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

F. Andrew Frame,[a] Elizabeth C. Carroll,[a] Delmar S. Larsen,[a] Michael Sarahan,[a] Nigel D. Browning[b] and Frank E. Osterloh*[a]

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CdSe nanoribbons show catalytic activity for photochemical hydrogen evolution from aqueous Na_2S/Na_2SO_3 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 sulfide[2–5] and zinc sulfide[6,7] were the first two metal sulfides studied for this reaction. Both are prone to photocorrosion under bandgap irradiation[8–10] but can produce H_2 from aqueous solutions containing sacrificial electrons donors, such as Na_2S and Na_2SO_3.[5,7] Using Pt particles as co-catalysts, quantum efficiencies of up to 25% in the case of CdS[5] and 90% in the case of ZnS can be achieved.[7] In contrast, metal sulfides based on indium,[11–14] tungsten[15] and bismuth[16] 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 nanosheets,[18,19] we show here that photocatalytic hydrogen evolution from water can be achieved with CdSe nanoribbons in the presence of Na_2S/Na_2SO_3 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).[20] The ribbons grow in the $000\bar{1}$ direction and are composed of CdSe wurtzite fragments (Fig. 1A) terminated at the top and bottom by $11\bar{2}0$ lattice planes and on the sides by $1\bar{1}00$ planes. TEM data (Fig. 1B,C) confirms that the ribbons are approximately 1.4 nm thick and form stacks in the $11\bar{2}0$ 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 deionized 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 $\lambda < 460$ 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 H_2 amount of 18.4 μmol after 5 h.

The increase in the H_2 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

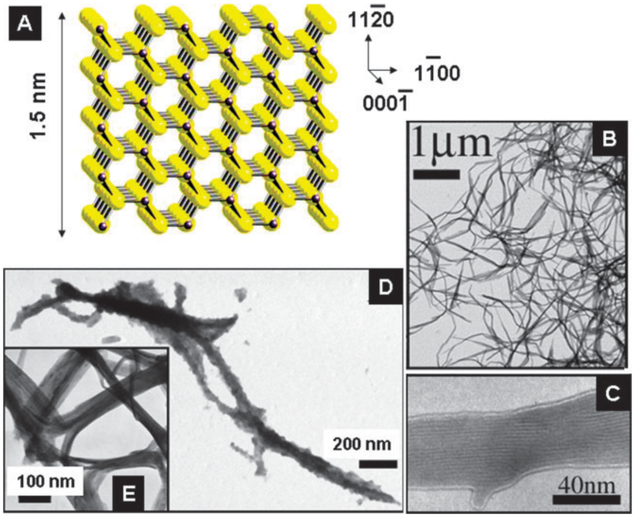

Fig. 1 Structure (A, schematic), and morphology of the CdSe ribbons: (B,C) as synthesized (note that the object in C is a stack of multiple ribbons), (D) after 5 h irradiation in water, (E) after 5 h irradiation in aqueous 0.1 M Na_2S/Na_2SO_3. The arrows in (A) indicate crystallographic directions of the lattice.

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[a] *Department of Chemistry, University of California, One Shields Avenue, Davis, CA 95616, USA. E-mail: fosterloh@ucdavis.edu; Tel: +1 (530) 754-6242*
[b] *Department of Chemical Engineering & Materials Science, One Shields Avenue, Davis, CA 95616, USA. E-mail: nbrowning@ucdavis.edu; Tel: +1 (530) 754-5358*

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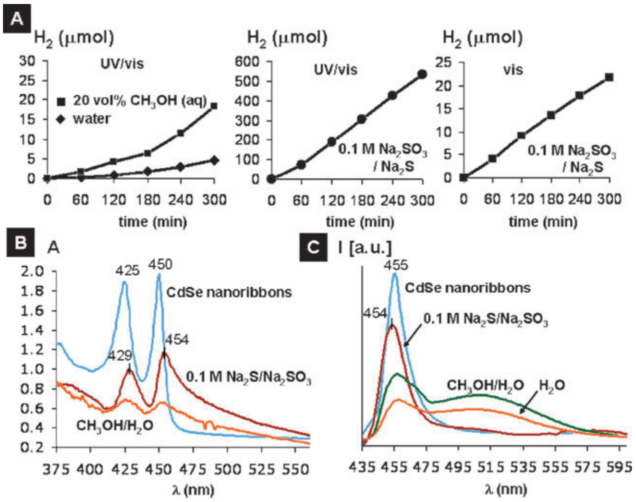

Fig. 2 (A) Hydrogen evolution from 10 mg of CdSe nanoribbons in various media. (B) UV/Vis spectra of CdSe before and after irradiation. (C) Fluorescence spectra of CdSe nanoribbons before and after irradiation.

