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Synthesis and optical properties of zeolite–semiconductor composites—New photocatalysts

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Abstract

The CdS:zeolite composites were synthesized using original method from thiourea complexes. DRIFT, UV–vis and X-ray studies confirm the formation of both CdS nanoparticles and more bulky agglomerates. The nanocomposites CdS:Hbeta with various nanoparticles sizes were obtained.

Keywords: Zeolite; Cadmium sulfide; Thiourea complex

1. Introduction

Nanotechnology develops stormy last 20 years and finds new areas of application. Nanosized semiconductor particles can be more active in the photocatalysis, than films and microparticles, due to the their small size [1,2]. Herron et al. [3] and Wang and Herron [4] have shown fundamental possibility of synthesis of semiconductor nanoparticles inside of the zeolite pores. For synthesis of composites the authors used ion exchange of the zeolite with cadmium nitrate in aqueous solution followed by H_2S treatment. Even at high concentration no CdS particles on the surface of the zeolite were detected by X-ray photoelectron spectroscopy. That indicates on a formation of particles immediately inside the zeolite pores due to the ion exchange. Later this procedure was extended to the synthesis of others semiconductors in other sodalites [5].

The use of thiourea complexes as precursors seems to be interesting, because at the thermal decomposition of these complexes existing Cd–S bond and its environment is “inherited”. The use of thiourea complexes of different structure allows to control the structure of obtained semiconductor materials. The zeolite matrix is perspective as stable host for the different nanoobjects. These materials are supposed to be promising photocatalysts for hydrogen generation from the water [1].

However, there is need to develop the synthesis procedures, where the particle’s size can be controlled. Therefore, the aim of the present work is to synthesize nanoparticles in zeolitic host from the thiourea complexes adapting a procedure already described for thin solid semiconductor films on the glass and ceramic substrates [6].

2. Experimental

The composites of zeolites (Hbeta (Si/Al = 12.5, Südchemie), NH_4ZSM-5 (Si/Al = 45, AlSi Penta) and HY (Si/Al = 28, Akzo-Nobel)) with CdS nanoparticles have been prepared according to the original methodic from thiourea complexes. For preparation of thiourea complexes we used $CdCl_2{\cdot}2H_2O$ and thiourea (chemically pure). Two modifications of the synthesis were used.

1. Adsorption of chloride thiourea complex of cadmium $[Cd(SC(NH_2)_2)_2Cl_2]$ from aqueous solution on the zeolite followed by thermal decomposition of the adsorbed complex at 220 °C with formation of finely dispersed cadmium sulfides and elimination of gaseous products (Eq. (1)):

$$[Cd(SC(NH_2)_2)_2Cl_2] \xrightarrow{220\,^{\circ}C,\,air} CdS + 2N_2\uparrow + 2HCl\uparrow + H_2S\uparrow + 2CO_2\uparrow + 2H_2O\uparrow \quad (1)$$

The zeolite samples were treated in 0.05 M solution of the complex for 24 h. We studied both the samples with excess

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of complex on the surface and samples without the complex on the surface (thoroughly washed).

2. Synthesis of the thiourea complex inside the zeolite pores. Solid state ion exchange between the zeolite and cadmium chloride (3.4 mass%) were performed at 500 °C in a muffle furnace (Eq. (2)):

$$2\text{Z–OH} + \text{CdCl}_2 \xrightarrow{500\,^\circ\text{C}, 24\,\text{h}} (\text{Z–O})_2\text{Cd} + 2\text{HCl} \uparrow, \qquad (2)$$

where Z–OH is the zeolite framework with bridged OH groups.

