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

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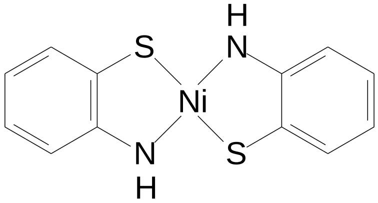
Materials

Oleic acid (**OA**, technical grade, 90%), cadmium oxide (99.5%), trioctylphosphine (**TOP**, 97%), sulfur (reagent grade, powder purified by sublimation, 100 mesh), sodium sulfide hydrate (>60%, scales), dimethyl sulfoxide (99.9%) were purchased from Sigma-Aldrich and used as received. Dibenzyl ether (**DBE**, 99%, Acros Organics), 2-aminothiophenol (98%, Acros Organics), L-ascorbic acid (>99%, Fisher Chemical), $NiCl_2•6H_2O$ (98,5%, reagent grade), sodium sulfite (98%, for analysis), potassium hydroxide (pure), nickel(II)-acetylacetonate (>99%, Merck) and $H_2PtCl_6•6H_2O$ (pure, Pt content 37.98%) were used without further purification.

Synthesis of nickel bis(2-aminobenzenethiolate) ([Ni(abt)$_2$])



$C_{12}H_{10}N_2S_2Ni$

2-Aminothiophenol (500 mg, 4 mmol) and potassium hydroxide (224 mg, 4 mmol) were dissolved in 10 ml of 20% aqueous ethanol. To this solution, a solution of $NiCl_2•6H_2O$ (475 mg, 2 mmol) in 8,3 ml of water and 3,4 ml of 13.3 M aqueous ammonia was added dropwise with stirring. A yellow colored precipitate was formed immediately. The solution was stirred for 30 min, and then the precipitate was collected by filtration. The precipitate was suspended in 30 ml of water containing 400 mg of potassium hydroxide, and the air was blown over the solution for 6 h, resulting in formation of dark blue precipitate. The precipitate was collected by filtration, washed with water, and dried *in vacuo* over P_20_5. The final product was obtained as a deep blue powder after the Soxhlet extraction with diethyl ether.

Characterization

The composition of NCs was determined by atomic absorption spectrophotometer (KVANT–2AT). UV-visible spectra were recorded using a UV-visible spectrophotometer Varian Cary 100 Scan. Transmission electron microscopy studies were carried out on a LEO 912 AB OMEGA instrument (Carl Zeiss) with an accelerating voltage of 100 kV.

X-ray diffraction studies were carried out by means of a D8 Advance Vario diffractometer (Bruker AXS) equipped with a Ge(111) monochromator and a LynxEye position_sensitive detector in the Θ—2Θ transmission geometry using the CuKα_1 radiation and an angular range of 10—120˚ with a step of 0.01˚. The samples were deposited on the Kapton film (DuPont). Diffraction patterns were processed using the TOPAS 4.2 program package.

The hydrogen content was analyzed with a Chrom-5 chromatograph equipped with a column 1 m long packed with molecular sieves 13X 100/120 mesh and a thermal conductivity detector.

