

OBTAINING OF NANOPARTICLES OF CDS BY PHOTOLYSIS OF $\text{Na}_4[\text{Cd}(\text{S}_2\text{O}_3)_3]$ AQUEOUS SOLUTIONS

K.V. Obmuch

Scientific advisor: PhD, Associate professor N.B. Egorov

Language advisor: Senior teacher N.N. Zyablova

Tomsk Polytechnic University, Russia, Tomsk, Lenin str., 30, 634050

E-mail: kvo@tpu.ru

Abstract

On the basis of X-ray diffraction and chemical analysis data, it was found that cadmium sulfide exhibiting the "size effect" is formed during the UV irradiation of aqueous solutions of cadmium thiosulfate. Sulfate ions and hydrogen ions accumulate in the aqueous solution. It was shown that the yield of cadmium sulfide is affected by the concentration of thiosulfate ions in the solution. The overall equation of photolysis of cadmium thiosulfates is proposed.

Thiosulfates of transition and heavy metals are interesting for their different stereochemistry, catalytic properties and capable to forming metals or metal sulfides during decomposition. The latter property allows the use of compounds of thiosulfate as precursors for the synthesis of nanoparticles of the respective metals or metal sulfides. Currently, the nanoparticles of metals and metal sulfides have a greater interest associated with their optical, catalytic, photocatalytic, electrical and biological properties.

Among ordinary semiconductors, cadmium sulfide (CdS) as a result of nearly perfect single crystal form - one of the most used and studied semiconductors. Under normal conditions, grained CdS is a direct wide band gap semiconductor with a cubic structure. At a temperature of 300 K band gap grained monocrystalline and polycrystalline CdS foil 2.42 eV. CdS nanoparticles are proposed as a material for photoresists phosphors and scintillators.

Irradiation of aqueous solutions of thiosulfates of heavy metals (Pb, Cd, Ag) UV light results in their decomposition with the formation of solid products [1, 2]. Photolysis of aqueous solutions of a complex lead thiosulfate [1] proposed as a photosensitive base for visible direct-darkening photographic image [3] has been most extensively studied. The photolysis of solutions of the complex lead thiosulfate results in the formation of lead sulfide, lead sulfate, and elemental sulfur [4]. In addition, hydrogen ions accumulate in the solution.

In this work, we investigated the possibility of obtaining nanoparticles of cadmium sulfide in the photolysis.

EXPERIMENTAL

Cadmium thiosulfate solutions were obtained by mixing aqueous solutions of sodium thiosulfate and cadmium chloride.

A DRT-350 mercury quartz lamp with unfiltered radiation was used as a source of UV light.

X-ray diffractograms were recorded on a Shimadzu XRD 6000 diffractometer, $\text{CuK}\alpha$ -radiation. In this case, the concentrations of the initial sodium thiosulfate and cadmium chloride solutions were 1 mol/l.

Cadmium sulfide formed during photolysis was separated by centrifugation. The CdS formation procedure was repeated Repeatedly to obtain an amount sufficient for analysis.

The cadmium content in the products was determined by chelatometric titration with disodium ethylenediamine tetraacetate. A mixture of Eriochrome Black with sodium chloride was used as an indicator [5]. For sulfur determination, the photolysis products were treated with aqua regia. In this case, all sulfur present in the precipitate was converted into sulfate sulfur, which was determined by the gravimetric method after the precipitation of sulfate ions with a barium chloride solution [6].

Electronic absorption spectra (EAS) were recorded in a quartz cell with an optical path length of 1 cm on an Uvikon-943 spectrophotometer in the range λ 190–900 nm. The concentration of cadmium thiosulfate solutions in spectral measurements was 10^{-3} mol/l.

The IR spectra of solid photolytic products were recorded with a Nicolet-5700 IR Fourier spectrometer in the range $400\text{--}4000\text{ cm}^{-1}$. The samples were prepared in the form of potassium bromide disks.