Exchanged zeolites were treated by aqueous solution of thiourea $SC(NH_2)_2$ resulting in the formation of the chloride complex of cadmium (Eq. (3)). Then the samples were thoroughly washed and dried at 80 °C.

$$(\text{Z–O})_2\text{Cd} + 2\text{SC}(\text{NH}_2)_2 \xrightarrow[\text{H}_2\text{O}]{} [(\text{Z–O})_2\text{Cd}(\text{SC}(\text{NH}_2)_2)_2] \qquad (3)$$

The thermal decomposition of the thiourea complex at 220 °C led to a formation of CdS nanoparticles inside the zeolite pores and elimination of gaseous products (Eq. (4)).

$$[(\text{Z–O})_2\text{–Cd–}(\text{SC}(\text{NH}_2)_2)_2] \xrightarrow{200\,^\circ\text{C}, \text{air}} 2\text{Z–OH} + \text{CdS} + 2\text{N}_2 \uparrow + 2\text{CO}_2 \uparrow + \text{H}_2\text{S} \uparrow + 2\text{H}_2\text{O} \qquad (4)$$

For the comparing, as reference sample, also CdS composites were synthesized by traditional procedure applying solid state ion exchange between zeolite and cadmium chloride followed by treatment with H_2S [3].

The samples were characterized by DRIFT and UV–vis spectroscopy.

DRIFT-study of the samples was performed with a FTIR-spectrometer (Bruker Equinox 55) under N_2 flow in the range of 700–8000 $\mathrm{cm^{-1}}$ in the temperature interval 50–600 °C with the temperature control by thermoprogrammed regulator HT MC1. The comparison of spectra was made at 500 °C, because at this temperature adsorbed water, which wide IR-bands make some problems at the interpretation, is already removed. All spectra were normalized on the maximal intensity at ~8000 $\mathrm{cm^{-1}}$, where no absorption bands for the zeolite samples are. The spectra in this area are similar and normalization allows making half quantitative comparison. For the calculation of the optical density by the totally light absorption we have used equation [7]:

$$A = -\log R_\infty, \qquad (5)$$

where R_∞ is the reflection coefficient and A is the optical density.

The UV–vis reflectance measurements of the samples were performed on the UV–vis spectrometer Perkin-Elmer 555 with Ulbrecht sphere and Shimadzu PC3100. The absorbance was calculated from reflectance data using assumption about additive dependence of reflectance for a mixture. For interpretation of data we have used dependence $(\alpha h\nu)^2$ versus $h\nu$ plots, which allows to characterize the semiconductor properties [8]. In these coordinates the linear part of curve was extrapolated to $(\alpha h\nu)^2 = 0$, that give a value of band gap E_g.

The measurements of X-ray diffraction were conducted on device DRON (Cu Kα).

3. Results and discussion

3.1. DRIFT properties

Parent zeolites, ion exchanged and nanocomposites with semiconductor were studied by the DRIFT spectroscopy. The spectra of activated Hbeta zeolite is given in Fig. 1 (spectrum 1). The OH stretching vibration region the of bridged Si(OH)Al (3600 $\mathrm{cm^{-1}}$) [9], terminal silanol groups (3740 $\mathrm{cm^{-1}}$) and isolated terminal AlOH groups (3780 $\mathrm{cm^{-1}}$) were observed. The change of intensity for the band of bridged hydroxyl and AlOH groups for the samples admixed with cadmium salt (Cd-Hbeta zeolite) can be explained in term of solid state exchange of the metal ions with the corresponding hydroxyl groups (Fig. 1, spectrum 2). This effect is more detailed described in the forthcoming publication [10].

The adsorption of thiourea on Hbeta or Cd-Hbeta is accompanied by the appearance of intensive bands at 1672 $\mathrm{cm^{-1}}$ and 3217, 3300, 3390, 3487 $\mathrm{cm^{-1}}$ in the DRIFT spectra (Fig. 2). Taking into account that the free metal–thiourea complex decomposes at $T = 220$ °C the presence of the corresponding absorption bands indicates on the stabilizing influence of the zeolite framework, taking into account that the spectra were recorded at 500 °C. During thermal decomposition of complexes synthesized by ion exchange with followed thiourea treatment, a restoration of bridged and isolated terminal OH groups is observed (Fig. 2). This fact allows to suppose that the complex formation takes place inside the zeolite channels. The increase of the intensities of OH groups (bridged, silanol, aluminium) indicates that the coordination sphere of cadmium ions located

