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Remarkable improvement in visible-light induced hydrogen generation by ZnO/Pt/Cd$_{1-y}$Zn$_y$S heterostructures through substitution of N and F in ZnO

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The performance of ZnO/Pt/Cd$_{1-y}$Zn$_y$S (y= 0.0, 0.2) heterostructures in generating hydrogen on visible light irradiation is substantially improved if ZnO is co-substituted
10 **with N and F, since such anion substitution results in intense visible light absorption and decrease in the band gap.**

Visible-light-induced hydrogen generation using semiconductor nanostructures is assuming considerable importance in the last few years.[1] Metal oxides such as ZnO, TiO$_2$ and SrTiO$_3$ have
15 been used for the generation of hydrogen by ultraviolet irradiation.[2-4] Since 40 % of the solar irradiation is in the visible region, it is important to explore ways of exploiting visible-light-induced generation of hydrogen for purposeful beneficiation of solar energy. Photocatalytic systems such as TiO$_2$-CdS, TiO$_2$-
20 CdS-Pt, Cu(OH)$_2$/TiO$_2$, MoS$_2$-grahene/TiO$_2$, reduced graphene oxide-Zn$_{1-x}$Cd$_x$S, CdS-Graphene-Pt, ZnO/CdS/Pt, Zn$_{1-x}$Cd$_x$S and Cu$_2$MoS$_4$ with a wide range of yields of hydrogen as well as of quantum yields have been reported.[5-18] In this context, the work of Alivisatos and co-workers is noteworthy.[19] These workers
25 have developed a multi-component heterostructure of CdSe/CdS/Pt in which CdS nanorods act as the active catalyst and CdSe and Pt act as hole and electron traps. These nanostructures have shown high activity towards hydrogen production with 40 mmol h^{-1} g^{-1} and an apparent quantum yield
30 of 20% at 450 nm. It has been shown recently that semiconductor nanostructures of the type ZnO/Pt/CdS and ZnO/Pt/Cd$_{0.8}$Zn$_{0.2}$S which are analogous to CdSe/CdS/Pt can be effectively produce high yields of hydrogen with good quantum yields.[20] Since ZnO does not absorb in visible region, we considered it worthwhile to
35 modifying it so as to induce visible absorption by doping N and F in the oxide. Such co-doping is important since doping with N alone creates anion vacancies[21] and doping with F alone has negligible effect on the electronic structure.[22, 23] Co-doping of N and F in ZnO gives rise to intense absorption in the visible
40 region, bringing down the band gap of the oxide. We have used N, F-codoped ZnO for visible-light-induced generation of hydrogen and compared the results with those obtained with undoped ZnO. The results are indeed most encouraging.

In Figure 1, we show a schematic representation of the
45 photocatalytic hydrogen evolution by ZnO$_{1-x}$(N,F)$_x$/Pt/CdS heterostructures. Both CdS and ZnO$_{1-x}$(N,F)$_x$ absorb in the visible region. Upon visible light irradiation, these