The pH value was measured with an EV-74 ion meter using a glass electrode with a silver/silver chloride reference electrode.

RESULTS AND DISCUSSION

During UV irradiation, aqueous cadmium thiosulfate solutions take a brown–green color. Elemental analysis of the precipitate produced by the photolysis showed that the Cd : S ratio in the solid is not constant and depends on a procedure and duration of its washing. Examination of the obtained precipitate by means of IR spectroscopy showed that absorption bands at 1149 , 1004 , and 628 cm^{-1} , characteristic of the thiosulfate ion [7], and absorption bands at 3469 and 1622 cm^{-1} characteristic of water are present in the IR spectrum. Repeated washing with water and water acidified to pH 2 does not result in the removal of thiosulfate ions from the photolysis product (Fig.1, curve 1).

It is impossible to remove impurities from the photolytic precipitate unless the solid is subjected to longterm heating in water or in 0.1 M HCl (Fig.1, curve 2). In this case that, the color of the photolysis product changes from brown–green to bright yellow.

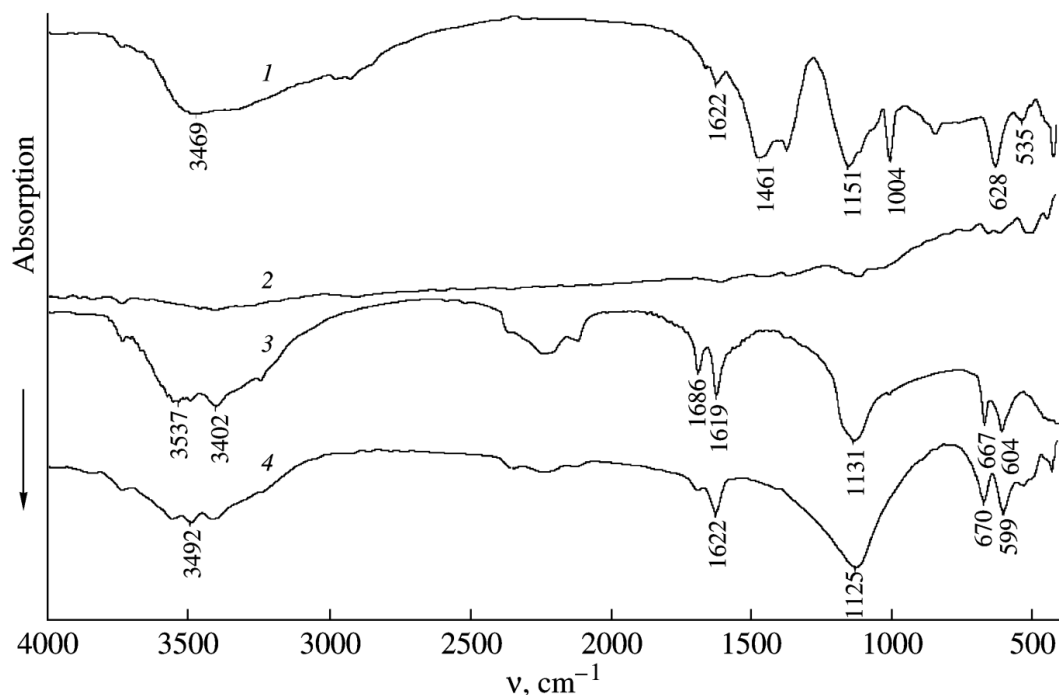


Fig.1. IR spectra of (1) the cadmium thiosulfate photolysis product, (2) the cadmium thiosulfate photolysis product washed by heating in 0.1 M HCl, (3) the precipitate obtained via addition of a CaCl₂ solution to a photolyzed cadmium thiosulfate solution, and (4) calcium sulfate.

As shown in table of X-ray diffraction data, the cadmium thiosulfate photolysis product washed by heating in 0.1 M HCl produces a set of reflections including the basic reflections of CdS.