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.[22] When irradiation of the CdSe nanoribbons is performed in 0.1 M aqueous Na_2S, 0.1 M Na_2SO_3, an increase in hydrogen evolution can be observed. Under these conditions 107 μmol h^{-1} of H_2 are evolved steadily for 5 h, corresponding to an apparent quantum efficiency (QE) of ~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 μmol h^{-1}). Considering the reduced quantum flux of the filtered light (1.80×10^{-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.[17] The bandgap of bulk CdSe is 1.7 eV and reported flatband potentials for it range from −0.6 V (NHE) at pH = 7[24] to −0.2 V (NHE) at pH = 0.[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 order to identify the spectroscopic and photocatalytic events following photoexcitation of the CdSe ribbons, femtosecond transient absorption (TA) signals were measured. The 1 ps transient spectrum (Fig. 3) for the CdSe ribbons can be decomposed into contributions from bleaching of the 1P (425 nm) and 1S (450 nm) exciton bands (Fig. 2B), a photo-induced absorption below 420 nm and at 440 nm, and a broad stimulated gain component extending beyond 700 nm. The latter directly represents the population of trapped electrons responsible for the long-wavelength tail of the photoluminescence spectra (Fig. 2C). Unlike CdSe nanoparticles,[26] the CdSe nanoribbons exhibit deeply trapped electrons, which we believe are responsible for the observed photocatalytic activity.

Contrasting the TA kinetics for CdSe ribbons in water (red curve) and in 0.1 M Na_2S/Na_2SO_3 solution (blue curve) demonstrates that the addition of the hole scavenger leads directly to a relative increase of trapped electrons that are formed almost instantly. As with previous applications of hole scavengers to semiconductor systems, this increase in trapped electrons is ascribed to the inhibition of recombination dynamics caused by the photo-reduction of holes by Na_2S/Na_2SO_3.[18,19,27,28] The enhancement of the lifetime of trapped electron populations (Fig. 3B) with the sacrificial electron donor increases the H_2 evolution rate. The complete wavelength- and time-resolved TA signals are obscured by secondary non-linear dynamics and a full discussion will be presented elsewhere.

In conclusion we have shown that CdSe nanoribbons have photocatalytic activity for hydrogen production from water in the presence of Na_2S/Na_2SO_3 as sacrificial electron donors under UV and visible light. This is the first example of

Table 1 Photochemical hydrogen generation

Experiment	CdSe used/ μmol	Initial/ final pH	Total H_2 produced/μmol	H_2 produced/ μmol h^{-1}	QE (%)[c]	Cd^{2+} (aq) post irradiation/μmol l^{-1}[a]
Pure water	45.92	10.30/9.55	4.62	0.92	0.09	6.7 (0.2)
20% CH_3OH (aq)	50.34	10.37/8.24	18.36	3.67	0.35	3.8 (0.2)
0.10 M Na_2SO_3 : 0.11 M Na_2S(aq)	48.15 (53.61)[b]	13.22/13.30	533.9 (21.8)[b]	106.79 (4.36)[b]	10.19 (13.4)[b]	1.08 (0.03)

[a] 8.2×10^{-2} μmol l^{-1}for non-irradiated sample. K_{SP}(CdSe) = 6.3×10^{-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.[19]

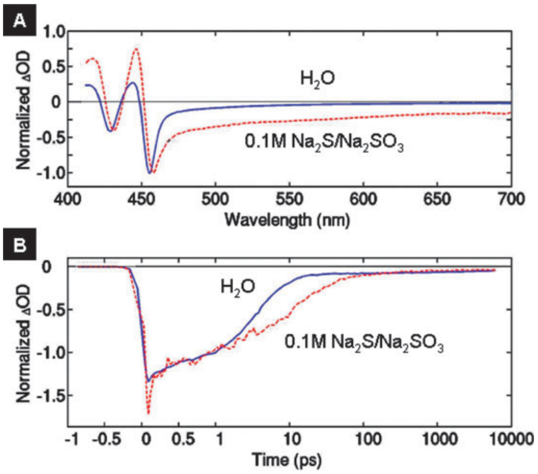

Fig. 3 (A) Normalized transient spectra of CdSe ribbons in water and 0.1 M Na_2S/Na_2SO_3 1 ps following 400 nm excitation. (B) Kinetics probed at peak of 1S exciton bleach of CdSe (455 nm in water, 458 nm in Na_2S/Na_2SO_3), normalized at 1 ps.

