test of CQDs solution with different quality of $BiVO_4$.

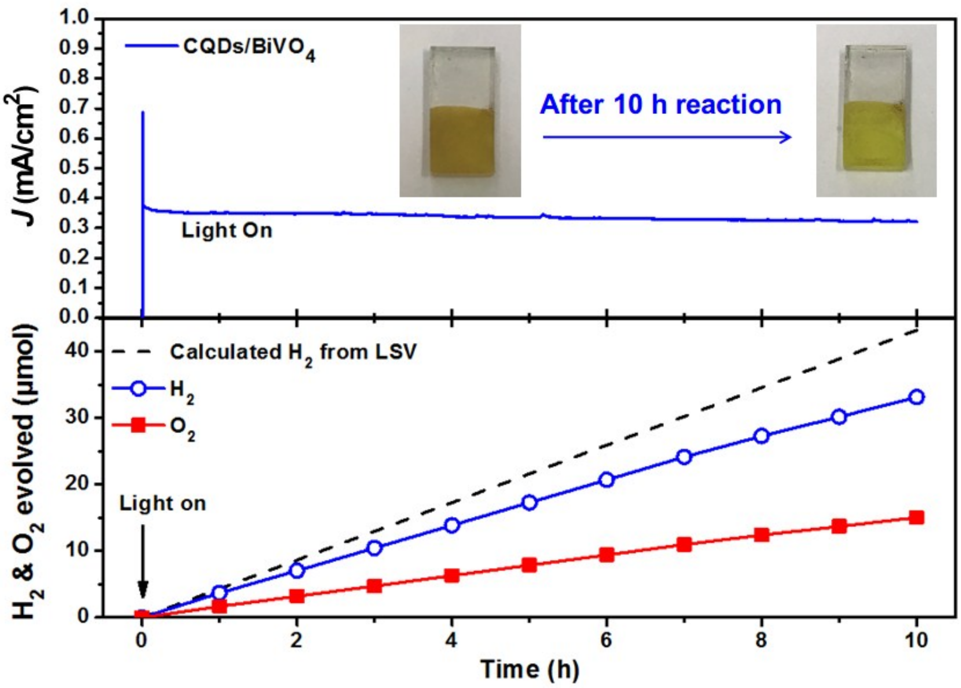



**Figure S15.** Operational stability of the CQDs/$BiVO_4$ photoanode. (Top) Chronoamperometry (*i*–*t*) curves of CQDs/$BiVO_4$ photoanode collected at 0.6 V vs. RHE under AM 1.5G illumination in potassium phosphate electrolyte without hole scavenger (pH 7). (Bottom) $H_2$and $O_2$evolution of NFCB photoanode at 0.6 V vs. RHE; dashed curves indicate the $H_2$and $O_2$evolution with about 75% Faraday efficiency.