Chemical analysis of the precipitate cleaned of thiosulfate ions by washing showed that it has a Cd : S molar ratio of 1 : 1. Thus, it should be concluded that the base substance forming the solid product during the photolysis of cadmium thiosulfate aqueous solutions is CdS.

Table 1. XRD data for the product of photolysis washed by heating in 0.1 M HCl.

CdS [8]		Photolysis product	
2θ	I, %	2θ	I, %
26.514	100	26.53	100
30.709	22	30.71	20
43.983	47	43.98	44
52.094	35	52.10	36
54.598	5	54.61	10

Figure 2 presents the differential electronic absorption spectra of CdS formed in the photolysis of cadmium thiosulfate at a concentration of 10⁻³ mol/l. As is apparent from Fig. 2, the maximum of CdS absorption is at 260 nm. The edge of the absorption band in the case of crystalline CdS occurs at 400 nm.

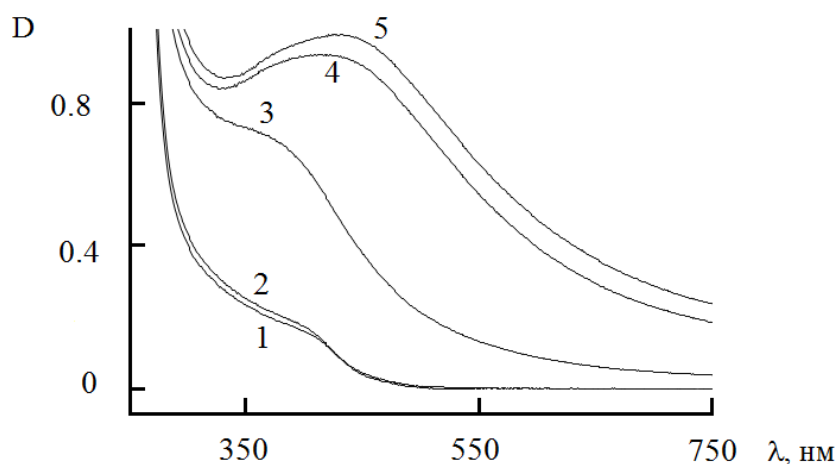


Fig. 2. Electronic absorption spectra of CdS formed during the photolysis of a 10^{-3} mol/l cadmium thiosulfate solution ($\text{Cd}^{2+} : \text{S}_2\text{O}_3^{2-} = 1 : 2$) for (1) 1, (2) 2.5, (3) 5, (4) 7 and (5) 9 min of irradiation.

It is known [9] that a shift of a maximum in an optical spectrum toward shorter wavelength is the “size effect” and manifests the formation in a system of nanoparticles with a higher value of the band gap energy than in the case of corresponding bulk specimens. Thus, it may be concluded that the product of the UV photolysis of aqueous cadmium thiosulfate solutions is CdS nanoparticles exhibiting the size effect.

It is known [10] that the electronic and structural properties of CdS particles change with a decrease in their size and these changes affect their physical and chemical properties. The difficulty of washing thiosulfate ions off CdS formed during photolysis indicates its high capability to adsorb charged ions on the surface. It may be assumed that, being adsorbed on the surface of CdS, thiosulfate ions create a shell around CdS and thereby impede the aggregation of the particles.

According to published data [7], the ν_a vibration mode at $>1175 \text{ cm}^{-1}$ (S bridging), $1175\text{--}1130 \text{ cm}^{-1}$ (S coordinated), $\sim 1130 \text{ cm}^{-1}$ (ionic $\text{S}_2\text{O}_3^{2-}$), $<1130 \text{ cm}^{-1}$ (O coordinated), as well as a shift in the ν_s (SO_3) vibration above 1000 cm^{-1} (S coordinated) and below 1000 cm^{-1} (O coordinated), is most useful in determining the structure of the thiosulfate ion in compounds with heavy metals on the basis of IR data. The band frequencies in the IR spectrum of the cadmium thiosulfate photolysis product (Fig. 1, curve 1) indicate that thiosulfate ions are coordinated to CdS through a sulfur atom, with the thiosulfate ion acting as a monodentate ligand.

