First demonstration of CdSe as a photocatalyst for hydrogen evolution from water under UV and visible light†

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CdSe nanoribbons show catalytic activity for photochemical hydrogen evolution from aqueous Na2S/Na2SO3 solution under irradiation with ultraviolet and visible light.

The ability to use photochemical energy to decompose water into hydrogen and oxygen is of interest as a potential technology for solar energy utilization. Many metal oxides are known to catalyze the reaction, but their bandgaps are suitable only to absorb the ultraviolet portion of the solar spectrum.1 Metal sulfides have smaller bandgaps and are thus particularly interesting as photochemical water splitting catalysts. Cadmium sulfide2–5 and zinc sulfide6,7 were the first two metal sulfides studied for this reaction. Both are prone to photocorrosion under bandgap irradiation8–10 but can produce H2 from aqueous solutions containing sacrificial electrons donors, such as Na2S and Na2SO3.5,7 Using Pt particles as co-catalysts, quantum efficiencies of up to 25% in the case of CdS2 and 90% in the case of ZnS can be achieved.7 In contrast, metal sulfides based on indium,11–14 tungsten15 and bismuth16 have lower efficiencies, even in the presence of sacrificial electron donors. Metal selenides, and CdSe in particular, do not catalyze the reaction at all.17 As part of our continuing study of photochemical water splitting with semiconductor nanostructures,18,19 we show here that photocatalytic hydrogen evolution from water can be achieved with CdSe nanoribbons in the presence of Na2S/Na2SO3 as sacrificial electron donors and using ultraviolet or visible light. The nanoribbons were synthesized according to the protocol by Joo et al. and characterized via TEM, UV/Vis and fluorescence spectroscopy (Fig. 1 and 2). The ribbons grow in the 001 direction and are composed of CdSe wurtzite fragments (Fig. 1A) terminated at the top and bottom by 1120 lattice planes and on the sides by 1100 planes. TEM data (Fig. 1B,C) confirms that the ribbons are approximately 1.4 nm thick and form stacks in the 1120 direction (see also Joo et al.20). The small thickness causes strong quantum confinement leading to an extended bandgap of 2.7 eV. As a consequence the absorption edge and fluorescence maximum are blue shifted to 460 nm and 455 nm, respectively. For catalytic measurements ~10 mg (exact amounts in Table 1) of the ribbons dispersed in 50 ml of de-ionized water were placed in a quartz flask that was directly connected to a gas chromatograph. The mixture was degassed with three evacuation/Ar backfill cycles, backfilled with Ar to a pressure of ~600 Torr, and irradiated with light from four 175 W low pressure Hg lamps. Over the course of 5 h, hydrogen evolved at a nearly constant rate of 0.92 μmol h−1 to a final value of 4.62 μmol (Fig. 2A and Table 1). The quantum efficiency (QE) for this process is 0.09% based on a photon flux of 5.92 × 10−7 mol s−1 for this lamp configuration, measured at 250–500 nm. The actual QE is higher, because only light with λ < 460 nm is absorbed by the catalyst.19 When the reaction was performed in 20% aqueous methanol, a known sacrificial electron donor,21 the hydrogen evolution rate was about three to four times higher, producing a total H2 amount of 18.4 μmol after 5 h.

The increase in the H2 rate indicates that the CdSe nanoribbons are able to photooxidize methanol. In both water and aqueous methanol solution, the CdSe nanoribbons undergo a color change during irradiation from bright yellow to orange, indicating decomposition of the semiconductor. UV/Vis spectra (Fig. 2B,C) do reveal a broadening of the characteristic absorption bands due to CdSe.
absorption bands at 425 and 450 nm, and diminished fluorescence intensity at 455 nm. A TEM of the catalyst recovered from the reaction mixture shows that the ribbon morphology of the material (Fig. 1D) is destroyed. Based on atomic absorption spectroscopy, irradiation increases the Cd$^{2+}$ ion concentration in the reaction mixture (Table 1). This suggests that the CdSe ribbons undergo photodecomposition into Cd$^{2+}$ and Se, similar to bulk CdSe.\(^2\) When irradiation of the CdSe nanoribbons is performed in 0.1 M aqueous Na$_2$S/0.1 M Na$_2$SO$_3$, an increase in hydrogen evolution can be observed. Under these conditions 107 $\mu$mol h$^{-1}$ of H$_2$ are evolved steadily for 5 h, corresponding to an apparent quantum efficiency (QE) of $\sim$10%.