Results

Optical properties of NCs

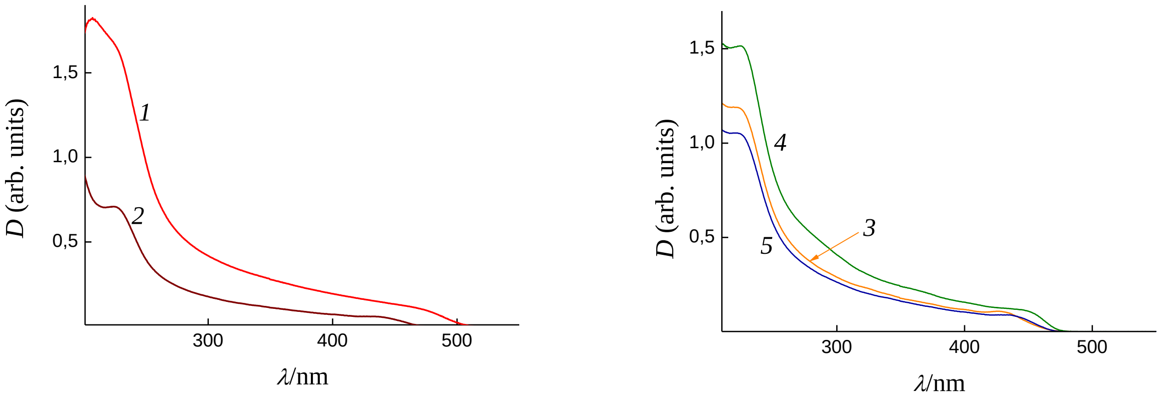


Figure S1 Absorption (*a*) spectra of NCs dispersions for samples CdS#17 (*1*), CdS#21 (*2*), CdS#22 (*3*), CdS#23 (*4*), and CdS#24 (*5*) in *n*-hexane.

Tauc plots of ($\alpha h\nu$) versus ($h\nu$) were used to estimate the optical band gap (Eg) for CdS. The relationship between the absorption coefficient and the incident photon energy of semiconductors are expressed through the following equation:

$$(\alpha h\nu) = A\,(h\nu - Eg)^n$$

Where Eg is the gap between valence band and conduction band, α is the absorption coefficient, A is a constant, and n is 0.5 for CdS. The optical Eg is determined by extrapolation of the straight portion of the plot onto the energy axis. The energy values for various wavelengths were calculated through the formula: $h\nu = 1.2405 \cdot 10^{3} \cdot \lambda^{-1}$.

X-ray diffraction (XRD) study

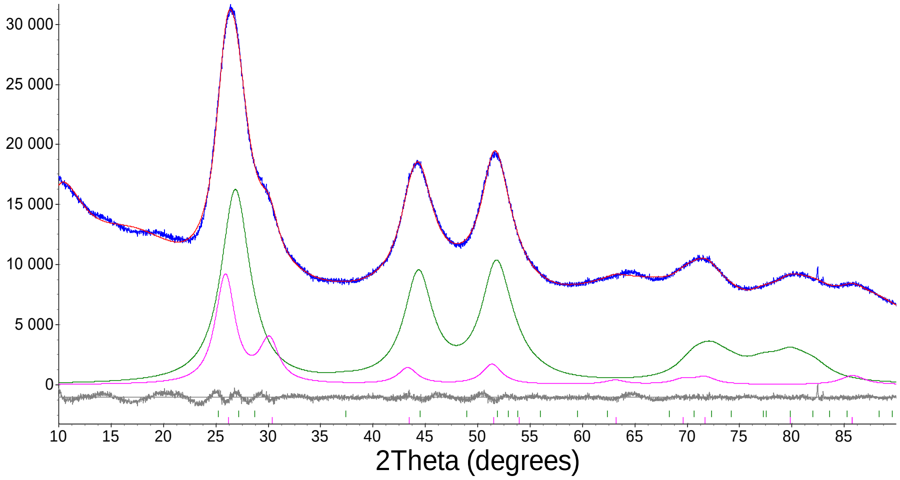


Figure S2 Typical XRD pattern (CdS#21). Blue and red lines correspond to the experimental and estimated plots accordingly. Green and pink lines demonstrate the contributions of hexagonal and cubic phases accordingly.

Table S1 Parameters of CdS phases.

Sample	Cubic			Hexagonal			
	a/Å	D/nm	Content (wt%)	a/Å	c/Å	D/nm	Content (wt%)
CdS#17	5.871(5)	4.3(1)	40	4.065(3)	6.559(7)	3.8(1)	60
CdS#21	5.863(10)	4.4(2)	25	4.067(4)	6.548(10)	2.9(1)	75
CdS#22	5.929(17)	4.2(1)	25	4.072(11)	6.581(19)	3.3(1)	75
CdS#23	5.895(11)	4.5(1)	24	4.067(5)	6.556(14)	3.3(1)	76
CdS#24	5.884(5)	4.4(1)	30	4.070(2)	6.559(5)	3.4(1)	70

The study of photocatalytic activity polymer-coated NCs in H_2 evolution reaction

Apparent quantum yield (*QY*) of H_2 evolution was calculated using the following equation: QY (%) = $2 \times 100 \cdot N_A \cdot V \cdot c \cdot h \cdot \lambda^{-1} \cdot W^{-1}$. Here, N_A is Avogadro constant, V is the rate of H_2 evolution, c is speed of light in vacuum, h is Planck's constant, λ is the wavelength (445 nm) and W is the power of incident light absorbed. When determining the turnover frequency (TOF), it was the fact taken into account that only some NCs particles were irradiated. Those particles placed within the cylinder with the diameter equal to the diameter of the laser beam (6 mm) and the height equal to that of the reaction solution (20 mm). The fraction of the irradiated particles was calculated as a ratio of this cylinder volume (0.57 ml) to the total solution volume (10 ml).

