Cu$_2$ZnSnS$_4$-Ag$_2$S Nanoscale p-n Heterostructures as Sensitizers for Photoelectrochemical Water Splitting

Supporting Information

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<th>Table S1.</th>
<th>CZTS and CZTS-Ag$_2$S atomic composition obtained from EDX analysis.</th>
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<td></td>
<td>Cu (%)</td>
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<tr>
<td>CZTS</td>
<td>22</td>
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<tr>
<td>CZTS-Ag$_2$S (Sample H1)</td>
<td>22</td>
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<tr>
<td>CZTS-Ag$_2$S (Sample H2)</td>
<td>17</td>
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<td>CZTS-Ag$_2$S (Sample H3)</td>
<td>16</td>
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Figure S1. XPS spectra of CZTS-Ag$_2$S nano-heterostructures.
**Figure S2.** Selection of HRTEM micrographs showing some single crystalline and polycrystalline Ag$_2$S NPs attached to CZTS NPs. They all seem to have the epitaxial relation.
**Figure S3.** XRD patterns of CZTS nanoparticles and CZTS-Ag$_2$S nanoparticles obtained with an excess amount of Ag$^+$. Only the XRD peaks corresponding to the Ag$_2$S and most probably also metal Ag crystal structures were obtained after the full cation exchange reaction. Reference patterns of wurtzite CZTS (JCPDS: 00-005-0492), Ag$_2$S (JCPDS: 00-003-0844) and Ag (JCPDS: 00-004-0783) are also shown as reference.
Figure S4. TEM micrographs of CZTS nanoparticles before (left) and after (right) full cation exchange with Ag\(^+\) ions.

Figure S5. HRTEM micrograph showing the presence of several NPs, detail of the single crystalline NP indicated with red square and its corresponding power spectrum.

We identified another phase of Ag\(_2\)S, which has a primitive orthorhombic lattice (space group = P2\(_1\)2\(_1\)2\(_1\)) with lattice parameters of a = 0.6725 nm, b = 0.4148 nm and c = 0.7294 nm. The abundance of this phase is about the same with the above presented monoclinic Ag\(_2\)S phase. A HRTEM micrograph showing the presence of a single crystalline Ag\(_2\)S attachment is presented in Fig. S5. On the right, detail of the red squared region and its corresponding power spectrum, which reveals that this NP has the orthorhombic Ag\(_2\)S phase and visualized along its [021] axis, are shown.
Figure S6. UV-vis absorbance spectra of CZTS nanocrystals and CZTS-Ag$_2$S nanoheterostructures (Sample H2).

Figure S7. (a) Mott-Schottky plot of TiO$_2$; (b)Mott-Schottky plot of CZTS-Ag$_2$S-sensitized TiO$_2$. 
Figure S8. The linear extrapolations of plots of $(\alpha h \nu)^2$ vs. photon energy for CZTS (a), CZTS-Ag$_2$S H1 (b), CZTS-Ag$_2$S H2 (c) and CZTS-Ag$_2$S H3.