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Formation and photocatalytic properties of Q-sized nanoparticles of various transition metal sulphides in the inner cavities of lecithin vesicles modified with sodium dodecylsulphate

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Abstract

Modification of lecithin vesicles by the incorporation of the ionogenic surface-active compound sodium dodecylsulphate into the lipid membrane influences the growth of ultrafine (40 Å or less) semiconductor sulphide particles inside the cavities of the vesicles. Particles of CdS, CuS_x, PbS and ZnS can be synthesized by encapsulating EDTA-metallocomplex precursors in the vesicle cavities and adding sulphide anions to the water phase outside the cavities. The optical spectra of CdS aggregates synthesized by this method differ significantly from those of CdS inside "unmodified" vesicles, and possess two distinct exciton maxima characteristic of cluster-like Q-sized sulphide nanoparticles of approximately 10 Å. The spectral shapes of these aggregates remain unchanged during growth; the sulphide nanoparticles formed exhibit a planar or "crumbly" structure, the particles being bound to both dodecylsulphate and EDTA anions. The concentration of dodecylsulphate in the membrane and the solution pH and temperature strongly affect the initial rate of CdS particle growth. The Q-sized CdS and CuS_x particles in the inner cavities of the lipid vesicles appear to be photocatalytically active in a process of vectorial electron phototransfer through the lipid–water interface to cetylviologen incorporated into the membrane.

Keywords: Q-sized semiconductors; CdS; CuS_x; ZnS; PbS; Lipid vesicles; Vectorial electron transfer

1. Introduction

Recently, we have investigated the controllable growth and photocatalytic properties of ultrasmall transition metal sulphide particles incorporated into the internal cavities of lecithin vesicles [1]. Such semiconductor particles exhibit pronounced photocatalytic activity for vectorial electron phototransfer across the bilayer lipid membrane, and are therefore promising candidates for artificial reaction centres mimicking the reaction centre of natural photosynthesizing organisms.

It is expected that the efficiency of semiconductor nanoparticles for electron phototransfer to molecular electron relays incorporated into the lipid bilayer will increase with tighter bonding of these nanoparticles to the bilayer. In this work, we have investigated the influence of the modification of lecithin vesicles by the ionogenic surface-active compound sodium dodecylsulphate on the properties of the transition metal sulphide particles formed in the cavities of the vesicles. It is shown that modification allows Q-sized cluster-like or "crumbly" planar sulphide aggregates to be produced with a well-pronounced quantum nature observed by UV–visible spectroscopy. Nanoparticles of CdS were investigated, together with other transition metal sulphides which may be expected to exhibit photochemical activity.

2. Experimental details

2.1. Materials

Sodium sulphide (Na_2S) and sodium ethylenediaminetetraacetate (Na_2H_2EDTA) were "pure" grades from Reakhim. Ethanol and toluene were "chemically pure" grades and were used without further purification. Distilled water was used for the preparation of all aqueous solutions. The pH of the outer (with regard to the vesicular cavity) solution was maintained by borate buffer (pH 8.0–9.0) [2]. The compounds used for the preparation of borate buffer were "pure for analysis" and "chemically pure" grades.

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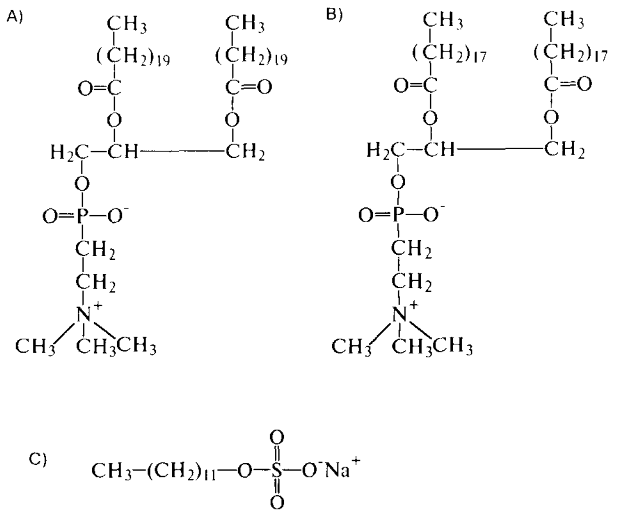

Fig. 1. Structural formulae of DPL (A), DML (B) and NaDS (C).

2.1.1. Metal precursors

Potassium salts of copper and cadmium ethylenediaminetetraacetate (K_2[CdEDTA] and K_2[CuEDTA]) were synthesized in the Laboratory for Catalytic Methods of Solar Energy Conversion (LCMSEC) of the Boreskov Institute of Catalysis [1]. Na_2[ZnEDTA] and Na_2[PbEDTA] were synthesized as described in Refs. [3] and [4]. The composition of the compounds obtained was demonstrated by elemental analysis.

