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Mendeleev Commun., 2017, **27**, 310–312

Mendeleev Communications

Photocatalytic activity of CdS nanocrystals doped with Ni and stabilized by polymer shell

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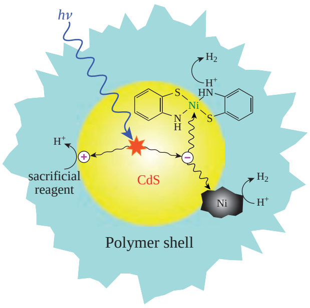
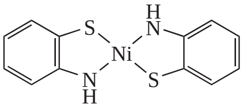
DOI: 10.1016/j.mencom.2017.05.032

Polymer-coated CdS nanocrystals were doped with nickel in different ways: (1) by thermal decomposition of Ni(acac)$_2$, (2) *via* photodeposition from NiCl$_2$ aqueous solution, and (3) using nickel bis(2-aminobenzenethiolate) complex in the polymer shell. The modification of nanocrystals with nickel resulted in threefold increase in the rate of hydrogen evolution in the aqueous Na$_2$S/Na$_2$SO$_3$ solution (pathways 1, 2) and 15- to 400-fold (pathways 3 and 2, respectively) increase in the aqueous solutions containing ascorbic acid.



Photocatalytic water splitting into hydrogen and oxygen using semiconductor photocatalysts is a promising and attractive approach to hydrogen generation and solar energy storage.[1] Earlier,[2] we have shown that CdS nanocrystals (NCs), stabilized with oleic groups and functionalized with an amphiphilic copolymer, can be used as photocatalysts for hydrogen evolution reaction (HER). Being promoted with small amount of Pt as a cocatalyst, they exhibited high specific photocatalytic characteristics.[3] However, Pt is expensive and it is desirable to replace it by another metal. According to publications,[4–7] Ni compounds can be used for this purpose in some cases.

Here we report the photocatalytic activity of polymer-coated NCs with Ni cocatalysts, which were deposited onto nanocrystals using three pathways: (1) in the course of their synthesis by thermal decomposition of nickel(II) acetylacetonate [Ni(acac)$_2$], (2) *via* photodeposition of Ni from NiCl$_2$ aqueous solution, and (3) through incorporating nickel(IV) bis(2-aminobenzenethiolate) complex [Ni(abt)$_2$] into the NCs polymer shell. Complex Ni(abt)$_2$ is known for its cocatalytic activity.[8]



Ni(abt)$_2$

NCs were prepared by thermal decomposition of cadmium(II) oleate in dibenzyl ether in the presence of sulfur and trioctylphosphine. Ni-doped NCs were obtained by the addition of Ni(acac)$_2$ to the reaction mixture after NCs formation followed by heating to 290 °C.[†] As a result, NCs with a different content of Ni were obtained (Table 1).

Table 1 Characteristics of Ni-doped NCs.

Entry	Sample	Concentration of Ni(acac)$_2$ solution (wt%)	Cd content[a] (wt%)	Ni content (wt%)	Diameter d/nm[b]	E_g/ eV[c]
1	CdS#17	0	52.10	0.0000	3.8 ± 1.1	2.63
2	CdS#21	1	41.93	0.0043	3.1 ± 0.6	2.68
3	CdS#22	3	39.78	0.0234	3.2 ± 0.6	2.73
4	CdS#23	9	42.53	0.0748	2.6 ± 0.8	2.69
5	CdS#24	27	45.59	0.2030	3.8 ± 0.8	2.65

[a] Obtained using atomic absorption spectroscopy. [b] Obtained using transmission electron microscopy (TEM). [c] The band gap was deduced from UV-VIS data using the formula:[10] $(\alpha h\nu) = A(h\nu - E_g)^n$, where α is absorption degree, A is the constant value, $n = 0.5$.

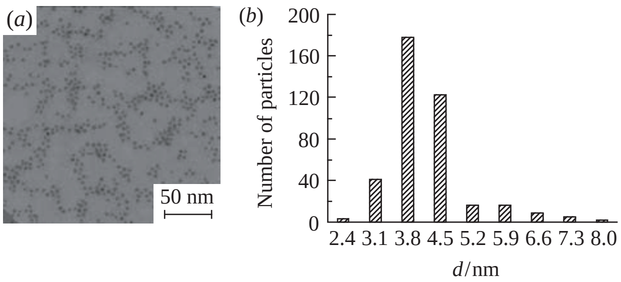


Figure 1 (*a*) TEM image and (*b*) size distribution histogram for CdS NCs (entry 5, Table 1).