The total molar amount of produced H$_2$ exceeds the molar amount of CdSe by a factor of 10, indicating that H$_2$ evolution is catalytic. The sacrificial electron donors somewhat reduce the decomposition of the nanoribbons, but do not prevent it entirely. The TEM of the recovered material (Fig. 1E) appears identical to the starting material, but the optical absorbance features are less intense and have shifted by 4 nm to longer wavelength (429 and 454 nm) while the fluorescence is shifted in the opposite direction from 455 nm to 454 nm. The Cd$^{2+}$ concentration in the liquid after irradiation is about four to six times lower compared to the other conditions. This shows that the sacrificial electron donors slow the photodecomposition of CdSe significantly. To test the activity of the catalyst in visible light, the reactor was encased in a UV filter (1.0 M aqueous NaNO$_2$) which transmits only light of $\lambda > 400$ nm. Under these conditions H$_2$ was continuously evolved, although at a lower rate (4.36 $\mu$mol h$^{-1}$). Considering the reduced quantum flux of the filtered light ($1.80 \times 10^{-8}$ mol s$^{-1}$), this corresponds to an apparent QE of 13.4%, i.e. slightly higher than under UV irradiation.

The observation of catalytic activity of the nanoribbons is remarkable because it contrasts sharply with that of bulk CdSe, which is inactive for the reaction.\(^1\) The bandgap of bulk CdSe is 1.7 eV and reported flatband potentials for it range from $-0.6$ V (NHE) at pH = 7\(^\text{24}\) to $-0.2$ V (NHE) at pH = 0.\(^\text{25}\) The inability of bulk CdSe to catalyze H$_2$ evolution from water even in the presence of reducing agents indicates a large overpotential for proton reduction on the CdSe surface. For CdSe nanoribbons proton reduction is possible because the effect of the overpotential is compensated by the increased bandgap.

In conclusion we have shown that CdSe nanoribbons have photocatalytic activity for hydrogen production from water in the presence of Na$_2$S/Na$_2$SO$_3$ as sacrificial electron donors under UV and visible light. This is the first example of

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**Table 1** Photochemical hydrogen generation

<table>
<thead>
<tr>
<th>Experiment</th>
<th>CdSe used/ (\mu)mol</th>
<th>Initial/ final pH</th>
<th>Total H$_2$ produced/ (\mu)mol</th>
<th>H$_2$ produced/ (\mu)mol h$^{-1}$</th>
<th>QE (%)$^\text{a}$</th>
<th>Cd$^{2+}$ (aq) post irradiation/(\mu)mol l$^{-1}$$^\text{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>45.92</td>
<td>10.3/9.55</td>
<td>4.62</td>
<td>0.92</td>
<td>0.09</td>
<td>6.7 (0.2)</td>
</tr>
<tr>
<td>20% CH$_3$OH (aq)</td>
<td>50.34</td>
<td>10.37/8.24</td>
<td>18.36</td>
<td>3.67</td>
<td>0.35</td>
<td>3.8 (0.2)</td>
</tr>
<tr>
<td>0.10 M Na$_2$SO$_3$ : 0.11 M Na$_2$S(aq)</td>
<td>48.15 (53.61)$^\text{c}$</td>
<td>13.22/13.30</td>
<td>533.9 (21.8)$^\text{d}$</td>
<td>106.79 (4.36)$^\text{e}$</td>
<td>10.19 (13.4)$^\text{f}$</td>
<td>1.08 (0.03)</td>
</tr>
</tbody>
</table>

$^a$ 8.2 $\times$ 10$^{-2}$ $\mu$mol l$^{-1}$ for non-irradiated sample. $K_{SP}$(CdSe) = 6.3 $\times$ 10$^{-36}$ from ref. 23. $^b$ Separate experiment with 1.0 M NaNO$_2$ (aq) longpass filter $\lambda > 400$ nm. $^c$ Actual values are higher because catalysts only absorb at wavelengths below 460 nm, while ferrioxalate actinometry measures photons at 250–500 nm. $^d$
photocatalytic water reduction by CdSe, or by any metal selenide. These results demonstrate that size confinement effects can establish catalytic properties of an otherwise non-catalytic material. This is analogous to the appearance of catalytic properties in gold nanoclusters on titania.29

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Notes and references