Supporting information

Nano-design of quantum dot-based photocatalysts for hydrogen generation using advanced surface molecular chemistry

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As shown in Figure S1, we attempted to provide evidence of the functionalization of the CdSe quantum dots (without ZnS shell). The S 2p photoemission signal overlaps with the Se 3p signal from CdSe. The spectrum consists of three (S 2p\textsubscript{3/2}–S 2p\textsubscript{1/2}) spin-orbit doublets and one (Se 3p\textsubscript{3/2}–Se 3p\textsubscript{1/2}) spin-orbit doublet. The doublet separation at 5.8 eV and a fixed area ratio equal to 2:1 were used for the (Se 3p\textsubscript{3/2}–Se 3p\textsubscript{1/2}) doublet. The S 2p\textsubscript{3/2} components were located at binding energy values of 162.0, 163.6 and 168.3 eV, respectively. The peaks at 163.6 and 168.3 eV correspond to unbound thiols and sulfates, respectively, whereas the new peak located at 162.0 eV is assigned to Cd-S bonds.\textsuperscript{1-3} CdSe quantum dots capped with mercaptopropyl porous phosphate heterostructure (PPH-SH) show similar structures at the same binding energy that corresponds to the formation of PPH-S-CdSe nanocomposites.\textsuperscript{2} Furthermore, the binding energies of the Se 3p\textsubscript{3/2} component at 160.2 eV and the Cd 3d\textsubscript{5/2} component at 405.2 eV (results not shown) are in good agreement with previously reported values for CdSe.\textsuperscript{4-6}
Figure S2. High resolution XP spectra of the wide scan and detailed spectra for each component of Ti-2.
Figure S3. High resolution XP spectra of the wide scan and detailed spectra for each component of Ti-3.
**Figure S4.** a) Size distribution and b) EDS spectrum of the Au/Pt alloy NCs.

**Figure S5.** EDS spectrum of the Ti-4 sample.
Figure S6. Photon irradiance of the light source (ASAHI) over the full wavelength range used and with band pass filters for QE measurements.

Figure S7. Hydrogen evolution of Au/Pt-TiO$_2$-CdSe complexes.

Average evolution rate of hydrogen: 9.8 µmol h$^{-1}$. 
Figure S8. Hydrogen evolution of Au/Pt-CdSe@ZnS complexes.

Average evolution rate of hydrogen: 15.6 μmol h⁻¹.

Figure S9. Hydrogen evolution of CdSe@ZnS-TiO₂-Au/Pt complexes (Ti-4) in an aqueous MeOH solution (10% v/v).

Average evolution rate of hydrogen: 4.2 μmol h⁻¹. Amounts: 30 mg Ti-4 (590 nm) in 25 ml of an aqueous solution containing Na₂S (0.5 M) and Na₂SO₃ (0.5 M).
Figure S10. Photoluminescence of QDs, sample Ti-3 and sample Ti-4.
Table S1. Average sizes of different ZnS@CdSe QDs obtained from the chemical provider Sigma-Aldrich.

<table>
<thead>
<tr>
<th>PL peak</th>
<th>560 nm</th>
<th>590 nm</th>
<th>610 nm</th>
<th>640 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (nm)</td>
<td>3.4</td>
<td>4.0</td>
<td>5.2</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Note: The monolayer thickness of the ZnS shell was calculated according to the distance of 3.1 Å between consecutive planes along the [002] axis in bulk wurtzite ZnS. According to the manufacturer, a ZnS shell measuring 2 to 3 monolayers in thickness was epitaxially grown in solution on the CdSe core. Therefore, the average shell thickness was approximately 1.2–1.9 nm.[10]

Table S2. ICP data (wt%) for Ti-4 with ZnS@CdSe QDs of different sizes.

<table>
<thead>
<tr>
<th>Sample labels</th>
<th>Au</th>
<th>Pt</th>
<th>Se</th>
<th>Cd</th>
<th>S</th>
<th>Ti</th>
<th>Zn</th>
<th>ZnS@Cd Sea</th>
<th>Au + Ptb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-4 (QD560)</td>
<td>0.38</td>
<td>0.37</td>
<td>0.70</td>
<td>1.7</td>
<td>2.8</td>
<td>45.7</td>
<td>0.29</td>
<td>2.8</td>
<td>0.75</td>
</tr>
<tr>
<td>Ti-4 (QD590)</td>
<td>0.39</td>
<td>0.37</td>
<td>0.80</td>
<td>2.1</td>
<td>3.0</td>
<td>47.8</td>
<td>0.30</td>
<td>3.4</td>
<td>0.76</td>
</tr>
<tr>
<td>Ti-4 (QD610)</td>
<td>0.37</td>
<td>0.40</td>
<td>0.76</td>
<td>2.1</td>
<td>3.1</td>
<td>47.0</td>
<td>0.31</td>
<td>3.3</td>
<td>0.77</td>
</tr>
<tr>
<td>Ti-4 (QD640)</td>
<td>0.37</td>
<td>0.37</td>
<td>0.83</td>
<td>1.9</td>
<td>3.2</td>
<td>45.1</td>
<td>0.32</td>
<td>3.2</td>
<td>0.74</td>
</tr>
</tbody>
</table>

a The weight percent of ZnS was calculated based on Zn metal; b the sum of the Au and Pt weight percents.
Reference (Supporting information)