[†] In a typical experiment, oleic acid (3.6 mmol), CdO (1.2 mmol), and dibenzyl ether (9 ml) were placed in a flask, degassed by evacuation at 50 °C and heated under nitrogen flow. Trioctylphosphine was loaded by syringe upon reaching the temperature of 240 °C. After heating to 290 °C, the solution of sulfur (0.9 mmol) in dibenzyl ether (1.6 ml) was added. The mixture was stirred for 15 min and then cooled to room temperature. For modification of NCs with nickel, a solution of Ni(acac)$_2$ in dibenzyl ether was added to the reaction mixture cooled to 200 °C. Then the reaction mixture was heated again to 290 °C and cooled to room temperature. NCs were purified by precipitation with ethanol and dispersing in hexane (twice). NCs were isolated from insoluble residue as a transparent dispersion of yellow or yellow-green color *via* centrifugation.

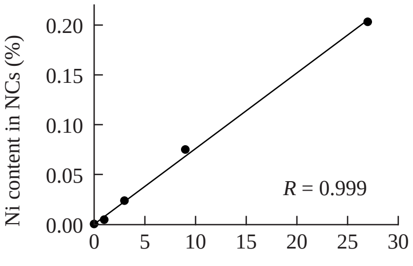


Figure 2 Plot of Ni content in NCs *versus* its relative amount in the reaction mixture.

Typical TEM image is shown in Figure 1. Size distribution and optical band gap of NCs are almost independent of the Ni content, which is practically linear with the amount of $Ni(acac)_2$ used in the reaction (Figure 2).

As follows from the X-ray powder diffraction data (see Online Supplementary Materials, Table S1), NCs consisted of cubic (24–30%) and hexagonal phases; other phases, which are not related to CdS, were not found. Besides, we could not determine the degree of Ni oxidation because of its insignificant content (0.2% or less) in these NCs. From the analysis of synthesis and literature data,[9] one can assume that Ni is present on the NCs surface in the form of NiO nanoclusters consisting of a small number of nickel ions. On the other hand, NiO can be either reduced to metallic Ni[5] or oxidized to Ni_2O_3[6] during photocatalytic reaction.

NCs, which were obtained by decomposition of cadmium(II) oleate, have hydrophobic oleic groups on the surface and, therefore, cannot be dispersed in water or polar solvents. To render them hydrophilic, we covered NCs with amphiphilic copolymer poly[2-(dimethylamino)ethyl metacrylate-co-stearyl metacrylate] quaternized using dimethyl sulfate.[11] As a result, stable water dispersions of polymer-coated NCs[‡] were obtained and used as the photocatalysts for HER.[§]

Modification of NCs with Ni led to 2.5-fold increase in the rate of HER in 0.1 M Na_2S and 0.15 M Na_2SO_3 basic aqueous solutions as sacrificial reagents (Figure 3). In the acidic media (10% aqueous ascorbic acid), this reaction proceeds significantly slower, but it is accompanied with substantial increase in the rate of HER (by a factor of > 400 as compared with that in the basic media). Such increase in the rate of HER can be explained by its relatively low value (3×10^{-3} μmol h^{-1} counted on 1 mg of polymer-coated NCs) in the absence of the above cocatalyst.

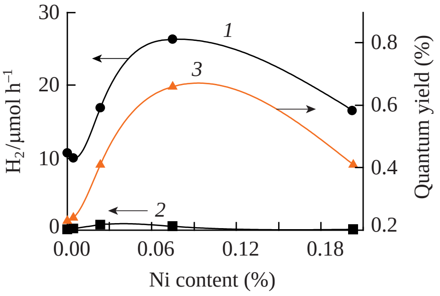


Figure 3 The rate and the quantum yield of HER for NCs promoted with different relative amounts of Ni in (*1*), (*3*) 0.1 M Na_2S and 0.15 M Na_2SO_3 aqueous solution at pH 13, and (*2*) 10% aqueous ascorbic acid at pH 2.