semiconductors generate electrons and holes in the conduction and valence bands respectively. The electrons in the conduction
50 band of CdS are transferred either to the conduction band of ZnO$_{1-x}$(N,F)$_x$ and then to the Pt or directly to the nanoparticles of the Pt co-catalyst where the reduction of proton to hydrogen occurs. The holes generated in the valence band are utilized by the Na$_2$S+Na$_2$SO$_3$ or benzyl alcohol used as sacrificial agents.
55 We have prepared ZnO$_{1-x}$(NF)$_x$ by treating the ZnO nanoparticles with NH$_4$F and NH$_3$ at high temperatures following the method described earlier with modifications.[21] The mixture of ZnO (diameter ~ 10 nm) and NH$_4$F was subjected to a two step heating process (100 °C and 600 °C) under a flow of NH$_3$ to
60 obtain N, F co-doping. The product was dispersed in water to deposit Pt followed by dispersion in methanol solution to prepare the heterostructures and configured CdS on nanostructures. (See supporting information). These hybrid nanoheterostructures were characterized by X-ray diffraction, transmission electron
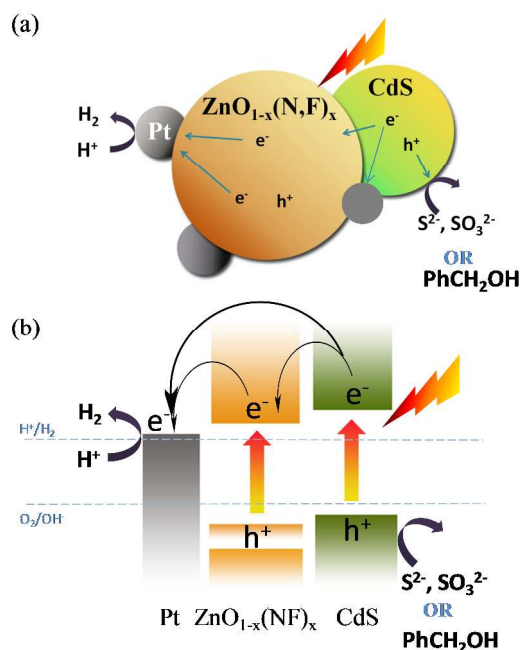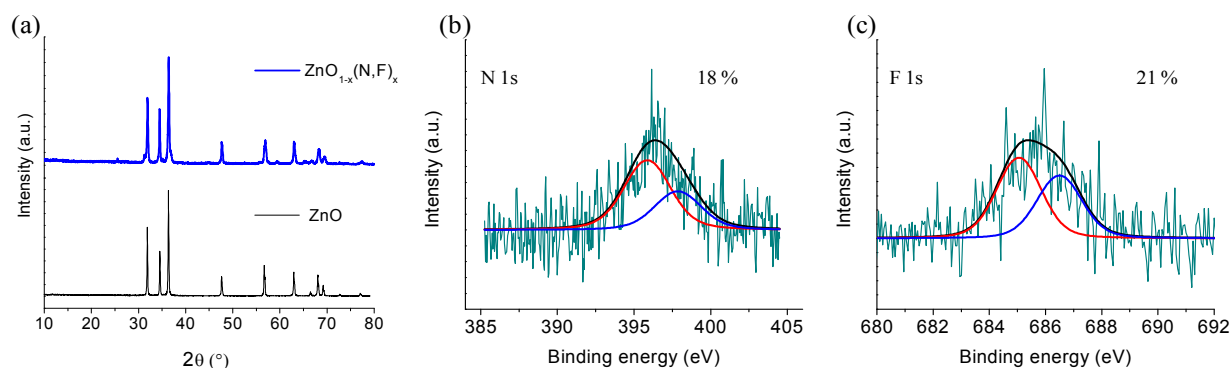
65 (a)

(b)

Figure 1. (a) Schematic representation of photocatalytic hydrogen evolution and (b) energy levels in ZnO$_{1-x}$(NF)$_x$/Pt/CdS heterostructures.

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Figure 2. (a) X-ray diffraction patterns of N, F co-doped ZnO and undoped ZnO. (b) and (c) High-resolution in X-ray photoelectron spectra of N 1s and F 1s peak of $ZnO_{1-x}(N,F)_x$ respectively. (total atomic percents were given with respect to amount of Zn).