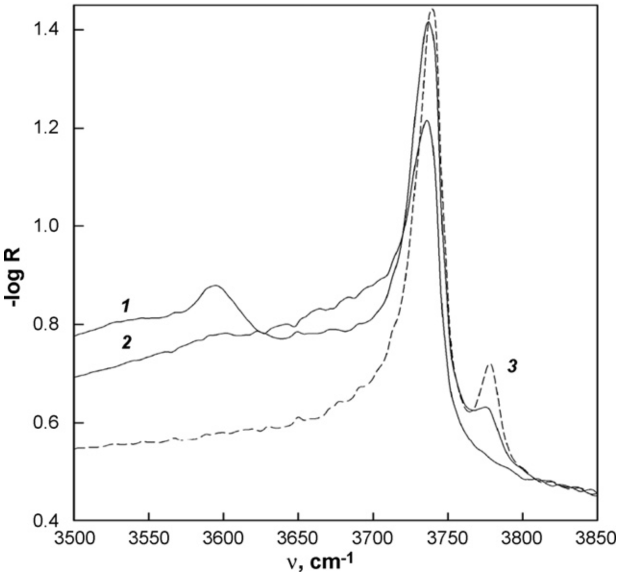

Fig. 1. DRIFT spectra of the zeolites: (1) Hbeta; (2) Cd-Hbeta; (3) calcined Hbeta.

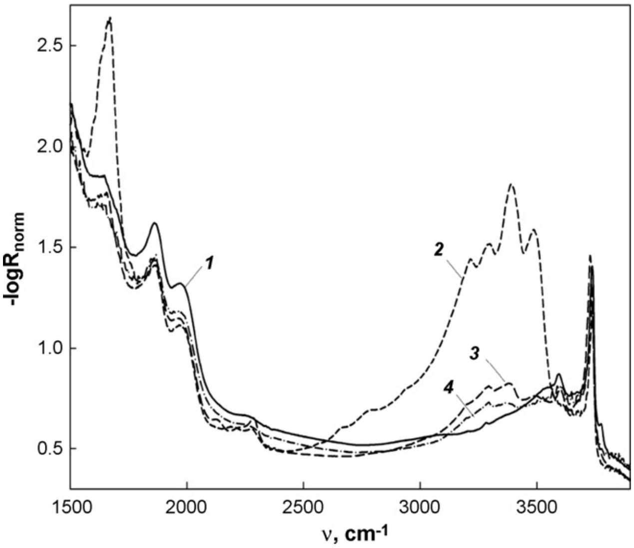

Fig. 2. DRIFT spectra of the zeolites: (1) Hbeta; (2) CdS:Hbeta, synthesized by method 1, not washed; (3) CdS:Hbeta, synthesized by method 1; (4) CdS:Hbeta, synthesized by method 2. Measurements at 500 °C.

on ion exchangeable positions in the zeolitic framework ions was changed, i.e. instead of cadmium ion protons are located again there.

The formation of complex between cadmium and thiourea from the solution is confirmed by a shift of intensive band 738 cm^{-1} for free thiourea to 727 cm^{-1} for the complex [$Cd(TU)_2Cl_2$], which is ascribed to C–S bond [11]. The bands of free thiourea are not observed. After thermal treatment at 220 °C of both adsorbed complex and synthesized inside the zeolite there such a band was not observed. This fact means a destruction of the C–S bond in the complex and a formation of CdS particles.

Taking into account the restoration of both bridged and isolated terminal aluminium OH groups (Fig. 2) after thermal treatment and presence of C–S bond, we can confirm the formation of the complexes inside the zeolite pores and the progress of reaction (3), as well as possible design of cadmium sulfide particles inside the zeolite pores.

3.2. *UV–vis properties of the composites*

The UV–vis reflection (Fig. 3) and absorption (Fig. 3, insertion) spectra show typical shape for the semiconducting materials. The absorption spectra have, besides the strong absorption peaks for bulk CdS structure (450–490 nm or 2.74–2.52 eV), small peaks, which can be assigning to nanoclusters of CdS (Fig. 3, insertion, marked with arrows). The positions of these peaks are about 280 nm (4.4 eV) for the nanocomposites, synthesized by method 1 and using H_2S treatment (Fig. 3, insertion, curves 1 and 3), and 234 nm (5.27 eV) for CdS:Hbeta, synthesized by method 2 (Fig. 3, insertion, curve 2).