As a rule, organic compounds having a long hydrocarbon radical and a terminal functional group in their molecules are admixed to a reaction medium for stabilization of nanosized particles.

PRODUCTS OF PHOTOLYSIS

In the given system, thiosulfate ions simultaneously both act as a source of sulfur for CdS formation and a stabilizer of CdS nanoparticles formed during photolysis.

It is known that, depending on the $\text{S}_2\text{O}_3^{2-}$ concentration in a solution containing Cd^{2+} ions, three thiosulfate compounds CdS_2O_3 , $[\text{Cd}(\text{S}_2\text{O}_3)_2]^{2-}$ and $[\text{Cd}(\text{S}_2\text{O}_3)_3]^{4-}$ can be formed [11]. A study of the dependence of the CdS yield on the $\text{S}_2\text{O}_3^{2-}$ concentration in a photolyzed system showed that the maximum

yield of CdS is observed at a $S_2O_3^{2-} : Cd^{2+}$ ratio of 2 to 3 (Fig. 3). This finding can be explained by a lower stability of $[Cd(S_2O_3)_2]^{2-}$ and $[Cd(S_2O_3)_3]^{4-}$ complexes toward UV irradiation in aqueous solutions, as compared with the photostability of CdS_2O_3 . A further increase in the amount of $S_2O_3^{2-}$ ions that are not included into the inner sphere of coordination complexes in the solution leads to a reduction in the yield of CdS, a change that is apparently caused by absorption of a portion of radiation by $S_2O_3^{2-}$.

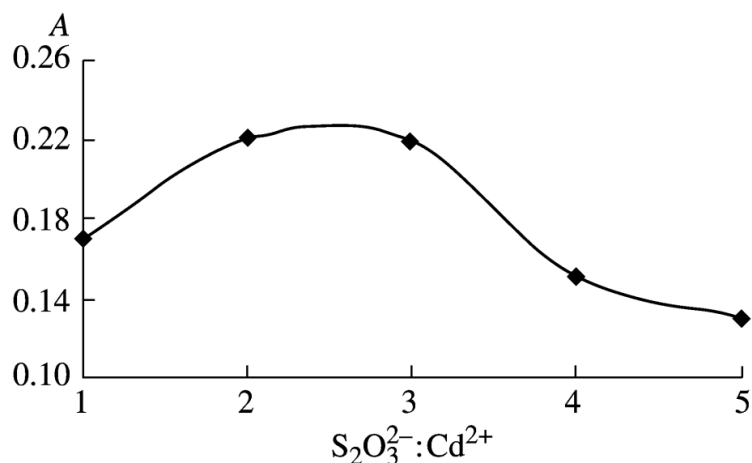


Fig. 3. Dependence of the absorbance at $\lambda = 260$ nm of photolytically produced CdS on the $Cd^{2+} : S_2O_3^{2-}$ molar ratio. The initial cadmium thiosulfate concentration is 10^{-3} mol/l and the irradiation time is 5 min.

Figure 1 (curve 3) shows the IR spectrum of a substance obtained after the addition of a $CaCl_2$ solution to the photolyzed cadmium thiosulfate solution. Preliminarily, CdS was separated by centrifugation. For comparison, Fig. 1 (curve 4) presents the IR spectrum of $CaSO_4$ prepared by adding $CaCl_2$ solution to a solution of Na_2SO_4 . As is seen from Fig. 1, the IR spectrum of the substance obtained from the photolyzed cadmium thiosulfate solution strongly resembles that of $CaSO_4$. This observation allows the conclusion that another product of cadmium thiosulfate photolysis is the sulfate ion SO_4^{2-} .

The initial cadmium thiosulfate solutions have a weak acid or neutral reaction (depending on the concentration of thiosulfate ions). During photolysis, hydrogen ions accumulate in the solutions (Fig. 4).