microscopy, X-ray photoelectron spectroscopy and UV-visible spectroscopy. We have subjected these hybrid nanostructures for photocatalytic hydrogen evolution studies using $Na_2S + Na_2SO_3$ or benzyl alcohol-acetic acid as the sacrificial agent. A 450 W Xe arc lamp (New Port, 6279 NS, ozone free and working at 400 W) was used for photocatalytic studies (See supporting information).
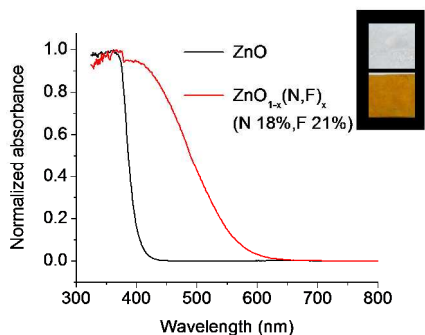
In Figure 2a we show the XRD patterns of ZnO and $ZnO_{1-x}(NF)_x$ to determine that both of them are in the hexagonal wurtzite structure with space group $P6_{3mc}$. N and F co-substituted ZnO sample shows a small decrease in the unit cell parameters.[21] Therein a small evidence for possible presence of very small quantities of impurity phases such as Zn_3N_2 or Zn_2NF. The population of N and F in $ZnO_{1-x}(N,F)_x$ were determined by X-ray photoelectron spectroscopy. The N 1s and F 1s signals are located at 396.3 and 685.7 eV respectively. The atomic percentage of N and F with respect to Zn were found to be 18 and 21 % respectively. The N 1s signal could be deconvoluted into two peaks at 395.8 and 398.0 eV (Figure 2b), assigned to N1s in O-Zn-N (~12 %) and absorbed -NH species (~6 %) respectively.[21] The F 1s signal was deconvoluted into two peaks positioned at 685.1 and 686.5 eV (Figure 2c), assigned to F 1s in O-Zn-F (~12%) and interstitial fluorine (~ 9 %) respectively.[21] Thus the composition of $ZnO_{1-x}(N,F)_x$ prepared by us was found to be $ZnO_{0.8}N_{0.1}F_{0.1}$. The N,F-cosubstituted material has a bright orange color. In Figure 3, we compare the electronic absorption spectrum of $ZnO_{0.8}N_{0.1}F_{0.1}$ with that of undoped ZnO. The absorption edge of the N,F doped sample occurs in the visible

region with a band gap of ~2.4 eV compared to 3.2 eV of undoped ZnO. The optical absorption cross section is likely to be band gap absorption rather than localized energy gap absorption.[24, 25]

TEM images of $ZnO_{0.8}N_{0.1}F_{0.1}$ show that the nanoparticles self-assemble giving rise to sheets of nanoparticles. TEM images of $ZnO_{1-x}(N,F)_x/Pt/CdS$ heterostructures are shown in Figure 4. Figure 4a shows the distribution of CdS nanoparticles and Figure 4b shows the presence of Pt metallic nanoparticles. We have assigned these nanoparticles located on two dimensional surfaces of $ZnO_{1-x}(N,F)_x$ as Pt and CdS nanoparticles based on the lattice fringes in HRTEM images (Figure 4c). The heterostructures competently expose the reaction centers to photocatalytic reaction solution to drive reduction as well as oxidation reactions.
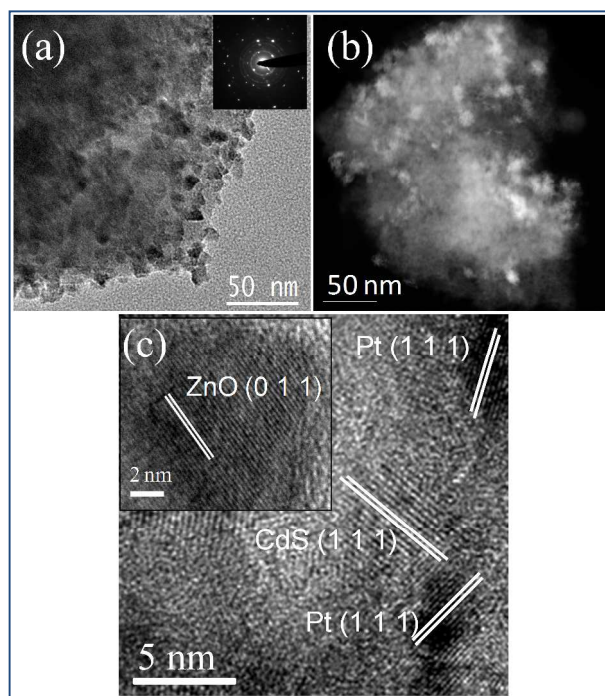
Figure 4. (a) TEM image (b) STEM image and (c) HRTEM image of $ZnO_{1-x}(N,F)_x/Pt/CdS$ nanostructures. (Inset in Figure 4c shows the lattice fringes of $ZnO_{1-x}(N,F)_x$ before depositing Pt and CdS).