2.1.2. Surface-active compounds

Lipid vesicles were prepared using DL-β,γ-dipalmitoyl-α-lecithin (DPL) and DL-β,γ-dimyristoyl-α-lecithin (DML), both from Fluka AG. Sodium dodecylsulphate ("pure" grade, Reakhim) (NaDS), used for membrane modification, was recrystallized from water before use. *N*,*N*′-Dihexadecyl-4,4′-dipyridinium dibromide (cetylviologen, $C_{16}VBr_2$) was synthesized and purified at LCMSEC as described in Ref. [1]. The structural formulae of the lipids and NaDS are given in Fig. 1.

2.2. Methods

2.2.1. Vesicle preparation

About 20 mg of lecithin, or a dried mixture of lecithin with sodium dodecylsulphate and/or cetylviologen, was dispersed in 1 ml of a 0.3 M aqueous solution of the desired metal precursor. The resulting mixture was treated by ultrasound (22 kHz) for 20 min, centrifuged for 10 min and then passed through a gel filtration column filled with Sephadex G-50 medium. KCl water solution (0.45 M) was used as eluent. The initial form of the suspension of lipid vesicles, containing metal precursor in the inner cavities, was further processed with aqueous sodium sulphide solution.

2.2.2. Optical measurements

The UV–visible optical absorption spectra were registered in single and cyclic regimes and processed by a Specord M400 spectrophotometer (Karl Zeiss Jena, Germany). The temperature measurements were carried out using a thermoregulated two-channel cell holder; during the measurements the solutions were stirred with a magnetic stirrer. The optical measurements during CdS particle growth were carried out at different temperatures in standard 1 cm quartz cells. The point of phase transition ("gel–liquid crystal") for the lipid used was within the temperature interval investigated.

The initial rate of CdS particle growth was determined as the change in the degree of conversion of the particular metal sulphide precursor at the initial time moment. The degree of conversion was calculated as the ratio of the current optical density of the sample (D) to that of the final registered state (D^f) at a certain wavelength. The final registered state was chosen 3000 s after the beginning of the measurements and is related to almost total conversion of the precursor.

Direct measurements of particle size were made by standard small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). For SAXS, the Kα line of Cu was used.

2.2.3. Stationary photolysis

Before the photochemical measurements, oxygen was removed from the samples by passing argon over the surface of the solution for 1 h. During this process, the solutions were stirred with a magnetic stirrer.

A high pressure mercury lamp (DRSh-500; 0.5 kW) was used as irradiation source. Irradiation was carried out directly in the cell compartment of the spectrophotometer (Shimadzu UV-300, Japan). The wavelength of irradiation, $\lambda = 365$ nm, was extracted by standard glass filters (SZS-21 and UFS-2). The change in optical density, caused by the accumulation of cation radicals $C_{16}V^{\cdot +}$, was monitored at $\lambda = 602$ nm ($\epsilon_{C_{16}V^{\cdot +}}{}^{602} = 12\,400$ M^{-1} cm^{-1} [1]). A standard glass filter (OS-11) was used to remove the scattered light with $\lambda \leqslant 600$ nm. In experiments with CuS_x, a continuous argon laser (ILA-120; Karl Zeiss Jena, Germany) with a wavelength of 458 nm was also used. The intensity of the incident light in both cases was measured with a bolometer (LM2; Karl Zeiss Jena, Germany).

The process quantum yield was calculated using the equation

$$\phi = \frac{w_0}{I_{abs}}$$

where w_0 is the initial rate of $C_{16}V^{\cdot +}$ accumulation (molecules s^{-1}) and I_{abs} is the intensity of the absorbed light (quanta s^{-1}). For CdS, $I_{abs} = I_0(1 - 10^{-D_{CdS}{}^{365}})$, where $D_{CdS}{}^{365}$ is the optical density of CdS at $\lambda = 365$ nm and I_0 is the intensity of the incident light.

3. Results and discussion

3.1. Formation of metal sulphide aggregates inside the inner cavities of lipid vesicles

On consecutive addition of the buffer and sodium sulphide solutions to the initial form of the lipid vesicle suspension in

0.45 M KCl, with the transition metal sulphide precursors inside the inner cavities of the vesicles, metal sulphide particles are formed according to the reaction

$$[\mathrm{MEDTA}]^{2-} + \mathrm{H_2S} \longrightarrow \mathrm{MS} + \mathrm{H_2EDTA}^{2-} \qquad (1)$$

where M≡Cd, Cu, Zn, Pb. This process can be readily observed by a change in the UV–visible absorption spectra in the wavelength range characteristic of the metal sulphides under investigation. The spectral shape does not change during particle growth. The same observation was also made in Ref. [1]. The constant shape of the sulphide particle spectrum is not easy to explain because, according to existing theories, the shape and absorption band edge of ultrasmall semiconductor particles should be dependent on the particle size [5–7].