The position of the peaks, which assigned to nanoparticles, correlate good with results of R. Ochoa-Landıı̆n et al. [12]. They have shown, that the CdS clusters in zeolite A show an adsorption peak around 290 nm, but no massive aggregates were found. But different position for different samples can indicate the existence of nanoclusters with a different size.

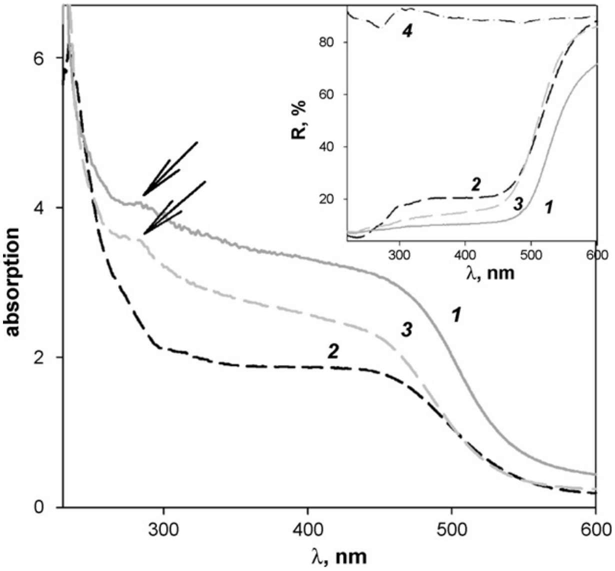

Fig. 3. UV–vis reflectance and absorbance (insertion) spectra for CdS:Hbeta: (1) synthesized by method 1; (2) synthesized by method 2; (3) synthesized by H_2S-treatment; (4) source Hbeta.

From the tight binding approximation for the band gap of small CdS crystallites [13] it was obtained, that CdS crystallites with size about <1 nm can have a band gap of 5.04 eV (absorption threshold at about 250 nm) and the energy of the first excitonic peak is 3.61 eV (absorption threshold at about 343 nm). We suppose, that these particles have semiconducting properties. This fact allows to determine the band gap E_g using the dependence of optical absorption α on the photon energy $h\nu$:

$$\alpha = \frac{k(h\nu - E_g)^{m/2}}{h\nu}, \qquad (6)$$

where k is the constant, and $m = 1$ for direct transitions and $m = 4$ for indirect transitions (for CdS the transition is direct).

In these coordinates the optical data show linear portion of dependence $(\alpha h\nu)^{2/m} = f(h\nu)$ for the transition, which extrapolation to $h\nu = 0$ gives the band gap of material.

For all of the composites we detected two linear parts of this dependence (Fig. 4) and calculated two values for the band gap, which are listed in Table 1. The first value was assigned to band gap of CdS of bulk structure, and the second—to CdS nanoparticles. The band gap values for samples from synthesis 1 are the smallest, because direct adsorption of the complex leads to a formation of big particles. For the samples, where synthesis was inside the zeolite pores, band gaps are always larger. Per-

Table 1
Band gap (E_g) for CdS:Hbeta composites calculated according data of Fig. 4

Sample	E_g for aggregates (eV)	E_g for nanoparticles (eV)
Synthesis 1	2.34	3.08
Synthesis 2	2.38	3.98
Synthesized using H_2S	2.42	3.61

E_g for $CdS_{bulk} = 2.4$ eV.