Table S2 Photocatalytic properties of Ni-promoted polymer-coated NCs.

Sample	Medium[a]	Method[b]	Amount of Ni used (wt%)	Ni content[c] •10^2 (wt%)	The rate of H_2 evolution/ µmol•h^{-1}	TOF/ h^{-1}	QY[d] (%)
CdS#17	SS	P	0.10		24.0±0.8	107	0.37
CdS#17	SS	P	0.25		31.4±0.7	140	0.52
CdS#17	AA	P	0.25		<0.1	<1	
CdS#17	SS	P	0.5		27.2±0.2	121	0.50
CdS#21	SS	S	1.0	0.43	9.1±0.3	40	0.24
CdS#21	AA	S	1.0		0.21±0.03	1	
CdS#17	SS	P	1.0		26.4±0.2	117	0.47
CdS#17	AA	P	1.0		<0.1	<1	
CdS#17	SS	P	2.0		21.8±0.7	97	0.35
CdS#17	SS	P	2.0		22.0±0.2	98	0.35
CdS#22	SS	S	3.0	2.34	16.8±0.7	75	0.41
CdS#22	AA	S	3.0		0.74±0.03	3	
CdS#17	SS	P	4.0		10.1±0.2	45	0.20
CdS#23	SS	S	9.0	7.48	26.2±1.0	117	0.66
CdS#23	AA	S	9.0		0.53±0.02	2	
CdS#24	SS	S	27.0	20.3	16.4±1.0	73	0.41
CdS#24	AA	S	27.0		<0.1	<1	
CdS#17	AA		0		<0.1	<1	<0.01
CdS#17[e]	AA		0		0.28±0.06	<1	<0.01
CdS#17	SS		0		10.6±0.1	47	0.23

[a] Dispersion of 0.57 mg photocatalyst in 10 ml of either 10% ascorbic acid (AA) or 0.1 M Na_2S and 0.15 M Na_2SO_3 (SS) aqueous solutions had been exposed onto the laser irradiation (445 nm, 1.9 W, 3.40 W•cm^{-2}) for 5-6 h at 25 °C. [b]Modification methods: S – during the NCs synthesis by $Ni(acac)_2$ decomposition; P – photoelectrochemical deposition from $NiCl_2$. [c] Of the CdS weight. [d]Apparent quantum yield. [e]100 mg of NCs had been taken.

Table S3 Photocatalytic properties of polymer-coated NCs promoted by [Ni(abt)$_2$].

Sample	Medium[a]	Amount of [Ni(abt)$_2$] used[b] (wt%)	Ni content[b] (wt%)	The rate of H_2 evolution/ µmol•h^{-1}	TOF/ h^{-1}
CdS#17	AK	16	3.1	0.43±0.1	2
CdS#17	AK	0	0	≤3•10^{-2}	<1
CdS#17	SS	2.3	0.44	12.4±0.17	55
CdS#17	SS	1.1	0.22	14.0±0.17	62
CdS#17	AK	32	6.2	0.47±0.01	2
CdS#17	AK	2.3	0.44	0.10±0.01	<1
CdS#17	AK	8.0	1.5	0.18±0.01	1
CdS#17	SS	13	2.5	7.30±0.10	32
CdS#17	SS	32	6.2	3.95±0.06	18

[a] Dispersion of 0.57 mg photocatalyst in either 10 ml of 0.5 M ascorbic acid and potassium ascorbate (pH = 4.5) or 0.1 M Na_2S and 0.15 M Na_2SO_3 (SS) aqueous solutions *(*exposed onto the laser irradiation) (445 nm, 1.9 W, 3.40 W•cm^{-2}) for 5-6 h at 25 ºC. [b] Of the CdS weight.