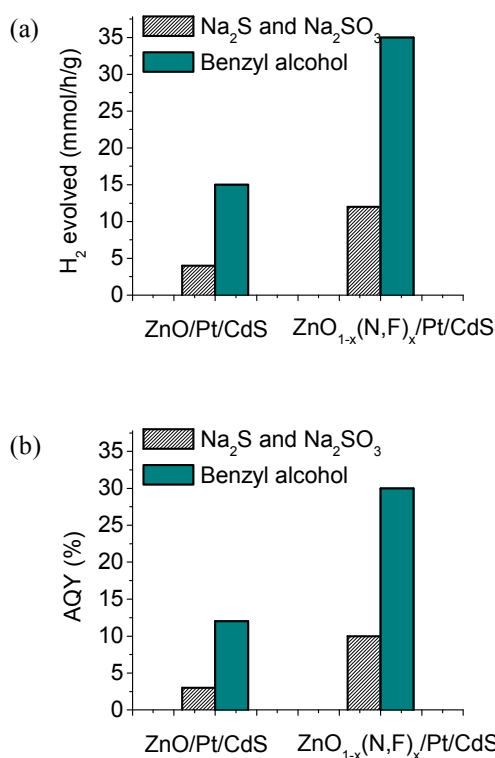
Figure 3. Comparison of UV-Visible absorption spectra of $ZnO_{1-x}(N,F)_x$ nanostructures and ZnO.(Inset shows the comparison of corresponding images).

Figure 5. Comparison of effect of co-doping of N and F in ZnO, on (a) hydrogen evolution and (b) AQY of ZnO/Pt/CdS (25 %) type hybrid nanostructures using Na_2S and Na_2SO_3 or Benzyl alcohol-acetic acid mixture as sacrificial agents under visible light irradiation.

We have observed the visible light induced hydrogen evolution with $ZnO_{1-x}(N,F)_x$/Pt alone although to a small extent. CdS nanoparticles alone exhibited a very weak hydrogen evolution activity. The $ZnO_{1-x}(N,F)_x$/Pt/CdS heterostructures however show good hydrogen evolution under visible light irradiation on employing Na_2S and Na_2SO_3 or benzyl alcohol as sacrificial agents. The best results were found when the CdS loading was 25 % relative to ZnO. Hydrogen evolution was continuous without any degradation of activity with time. In Figure 5 we compare the hydrogen evolution activity and apparent quantum yield obtained with these heterostructures with those containing undoped ZnO. With Na_2S-Na_2SO_3, the heterostructures with $ZnO_{1-x}(N,F)_x$ exhibited a hydrogen evolution of 12 $mmolh^{-1}g^{-1}$ with an AQY of 10 % where as with undoped ZnO the values were 4 $mmolh^{-1}g^{-1}$ and AQY of 3 % respectively (Table S2). These results confirms the synergic effect of $ZnO_{1-x}(N,F)_x$ and CdS in $ZnO_{1-x}(N,F)_x$/Pt/CdS.

Earlier experience, has shown the performance of heterostructures to improve substantially by the use of benzyl alcohol-acetic acid as the sacrificial agents.[20] We have, therefore, carried out experiments with this sacrificial agent. $ZnO_{1-x}(N,F)_x$/Pt/CdS along with benzyl alcohol in acetic acid medium(pH ~2.4), on illumination with visible light, showed hydrogen evolution of 35 $mmolh^{-1}g^{-1}$ with AQY of 30 %. ZnO/Pt/CdS under similar condition showed hydrogen evolution of 15 $mmolh^{-1}g^{-1}$ with AQY of 12% (Figure 5).
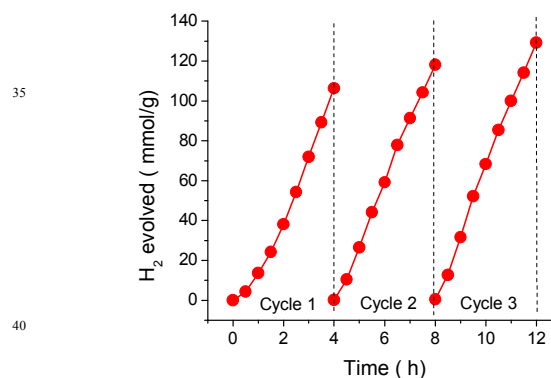
Figure 6. Function of photocatalytic activity with time $ZnO_{1-x}(NF)_x$/Pt/CdS (CdS 25 % with respect to ZnO) type hybrid nanostructures in presence of benzyl alcohol and acetic acid under visible light irradiation.

