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:

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

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

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

\[
\text{IPCE} = \frac{1240 \times I}{\lambda \times J_{\text{light}}},
\]

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

Light harvesting efficiency (LHE) can be expressed as:

\[
\text{LHE} = 1 - 10^{-A_{\lambda}},
\]

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

The maximum photocurrent density \(J_{\text{max}}\):

Firstly, the National Renewable Energy Laboratory (NREL) reference solar spectral irradiance at AM 1.5G (radiation energy (W·m\(^{-2}\)·nm\(^{-1}\)) vs. wavelength (nm))\(^3\) was converted to the solar energy spectrum in terms of number of photons (s\(^{-1}\)·m\(^{-2}\)·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·cm\(^{-2}\)).\(^1\)

Photocurrent assuming 100% APCE \(J_{\text{abs}}\) can be expressed as:
\[ J_{\text{abs}} = J_{\text{max}} \times \text{LHE}. \]

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

\[ J_{\text{PEC}} = J_{\text{abs}} \times \Phi_{\text{sep}} \times \Phi_{\text{OX}}. \]

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

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

where \( J_{\text{HS}} \) is the photocurrent density of sample with Na\(_2\)SO\(_3\) hole scavenger.

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

\[ \Phi_{\text{OX}} = \frac{J_{\text{PEC}}}{J_{\text{HS}}}. \]

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

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

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

**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/BiVO₄ photoanodes, SEM images of (b) BiOI, (c) BiVO₄ and (d) CQDs/BiVO₄.

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

**Figure S4. (a)** XRD patterns of FTO, BiVO₄, 2h-CQDs/BiVO₄, 4h-CQDs/BiVO₄ and
8h-CQDs/BiVO$_4$; (b) $J-V$ curves ofBiVO$_4$, 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$_2$SO$_3$ 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\textsubscript{4} and CQDs/BiVO\textsubscript{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/BiVO₄.

Figure S10. High-resolution XPS spectra of Bi₄f, Fe₂p, Ni₂p and C₁s.
Figure S11. The electron-hole separation yield of CQDs/BiVO₄ and NFCB photoanodes.

Figure S12. $J-V$ curves of the NFCB sample, Co-Pi/CQDs/BiVO₄ sample, and CoOₓ/CQDs/BiVO₄ sample recorded at a scan rate of 25mVs⁻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 BiVO₄.
Figure S15. Operational stability of the CQDs/BiVO₄ photoanode. (Top) Chronoamperometry ($i-t$) curves of CQDs/BiVO₄ photoanode collected at 0.6 V vs. RHE under AM 1.5G illumination in potassium phosphate electrolyte without hole scavenger (pH 7). (Bottom) H₂ and O₂ evolution of NFCB photoanode at 0.6 V vs. RHE; dashed curves indicate the H₂ and O₂ evolution with about 75% Faraday efficiency.

Figure S16. C₁s High-resolution XPS spectra of NFCB and CQDs/BiVO₄ 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$_4$ photoanode collected at 1.23 V vs. RHE under AM 1.5G illumination in potassium phosphate electrolyte without hole scavenger (pH 7).
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 BiVO\(_4\)-based photoanodes for PEC solar water splitting.

<table>
<thead>
<tr>
<th>Photoanodes</th>
<th>IPCE range of visible light</th>
<th>Photocurrent at 1.23 V vs. RHE</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiOOH/NiO/CoO(_x)/BiVO(_4)</td>
<td>420 nm-520 nm</td>
<td>3.5 mA/cm(^2)</td>
<td></td>
</tr>
<tr>
<td>Co(_3)O(_4)/BiVO(_4)</td>
<td>420 nm-520 nm</td>
<td>2.71 mA/cm(^2)</td>
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</tr>
<tr>
<td>BiOI/BiVO(_4)</td>
<td>420 nm-590 nm</td>
<td>3.27 mA/cm(^2)</td>
<td></td>
</tr>
<tr>
<td>NiOOH/FeOOH (W,Mo)-BiVO(_4)/WO(_3)</td>
<td>420 nm-500 nm</td>
<td>5.35 mA/cm(^2)</td>
<td></td>
</tr>
<tr>
<td>NiOOH/FeOOH/BiVO(_4)</td>
<td>420 nm-520 nm</td>
<td>~4.4 mA/cm(^2)</td>
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</tr>
<tr>
<td>NiOOH/FeOOH/N-BiVO(_4)</td>
<td>420 nm-550 nm</td>
<td>~5 mA/cm(^2)</td>
<td></td>
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<tr>
<td>BiVO(_4)/SnO(_2)/WO(_3)</td>
<td>420 nm-520 nm</td>
<td>2.5 mA/cm(^2)</td>
<td></td>
</tr>
<tr>
<td>CQDs/BiVO(_4)</td>
<td>-</td>
<td>~2.0 mA/cm(^2)</td>
<td></td>
</tr>
<tr>
<td>CQDs/TiO(_2)</td>
<td>420 nm-890 nm</td>
<td>~1 mA/cm(^2)</td>
<td></td>
</tr>
<tr>
<td>CoO(_x)/CQDs/BiVO(_4)</td>
<td>420 nm-790 nm</td>
<td>3.65 mA/cm(^2)</td>
<td>This work</td>
</tr>
<tr>
<td>Co-Pi/CQDs/BiVO(_4)</td>
<td>420 nm-790 nm</td>
<td>4.64 mA/cm(^2)</td>
<td>This work</td>
</tr>
<tr>
<td>NiOOH/FeOOH/CQDs/BiVO(_4)</td>
<td>420 nm-790 nm</td>
<td>5.99 mA/cm(^2)</td>
<td>This work</td>
</tr>
</tbody>
</table>

**References**