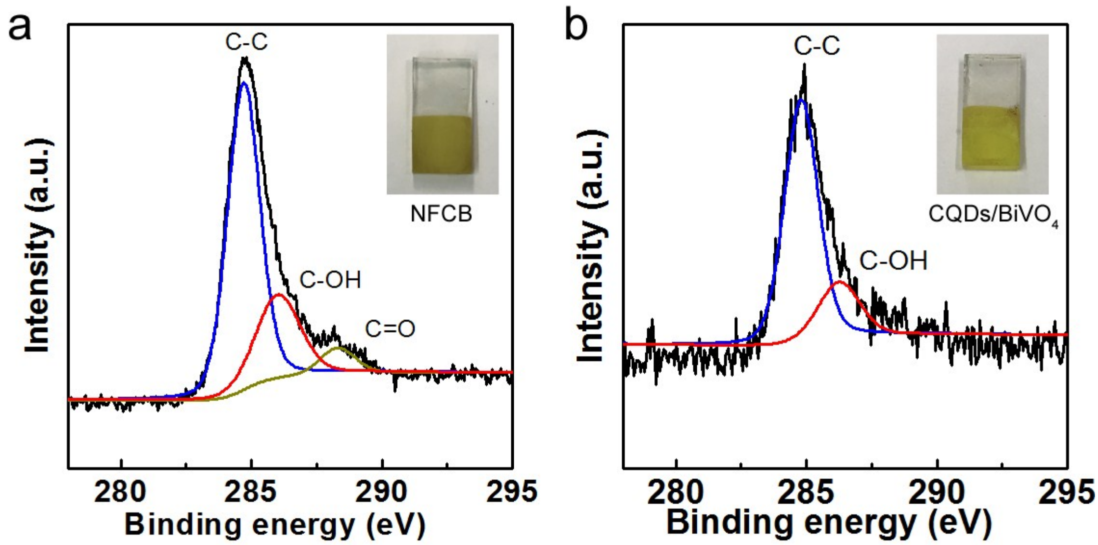



**Figure S16.** $C_{1s}$ High-resolution XPS spectra of NFCB and CQDs/$BiVO_4$ after 10 h reaction.

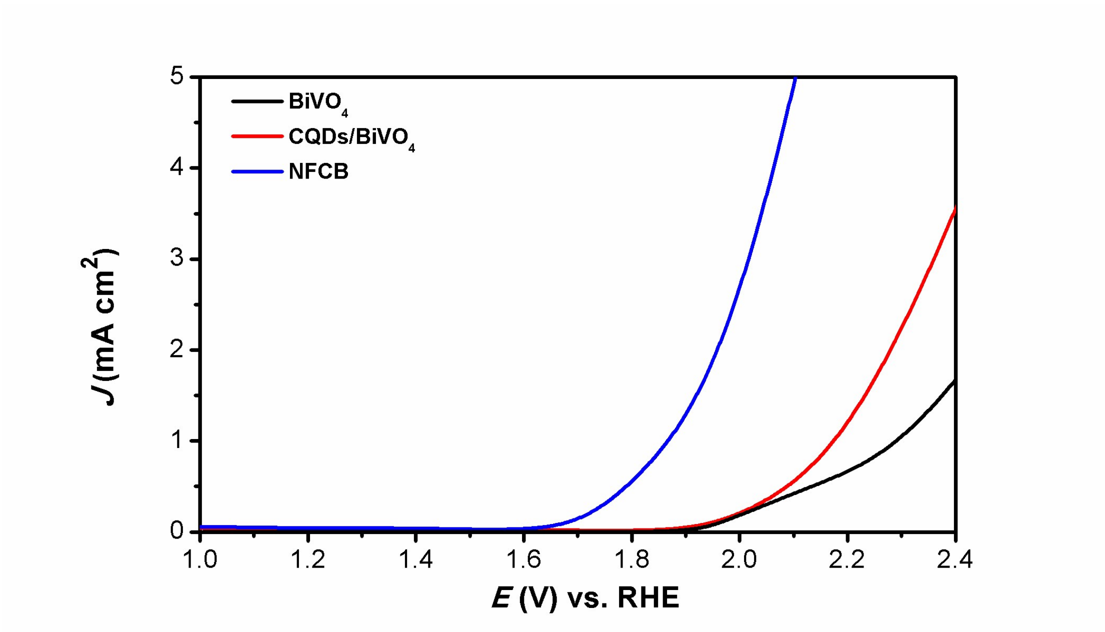



**Figure. S17**. *J-V* curves of the NFCB sample, CQDs/$BiVO_4$ sample, and $BiVO_4$ sample recorded at a scan rate of 25 $mVs^{-1}$ in potassium phosphate electrolyte with no hole scavenger (pH 7)