In [4], we have found that the formation of elemental sulfur (which was extracted by n-hexane from solid products) occurs during UV irradiation of aqueous solutions of a lead thiosulfate complex. Treatment of the solid products of cadmium thiosulfate photolysis with n-hexane did not show the presence of elemental sulfur.

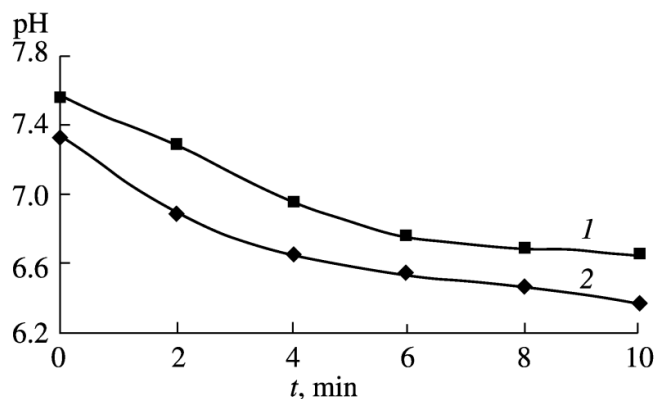
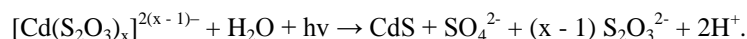


Fig. 4. Change in the pH of photolyzed (1) 0.1 M and (2) 0.01 M cadmium thiosulfate solutions. Molar ratio $\text{Cd}^{2+} : \text{S}_2\text{O}_3^{2-} = 1 : 2$.

Thus, the final products of photolysis of aqueous cadmium thiosulfate solutions are CdS , SO_4^{2-} , and H^+ . The results allow us to propose the following overall equation of cadmium thiosulfate photolysis processes:



On the basis of X-ray diffraction and chemical analysis data, it was found that cadmium sulfide exhibiting the “size effect” is formed during the UV irradiation of aqueous solutions of cadmium thiosulfate. Under certain conditions, is possible to obtain nanosized cadmium sulfide CdS .

REFERENCES

1. Egorov, N.B., Cand. Sci. (Chem.) Dissertation, Tomsk: TSU., 2003.
2. Egorov, N.B., Eremin, L.P., and Larionov, A.M., Abstracts of Papers, IX Mezhdunarodnaya konferentsiya “Fiziko-khimicheskie protsessy v neorganicheskikh materialakh”, (IX Int. Conf. on Physicochemical Processes in Inorganic Materials) Kemerovo, 2004, vol. 1, p. 129.
3. Eremin, L.P., USSR Inventor’s Certificate no. 1182901, Byull. Izobret., 1998, p. 365.
4. Eremin, L.P. and Egorov, N.B., Zh. Nauchn. Prikl. Fotogr., 2003, vol. 48, no. 2, p. 23.
5. Schwarzenbach, G. and Flaschka, H., Die komplexometrische Titration, Stuttgart: Ferdinand Enke, 1965.
6. Busev, A.I. and Simonova, L.N., Analiticheskaya khimiya sery (Analytical Chemistry of Sulfur), Moscow: Nauka, 1975.
7. Freedman, A.N. and Straughan, B.P., Spectrochim. Acta, 1971, vol. 27A, p. 1455.
8. Mirkin, L.I., Spravochnik po rentgenostrukturnomu analizu polikristallov (Handbook of X-ray Analysis of Polycrystals), Moscow: Fizmatgiz, 1961.
9. Gusev, A.I. and Rempel’, A.A., Nanokristallicheskie materialy (Nanocrystalline Materials), Moscow: Fizmatlit, 2000.
10. Gubin, S.P., Kataeva, N.A., and Khomutov, G.B., Izv. Akad. Nauk, Ser. Khim., 2005, no. 4, p. 811.
11. Lur’e, Yu.Yu., Spravochnik po analiticheskoi khimii (Analytical Chemistry Handbook), Moscow: Khimiya, 1979.