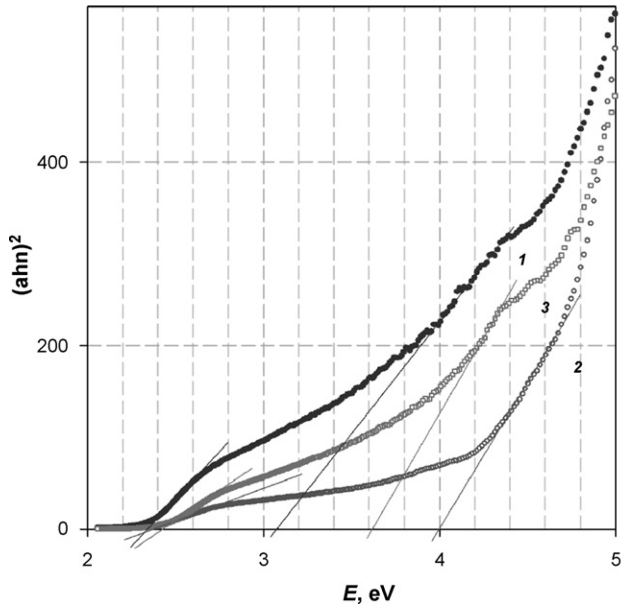

Fig. 4. Dependence $(\alpha h\nu)^2$ versus $h\nu$ for CdS:Hbeta: (1) synthesized by method 1; (2) synthesized by method 2; (3) synthesized by H_2S-treatment.

haps, this correlates with size of particles. This confirms, that the size of zeolite pores determines the size of CdS particles, and the particles, synthesized using adsorption of thiourea complex (synthesis 1) will be always larger then synthesized inside zeolite pores.

3.3. X-ray analysis of the samples

Fig. 5 shows XRD patterns for composites CdS:Hbeta, synthesized by adsorption of cadmium thiourea complex (1), by synthesis of this complex inside the zeolite pores (2) and, as reference sample, synthesized using H_2S. The data show a presence of both hexagonal (five peaks) and cubic structure (two peaks) of CdS in all of samples. The peaks for the composites, synthesized using thiourea complex, are similar. There are several broad peaks between $2\Theta = 40°$ and $55°$, respectively, which corresponds to CdS nanoparticles [14]. The peaks for the sample, synthesized using H_2S-treatment, are different from the peaks of samples, synthesized using thiourea complex: two peaks of hexagonal structure ((1 0 3) and (1 0 1)) practically are not observed.

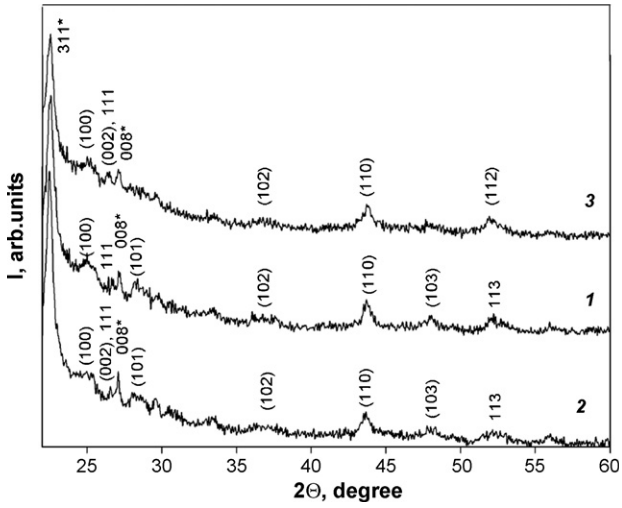

Fig. 5. XRD patterns for composites CdS:Hbeta: (1) synthesis 1; (2) synthesis 2; (3) reference sample, synthesis by H_2S processing; (*) Hbeta peaks; $(h\,k\,l)$ peak of hexagonal structure; $h\,k\,l$ peak of cubic structure.

From full width at half maximum of diffraction peak the average diameter of CdS particles in this direction can be calculated using formula:

$$D = \frac{\lambda}{\beta \cos\Theta}, \tag{7}$$

where λ is the wavelength of X-ray radiation and β is the full width at half maximum of diffraction peak. Calculated data are presented in Table 2 (the minimum values are written bold).