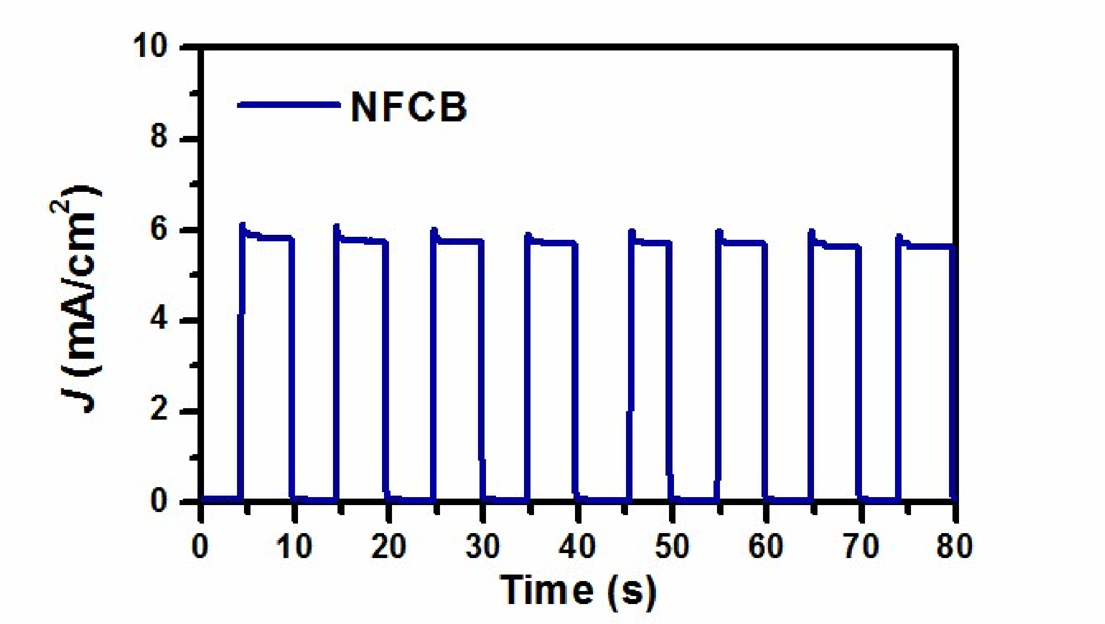
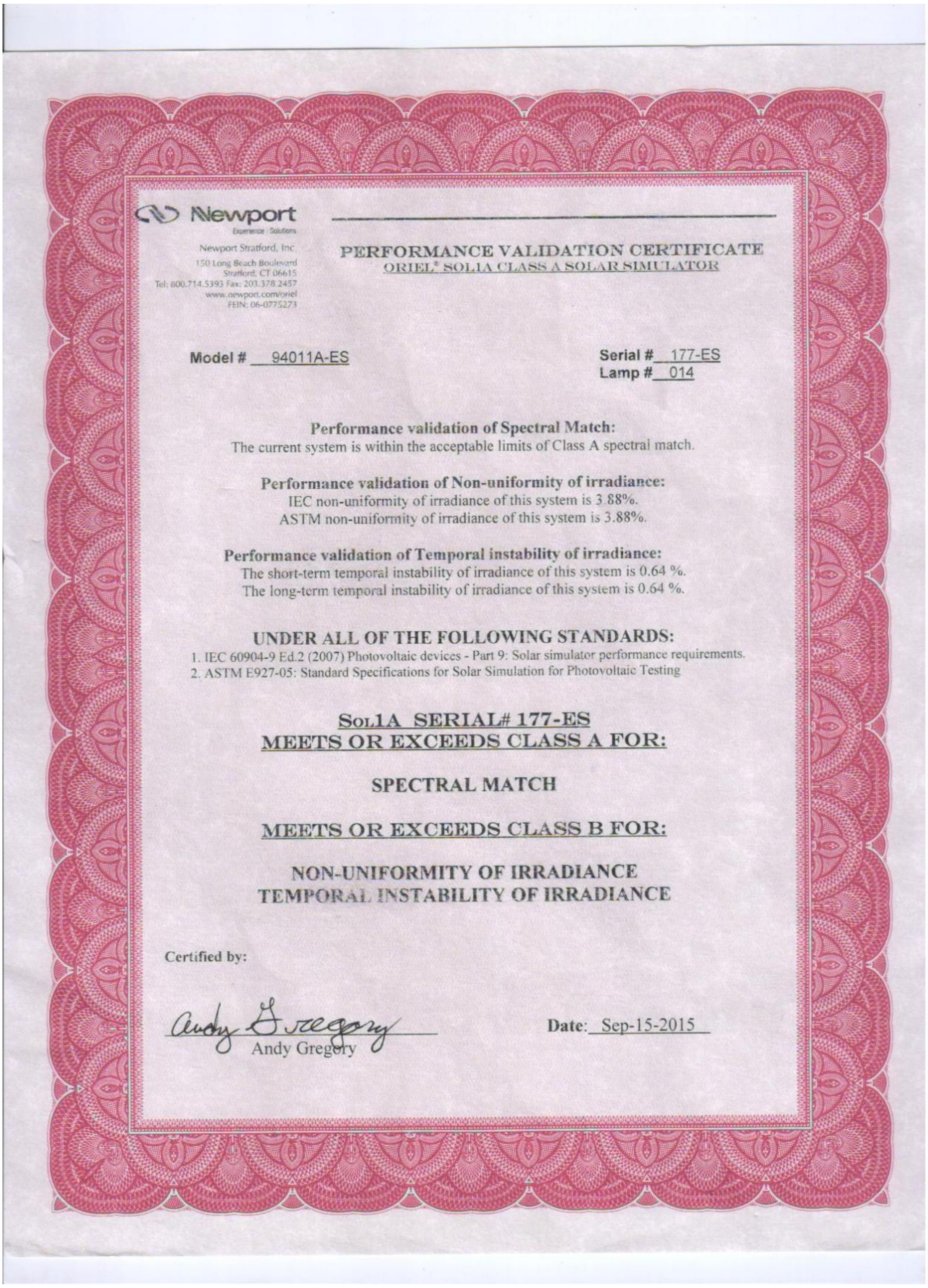