Figure 6 shows the stability and recyclability of $ZnO_{1-x}(N,F)_x$/Pt/CdS under visible light irradiation in the presence of benzyl alcohol-acetic acid. We have monitored the amount of hydrogen as a function of time. It shows slightly less activity initially and the amount of hydrogen increases linearly after 2h. After 4h, the reaction mixture was evacuated for removing the hydrogen and exposed to normal atmosphere for a few minutes. The resulting sample was subjected to further cycles of the reaction. Hydrogen evolution increased linearly for 4h in each case. The photocatalyst was remarkably stable and its activity was retained even after several reaction cycles.
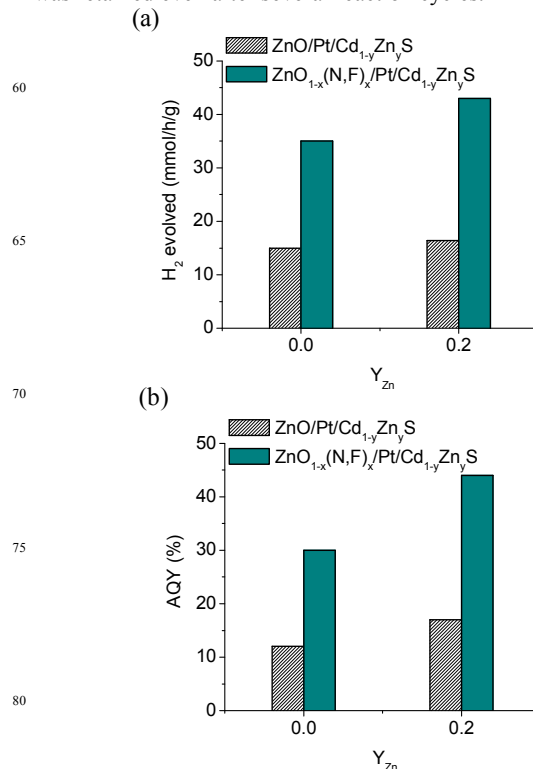
Figure 7. Comparison of (a) photocatalytic hydrogen evolution and (b) AQY of $ZnO_{1-x}(NF)_x$/Pt/$Cd_{1-y}Zn_yS$ and ZnO/Pt/$Cd_{1-y}Zn_yS$ in presence of aqueous solution of benzyl alcohol-acetic acid.

We have investigated the effectiveness of $ZnO_{1-x}(N,F)_x/Pt/CdS$ for the oxidation of benzyl alcohol. For this purpose the reaction mixture was transferred to a 100 mL separating funnel, the organic phase extracted in dichloromethane was subjected to GC-MS and NMR analysis (Figures S1 and S2). GC-MS data showed the presence of benzaldehyde and benzyl alcohol in the organic phase. The conversion of benzyl alcohol to benzaldehyde exactly comparable to the amount of H_2 evolved. Clearly, the photo-generated holes can be fruitfully utilized for the oxidation benzyl alcohol to benzaldehyde.

We have found that using $Cd_{1-y}Zn_yS$ (y=0.2) in place of CdS results in improved hydrogen evolution.[20] In Figure 7, we compare the hydrogen evolution results obtained with $ZnO_{1-x}(N,F)_x/Cd_{1-y}Zn_yS$ (x =0.2) compared those with undoped ZnO. With $Cd_{0.8}Zn_{0.2}S$, we observe a hydrogen evolution rate of 43 $mmolh^{-1}g^{-1}$ with AQY of 44 % under visible light irradiation. Substitution of Zn beyond the y= 0.2, increases the band gap of $Cd_{1-y}Zn_yS$ and reduces the fraction of visible light absorbed. These compositions show lower activities.

Conclusions

In conclusion, N and F co-substituted ZnO absorbs visible light and the $ZnO_{1-x}(N,F)_x$ /Pt/CdS (x= 0.2) heterostructure formed with it exhibits hydrogen evolution at a rate of 35 $mmolh^{-1}g^{-1}$ with an AQY of 30 % under visible light irradiation in the presence of benzyl alcohol-acetic acid as the sacrificial agent. Partial substitution of Zn in CdS further improves the performance of the heterostructure exhibiting a hydrogen evolution rate of 43 $mmolh^{-1}g^{-1}$ and AQY of 44 % under visible irradiation in the presence of benzyl alcohol-acetic acid. In Table S2, we have listed the results obtained by us with the relevant reports in the literature. We clearly see that heterostructures with N, F co-substituted ZnO are most effective in generating hydrogen with high rates and quantum yields. We believe that these results are of considerable significance.