The plots of the HER rate and the quantum yield depending on nickel content for NCs promoted with Ni showed a maximum as in the case of Pt cocatalyst.[3] Maximal rate of 26.2 μmol h^{-1} (TOF = 117 h^{-1}) was found for Ni content of 0.0748% in the basic solutions. The maximal rate of HER in the acidic media was 0.74 μmol h^{-1} (TOF = 3 h^{-1}) for Ni content of 0.0234%.

The addition of $NiCl_2$ to the reaction mixture led to an increase in the photocatalytic activity of the NCs dispersion in the basic solutions. The formation of Ni nanoparticles on the surface of NCs in this case apparently occurs through the electrochemical deposition with photoinduced electrons. This suggestion was confirmed by the shape of HER kinetic curves for NCs, which were obtained with and without $NiCl_2$ (Figure 4). An induction period (typically less than 1 h), attributed to the saturation of the aqueous solution with H_2, was observed in all kinetic experiments. However, in the first run (curve *1*) this period was longer than in the second run after H_2 removing (curve *2*). We believe it is due to the spending of part of the photoinduced electrons for the electrochemical reduction $Ni^{2+} + 2e^- = Ni$. After completion of this process, the rate of HER increases due to the catalytic effect[5] of Ni-containing nanoparticles formed and becomes the same as the rate observed in the second run (curve *2*). The dependence of the rate and the quantum yield of H_2 evolution on the Ni content in NCs (Figure 5) exhibits a maximum of 31.4 μmol h^{-1}

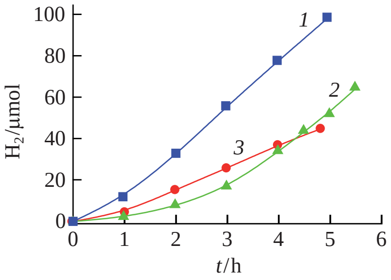


Figure 4 Kinetic curves of H_2 evolution with Ni (2%) promoted NCs (*1*) in the first run, (*2*) in the second run after H_2 removing, and (*3*) with non-promoted NCs, in 0.1 M Na_2S and 0.15 M Na_2SO_3 aqueous solution (pH 13).

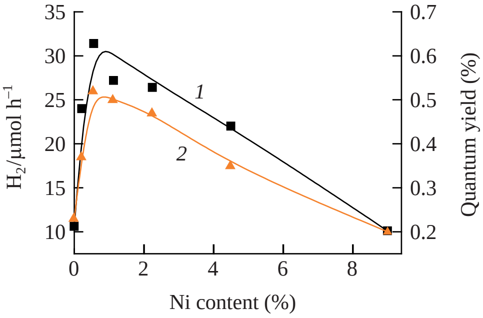


Figure 5 (*1*) The rate and (*2*) quantum yield of HER in the presence of NCs dispersions modified with different relative amounts of $NiCl_2$ in 0.1 M Na_2S and 0.15 M Na_2SO_3 aqueous solution at pH 13.

[‡] *Hydrophilization of NCs.* Dispersion of 1 mg of NCs in 0.5 ml of chloroform was immersed into a solution containing 3 mg of the copolymer in 0.5 ml of chloroform and 50 μl of methanol, followed by the addition of 100 μl of DMSO. The appropriate quantity of $Ni(abt)_2$ solution in DMSO was added, if required. The volatile components were removed *in vacuo*; the residue was then dispersed in the required amount of water and sonicated at 60 °C for 15 min.

[§] The H_2 evolution rate from 10 ml of 0.01% aqueous dispersion of polymer-coated NCs, containing 57% of CdS (3.94 mmol), was determined using illumination of 1.9 W laser (λ = 445 nm). The illuminated photocatalyst portion was equal to 0.057 of the load (*i.e.*, 32.5 μg or 0.225 μmol of CdS). Aqueous 0.1 M Na_2S and 0.15 M Na_2SO_3 mixture (pH 13), aqueous 10% ascorbic acid (pH 2), or the mixture of aqueous 0.5 M ascorbic acid and potassium ascorbate (pH 4.5) were used as a medium for absorption of the 'holes'. The reaction was carried out at 25 °C in 100 ml 3-necked glass reactor with a flat top and bottom, equipped with jacket, magnetic stirrer, septum stopper, and inlet and outlet for argon. The height of the illuminated dispersion layer, diameter of the laser beam, and the density of luminous flux were 20 mm, 6 mm, and 3.40 W cm^{-2}, respectively. Gas samples were taken from time to time using a 50–250 μl syringe equipped with the valve. H_2 content was determined by means of the previously calibrated gas chromatograph.