As can be seen, average size of particles is differ in different directions and bigger then zeolite pore size (for Hbeta pore sizes are 5.5 Å × 5.5 Å and 7.6 Å × 6.4 Å). This agrees with our hypothesis, that in the composites mainly big CdS particles are formed, and there is a little part of particles of size, commensurable with size of the zeolite pores. Thus, we have a distribution on CdS particles' size. The diameters differ depending on applied method of synthesis. Summary particles' size is the biggest for composite, which was obtained from synthesis 1 (adsorption of thiourea complex followed by its thermal decomposition).

As was shown by Gratzel [15], quantum size confinement becomes significant especially, when the particle size is smaller then the Bohr exciton radius, which is around 24 Å for CdS. As we can see, there are relative broad diffraction peaks (Fig. 5), and the average diameters (Table 2) do not show massive crystallites. But the results calculated from light absorption data show distinctly (Fig. 3) that big particles take place (more than 24 Å). Taking this into account, we supposed, that the determination of average particle size includes both very small particles ($\leq$1 nm) and big particles, since the peaks for both nano- and microparticles are at the same 2Θ position. We tried to calculate a contribution of both kinds of particles to any of XRD peaks, which are presented in. We used the ratio between intensities for the CdS bulk [14] and synthesized CdS particles. If only one

Table 2
Average diameter of CdS particles in CdS:Hbeta

Sample	$h\,k\,l$ of peak	Structure type	D (nm)
From synthesis 1	(1 0 2)	Hexagonal	**1.63**
	(1 1 0)	Hexagonal	15.47
	(1 0 3)	Hexagonal	12.71
	1 1 3	Cubic	6.43
From synthesis 2	(1 0 2)	Hexagonal	**2.54**
	(1 1 0)	Hexagonal	13.30
	(1 0 3)	Hexagonal	6.52
	1 1 3	Cubic	3.64
Synthesized using H_2S	(1 0 2)	Hexagonal	**2.18**
	(1 1 0)	Hexagonal	13.11
	(1 1 2)	Hexagonal	6.65

Table 3
Ratio between intensities of peaks for CdS:Hbeta composites

I (peak)	Sample			
	Synthesis 1	Synthesis 2	Synthesized using H_2S	CdS powder [14]
(1 0 0)	4.28	4.89	4.99	1.00
(0 0 2)		3.88	4.09	0.72
1 1 1	2.99	3.88	4.09	2.96
(1 0 1)	2.85	3.49	3.05	1.68
(1 0 2)	1.10	1.47	1.33	0.45
(1 1 0)	1.81	2.19	2.12	0.83
(1 0 3)	1.00	1.19	1.00	0.85
1 1 3	1.11	1.00	1.29	1.31

phase is present, the intensities of XRD peaks must be approximately similar. But if two phases are present, some of XRD peaks will be larger than for one phase.

Thus, using this assumption we can estimate a presence of bulky particles. For example, for CdS of bulk structure the ratio of intensities for XRD peaks (1 0 0) and (1 1 0) [14] is approximately 1, for CdS:Hbeta composites (see Table 3)—approximately 2, and for CdS nanoparticles of 5 nm size—within the range 3–5 [16,17]. Hence, by simple calculations we can obtain, that in synthesized CdS:Hbeta composites the quantity of CdS of bulk structure is within the range 50%.

Since the XRD data shown the average particles size only smaller then Bohr exciton radius, and the sizes are differ in different hkl direction, we can suppose, that the CdS particles have elongated form and can fill the zeolite channels. Similar results were reported by Herron et al. [3], who have been obtained CdS superclusters inside zeolites of X, Y and A type with pore size of 5 and 13 Å, which were claimed to be interconnected.

4. Conclusions

Thus, CdS:zeolite composites were synthesized using original method from thiourea complexes. All of used measurements confirm the formation of both CdS nanoparticles and more bulky agglomerates. Varying synthesis conditions nanocomposites with particles of different size can be obtained. Perhaps, CdS particles of elongated form can interconnect and form a three-dimensional network semiconductor structure inside the zeolite channels. This type of composite is expected to be a good photocatalysts due to their nanosize and regular structure [1].

Acknowledgements

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