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

1 F. E. Osterloh, *Chem. Mater.*, 2008, **20**, 35–54.
2 J. R. Darwent, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 1703–1709.
3 J. R. Darwent and G. Porter, *J. Chem. Soc., Chem. Commun.*, 1981, 145–146.
4 A. Mills and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 3659–3669.
5 N. Buhler, K. Meier and J. F. Reber, *J. Phys. Chem.*, 1984, **88**, 3261–3268.
6 S. Yanagida, T. Azuma and H. Sakurai, *Chem. Lett.*, 1982, 1069–1070.
7 J. F. Reber and K. Meier, *J. Phys. Chem.*, 1984, **88**, 5903–5913.
8 H. Platz and W. Schenk, *Angew. Chem.*, 1936, **49**, 0822–0826.
9 K. Gloor, *Helv. Chim. Acta*, 1937, **20**, 853–877.
10 H. Gerischer and E. Meyer, *Z. Phys. Chem. (N. F.)*, 1971, **74**, 302–18.
11 N. Zheng, X. H. Bu, H. Vu and P. Y. Feng, *Angew. Chem., Int. Ed.*, 2005, **44**, 5299–5303.
12 Z. B. Lei, G. J. Ma, M. Y. Liu, W. S. You, H. J. Yan, G. P. Wu, T. Takata, M. Hara, K. Domen and C. Li, *J. Catal.*, 2006, **237**, 322–329.
13 K. Kobayakawa, A. Teranishi, T. Tsurumaki, Y. Sato and A. Fujishima, *Electrochim. Acta*, 1992, **37**, 465–467.
14 A. Kudo, A. Nagane, I. Tsuji and H. Kato, *Chem. Lett.*, 2002, 882–883.
15 A. Sobczynski, A. Yildiz, A. J. Bard, A. Campion, M. A. Fox, T. Mallouk, S. E. Webber and J. M. White, *J. Phys. Chem.*, 1988, **92**, 2311–2315.
16 Y. Bessekhouad, M. Mohammedi and M. Trari, *Sol. Energ. Mater. Sol. C*, 2002, **73**, 339–350.
17 S. Kambe, M. Fujii, T. Kawai, S. Kawai and F. Nakahara, *Chem. Phys. Lett.*, 1984, **109**, 105–109.
18 E. C. Carroll, O. C. Compton, D. Madsen, D. S. Larsen and F. E. Osterloh, *J. Phys. Chem. C*, 2008, **112**, 2394–2403.
19 O. C. Compton, E. C. Carroll, J. Y. Kim, D. S. Larsen and F. E. Osterloh, *J. Phys. Chem. C*, 2007, **111**, 14589–14592.
20 J. Joo, J. S. Son, S. G. Kwon, J. H. Yu and T. Hyeon, *J. Am. Chem. Soc.*, 2006, **128**, 5632–5633.
21 K. Domen, A. Kudo, M. Shibata, A. Tanaka, K. Maruya and T. Onishi, *J. Chem. Soc., Chem. Commun.*, 1986, 1706–1707.
22 V. Marcu, R. Tenne and I. Rubinstein, *J. Electrochem. Soc.*, 1986, **133**, 1143–1148.
23 H. L. Clever, M. E. Derrick and S. A. Johnson, *J. Phys. Chem. Ref. Data*, 1992, **21**, 941–1004.
24 M. Fujii, T. Kawai and S. Kawai, *Chem. Phys. Lett.*, 1984, **106**, 517–522.
25 A. J. Nozik and R. Memming, *J. Phys. Chem.*, 1996, **100**, 13061–13078.
26 C. Burda and M. A. El-Sayed, *Pure Appl. Chem.*, 2000, **72**, 165–177.
27 Y. Tamaki, A. Furube, M. Murai, K. Hara, R. Katoh and M. Tachiya, *J. Am. Chem. Soc.*, 2006, **128**, 416–417.
28 S. N. Sharma, Z. S. Pillai and P. V. Kamat, *J. Phys. Chem. B*, 2003, **107**, 10088–10093.
29 M. Valden, X. Lai and D. W. Goodman, *Science*, 1998, **281**, 1647–1650.