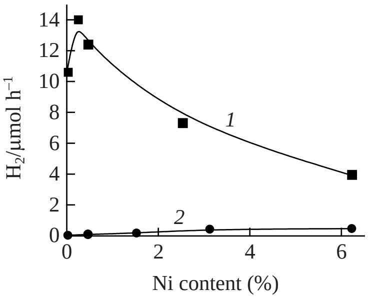


Figure 6 The rate of HER in the presence of NCs modified with different relative amounts of Ni(abt)$_2$ within their polymer shell in various media: (*1*) 0.1 M Na_2S and 0.15 M Na_2SO_3 aqueous solution at pH 13, (*2*) the mixture of 0.5 M aqueous solution of ascorbic acid and potassium ascorbate at pH 4.5.

(TOF = 140 h^{-1}, see Online Supplementary Materials) at 0.25% Ni content (from NCs weight).

Thus, Ni photoelectrochemical deposition from the reaction mixture containing $NiCl_2$ resulted in *ca*. threefold increase in the photocatalytic activity of NCs. It was shown earlier,[8] that complex Ni(abt)$_2$ behaves as an effective cocatalyst of HER for CdSe NCs in 0.5 M aqueous ascorbic acid and potassium ascorbate mixture at pH 4.5 (AK medium). The use of the NCs with polymer shell [poorly water-soluble Ni(abt)$_2$ complex was introduced into the shell at the stage of the shell formation] resulted in more than 15-fold increase in the rate of HER in AK medium (from $\leqslant 0.03$ to 0.43 μmol h^{-1}) at the relative concentration of this complex of 16% (3.1% Ni) (Figure 6).

A further increase in the relative amount of the nickel complex affected this rate only slightly. It should be noted that the above plot is different from that for Ni-promoted NCs with pronounced maximum (Figures 3 and 5). This is an evidence that Ni(abt)$_2$ participates in HER most likely without its decomposition, as a complex rather than a precursor of metallic Ni. In the basic media, after a slight growth in the rate of HER, a decrease by a factor of almost three was observed [relative concentration of Ni(abt)$_2$ of 2.3% (0.44% of Ni) to 32.0% (6.20% of Ni)]. In this case, the lack of catalytic effect of this complex may be explained by the absence of its catalytically active protonated form.[8] Thus, the doping of NCs *via* Ni(abt)$_2$ in the polymer shell (pathway 3) turned out to be the least effective of all tested approaches. Thermal decomposition of Ni(acac)$_2$ (pathway 1) and photodeposition from $NiCl_2$ aqueous solution (pathway 2) demonstrated almost the same results at the optimum Ni concentrations. However, the pathway 2 is technically easier.

The comparison of the rates of HER catalyzed by Ni- and Pt-promoted (21.3 μmol h^{-1})[3] NCs shows that the catalytic activity of the former particles is higher than that of the latter in the basic media. Meantime, the maximal rate of HER observed for Ni-promoted NCs in the acidic media is more than six times lower than that for Pt-promoted NCs (197 μmol h^{-1}) under the same reaction conditions.

The comparative analysis of our and literature data reveals that the coated with polymer Ni-promoted NCs possess relatively high catalytic activity in HER. Indeed, Ni_2O_3 deposited on the surface of 0.1 g of CdS by photodeposition[6] at the relative amount of Ni up to 13.2% increased the rate of HER to 445.6 μmol h^{-1} (TOF = 20 h^{-1}) in 30% methanol as the sacrificial reagent. When hierarchical 3D NiO–CdS binary heteroarchitecture photocatalyst[7] (0.2 g) consisting of nanoparticles and nanoscale fibers has been used in 0.25 M Na_2SO_3 and 0.35 M Na_2S aqueous mixture, this rate became 149 μmol h^{-1} (TOF = 3 h^{-1}), while those for bulk CdS and for CdS nanofibers were 14 and 52 μmol h^{-1}, respectively. The use of another Ni(OH)$_2$/CdS composite photocatalyst[12] prepared by the hydrothermal method provided the rate of HER equal to 5084 μmol h^{-1} g^{-1} (TOF = 23 h^{-1}) under an excitation with visible light (λ = 420 nm) at 23% concentration of Ni(OH)$_2$ in the composite.