**Figure. S18**. Operational stability of the NFCB photoanode. Chronoamperometry (*i–t*) curves of CQDs/$BiVO_4$photoanodecollected at 1.23 V vs. RHE under AM 1.5G illumination in potassium phosphate electrolyte without hole scavenger (pH 7).



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Serial # 177-ES
Lamp # 014

**Performance validation of Spectral Match:**
The current system is within the acceptable limits of Class A spectral match.

**Performance validation of Non-uniformity of irradiance:**
IEC non-uniformity of irradiance of this system is 3.88%.
ASTM non-uniformity of irradiance of this system is 3.88%.

**Performance validation of Temporal instability of irradiance:**
The short-term temporal instability of irradiance of this system is 0.64 %.
The long-term temporal instability of irradiance of this system is 0.64 %.

**UNDER ALL OF THE FOLLOWING STANDARDS:**
1. IEC 60904-9 Ed.2 (2007) Photovoltaic devices - Part 9: Solar simulator performance requirements.
2. ASTM E927-05: Standard Specifications for Solar Simulation for Photovoltaic Testing

**SOL1A SERIAL# 177-ES**
**MEETS OR EXCEEDS CLASS A FOR:**

**SPECTRAL MATCH**

**MEETS OR EXCEEDS CLASS B FOR:**

**NON-UNIFORMITY OF IRRADIANCE**
**TEMPORAL INSTABILITY OF IRRADIANCE**

Certified by:

Andy Gregory
Andy Gregory

Date: Sep-15-2015

**Figure. S19.** Performance validation certificate of AM 1.5G solar simulator (Newport, LCS 100 94011A)

**Move S1.** The water splitting device in potassium phosphate solution without hole scavenger (pH 7) (RT) at 0.6V vs. RHE under AM 1.5G irradiation (100 mW $cm^{-2}$).

**Table S1.** Summary of recent key advances in BiVO4-based photoanodes for PEC solar water splitting.

| Photoanodes | IPCE range of visible light | Photocurrent at 1.23 V vs. RHE | Ref. |
|---|---|---|---|
| $NiOOH/NiO/CoO_x/BiVO_4$ | 420 nm-520 nm | 3.5 $mA/cm^2$ | 5 |
| $Co_3O_4/BiVO_4$ | 420 nm-520 nm | 2.71 $mA/cm^2$ | 6 |
| $BiOI/BiVO_4$ | 420 nm-590 nm | 3.27 $mA/cm^2$ | 2 |
| NiOOH/FeOOH (W,Mo)-$BiVO_4/WO_3$ | 420 nm-500 nm | 5.35 $mA/cm^2$ | 7 |
| $NiOOH/FeOOH/BiVO_4$ | 420 nm-520 nm | ~4.4 $mA/cm^2$ | 1 |
| NiOOH/FeOOH/N-$BiVO_4$ | 420 nm-550 nm | ~5 $mA/cm^2$ | 8 |
| $BiVO_4/SnO_2/WO_3$ | 420 nm-520 nm | 2.5 $mA/cm^2$ | 9 |
| CQDs/$BiVO_4$ | - | ~2.0 $mA/cm^2$ | 10 |
| CQDs/$TiO_2$ | 420 nm-890 | ~1 $mA/cm^2$ | 11 |
| $CoO_x$/CQDs/$BiVO_4$ | 420 nm-790 nm | 3.65 $mA/cm^2$ | This work |
| Co-Pi/CQDs/$BiVO_4$ | 420 nm-790 nm | 4.64 $mA/cm^2$ | This work |
| NiOOH/FeOOH/CQDs/$BiVO_4$ | 420 nm-790 nm | 5.99 $mA/cm^2$ | This work |

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