Notes and references

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1. Z. Zou, J. Ye, K. Sayama and H. Arakawa, *Nature*, 2001, **414**, 625-627.
2. C. M. Janet, S. Navaladian, B. Viswanathan, T. K. Varadarajan and R. P. Viswanath, *J. Phys. Chem. C*, 2010, **114**, 2622-2632.
3. J. Yu, L. Qi and M. Jaroniec, *J. Phys. Chem. C*, 2010, **114**, 13118-13125.
4. T. K. Townsend, N. D. Browning and F. E. Osterloh, *Energy Environ. Sci.*, 2012, **5**, 9543-9550.
5. J. Yu and J. Ran, *Energy Environ. Sci.*, 2011, **4**, 1364-1371.
6. J. S. Jang, W. Li, S. H. Oh and J. S. Lee, *Chem. Phys. Lett.*, 2006, **425**, 278-282.
7. H. Park, W. Choi and M. R. Hoffmann, *J. Mater. Chem.*, 2008, **18**, 2379-2385.
8. L. Qi, J. Yu and M. Jaroniec, *Phys. Chem. Chem. Phys.*, 2011, **13**, 8915-8923.
9. J. Zhang, J. Yu, M. Jaroniec and J. R. Gong, *Nano Lett.*, 2012, **12**, 4584-4589.
10. J. Yu, Y. Yu and B. Cheng, *RSC Advances*, 2012, **2**, 11829-11835.
11. Q. Li, B. Guo, J. Yu, J. Ran, B. Zhang, H. Yan and J. R. Gong, *J. Am. Chem. Soc.*, 2011, **133**, 10878-10884.
12. Y. Li, Y. Hu, S. Peng, G. Lu and S. Li, *J. Phys. Chem. C*, 2009, **113**, 9352-9358.
13. C. F. Chi, Y. L. Lee and H. S. Weng, *Nanotechnology*, 2008, **19**, 125704.
14. Q. Li, H. Meng, P. Zhou, Y. Zheng, J. Wang, J. Yu and J. Gong, *ACS Catalysis*, 2013, **3**, 882-889.
15. P. D. Tran, L. H. Wong, J. Barber and J. S. C. Loo, *Energy Environ. Sci.*, 2012, **5**, 5902-5918.
16. P. D. Tran, M. Nguyen, S. S. Pramana, A. Bhattacharjee, S. Y. Chiam, J. Fize, M. J. Field, V. Artero, L. H. Wong, J. Loo and J. Barber, *Energy Environ. Sci.*, 2012, **5**, 8912-8916.
17. Q. Xiang, J. Yu and M. Jaroniec, *J. Am. Chem. Soc.*, 2012, **134**, 6575-6578.
18. Q. Xiang and J. Yu, *J. Phys. Chem. Lett.*, 2013, **4**, 753-759.
19. L. Amirav and A. P. Alivisatos, *J. Phys. Chem. Lett.*, 2010, **1**, 1051-1054.
20. S. R. Lingampalli, U. K. Gautam and C. N. R. Rao, *Energy Environ. Sci.*, 2013, **6**, 3589–3594.
21. R. Saha, R. Revoju, V. I. Hegde, U. V. Waghmare, A. Sundaresan and C. N. R. Rao, *ChemPhysChem*, 2013, **14**, 2672-2677.
22. H. Y. Xu, Y. C. Liu, R. Mu, C. L. Shao, Y. M. Lu, D. Z. Shen and X. W. Fan, *Appl. Phys. Lett.*, 2005, **86**, 123107-123103.
23. R. Gonzalez-Hernandez, A. I. Martinez, C. Falcony, A. A. Lopez, M. I. Pech-Canul and H. M. Hdz-Garcia, *Mater. Lett.*, 2010, **64**, 1493-1495.
24. M. Anpo and M. Takeuchi, *J. Catal.*, 2003, **216**, 505-516.
25. R. Van de Krol and M. Grèatzel, *Photoelectrochemical hydrogen production*, Springer, 2012.