In summary, Ni-promoted NCs with the concentration of Ni from 0.0043 to 0.2030 wt% have been obtained by thermal decomposition of Ni(acac)$_2$ in the course of NCs synthesis. Modification of polymer-coated crystals with Ni using thermal decomposition of Ni(acac)$_2$ or photoelectrochemical deposition from $NiCl_2$ aqueous solution enhances the photocatalytic activity. This activity depends on the relative amount of Ni exhibiting a concentration plot with a maximum. In the basic 0.1 M Na_2S and 0.15 M Na_2SO_3 aqueous solutions, threefold increase in the activity is observed. It is almost independent of the method of modification of the NCs. In the 10% ascorbic acid aqueous solution, the modification of NCs with Ni(acac)$_2$ results in more than 400-fold increase in the catalytic activity because of the low peculiar activity of NCs. The use of complex Ni(abt)$_2$ within NCs polymer shell in 0.5 M aqueous ascorbic acid and potassium ascorbate mixture results in more than 15-fold increase in the rate of HER at the relative amount of this nickel complex of 16%. However, the maximal achieved activity of Ni-promoted NCs is more than six times lower than that of Pt-promoted polymer coated CdS NCs.

This work was supported by the Russian Foundation for Basic Research (grant no. 15-29-01112).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2017.05.032.

References

1 M. Yu, W. D. McCulloch, Z. Huang, B. B. Trang, J. Lu, K. Amine and Y. Wu, *J. Mater. Chem. A*, 2016, **4**, 2766.

2 Yu. A. Kabachii, A. S. Golub’, A. S. Goloveshkin, S. S. Abramchuk, A. V. Shapovalov, M. I. Buzin, P. M. Valetskii and S. Yu. Kochev, *Russ. Chem. Bull., Int. Ed.*, 2014, **63**, 2355 (*Izv. Akad. Nauk, Ser. Khim.*, 2014, 2355).

3 Yu. A. Kabachii, S. Yu. Kochev, S. S. Abramchuk and P. M. Valetskii, *Russ. Chem. Bull., Int. Ed.*, 2016, **65**, 414 (*Izv. Akad. Nauk, Ser. Khim.*, 2016, 414).

4 Z. Han, F. Qiu, R. Eisenberg, P. L. Holland and T. D. Krauss, *Science*, 2012, **338**, 1321.

5 J. Yu, Y. Hai and B. Cheng, *J. Phys. Chem. C*, 2011, **115**, 4953.

6 X. Chen, W. Chen, P. Lin, Y. Yang, H. Gao, J. Yuan and W. Shangguan, *Catal. Commun.*, 2013, **36**, 104.

7 Z. Khan, M. Khannam, N. Vinothkumar, M. Deb and M. Qureshi, *J. Mater. Chem.*, 2012, **22**, 12090.

8 A. Das, Z. Han, W. W. Brennessel, P. L. Holland and R. Eisenberg, *ACS Catal.*, 2015, **5**, 1397.

9 Z. Chen, A. Xu, Y. Zhang and N. Gu, *Curr. Appl. Phys.*, 2010, **10**, 967.

10 J. Tauc, *Mater. Res. Bull.*, 1968, **3**, 37.

11 Yu. A. Kabachii, S. Yu. Kochev, N. D. Lenenko, V. I. Zaikovskii, A. S. Golub, M. Yu. Antipin and P. M. Valetskii, *Polym. Sci., Ser. B*, 2013, **55**, 95 (*Vysokomol. Soedin., Ser. B*, 2013, **55**, 243).

12 J. Ran, J. Yu. and M. Jaroniec, *Green Chem.*, 2011, **13**, 2708.

Received: 9th September 2016; Com. 16/5043