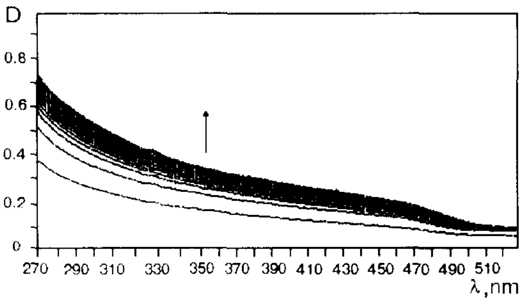

Fig. 2. Changes in the absorption spectrum of a suspension of pure DML vesicles, containing initially 0.3 M K_2[CdEDTA] in the cavities and borate buffer (pH 8.2) in the outer solution, on addition of 0.5 M Na_2S at 20 °C. The spectra were recorded at 150 s intervals.

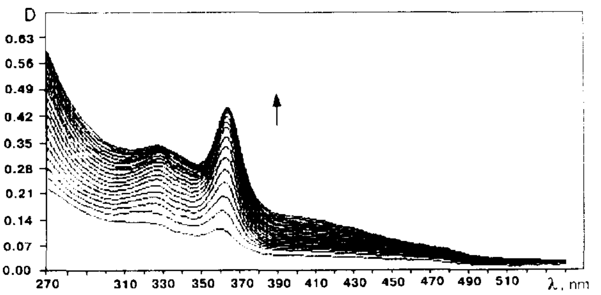

Fig. 3. Changes in the absorption spectrum of a suspension of NaDS-modified DML vesicles, containing initially 0.3 M K_2[CdEDTA] in the cavities and borate buffer (pH 8.2) in the outer solution, on addition of 0.5 M Na_2S at 20 °C; the molar fraction of NaDS in the membrane was 0.2. The spectra were recorded at 150 s intervals.

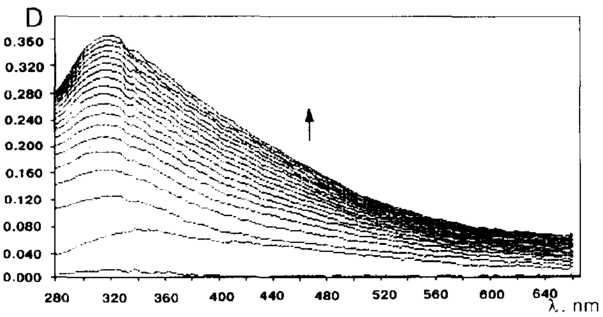

Fig. 4. Changes in the absorption spectrum of a suspension of NaDS-modified DML vesicles, containing initially 0.3 M K_2[CuEDTA] in the cavities, on addition of 0.5 M Na_2S. The other conditions are the same as in Fig. 3.

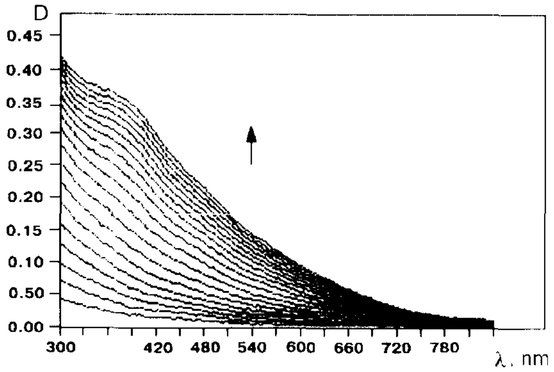

Fig. 5. Changes in the absorption spectrum of a suspension of NaDS-modified DML vesicles, containing initially 0.3 M Na_2[PbEDTA] in the cavities, on addition of 0.5 M Na_2S. The spectra were recorded at 300 s intervals. The other conditions are the same as in Fig. 3.

The most plausible explanation for the constant spectral shape is the formation of a thin lamellar sulphide structure covering the inner vesicle surface (or a set of ultrasmall sulphide-like clusters of constant composition and size), rather than a spherical semiconductor particle inside the vesicular cavity (see also, Ref. [1]). In this situation, both the shape and position of the absorption band edge should depend mainly on the smallest size (thickness) of the semiconductor particles formed, whereas the width of the semiconductor layer and the amount of sulphide clusters will not influence these parameters.

The optical spectral shape of CdS aggregates inside DML vesicles changes significantly on addition of NaDS incorporated into the lipid membrane (see Figs. 2 and 3). Indeed, instead of a non-structured absorption spectrum of a bulk semiconductor, two distinct maxima at $\lambda = 330$ nm and $\lambda = 364$ nm appear in the presence of NaDS. Such maxima are usually attributed to so-called "exciton" absorption of semiconductors and can be observed at room temperature for small semiconductor particles only [8]. For CdS, the reported size of the particles required for the observation of these two maxima was estimated as 10 Å [9]. It is expected that the addition of the ionogenic surfactant NaDS results in a more regular distribution of Cd^{2+} cations along the inner surface of the vesicular membrane. This may occur due to electrostatic adsorption of Cd^{2+} to the negatively charged surface of the modified membrane as a result of Cd^{2+}/Na^{+} cation exchange between $[\mathrm{CdEDTA}]^{2-}$ and NaDS. This "spreading" of Cd^{2+} cations along the membrane is fixed after processing the system with sulphide anions, resulting in the formation of a lamellar- or cluster-like structure composed of 100–1000 Cd cations. It should also be noted that the exciton maxima are observed only in the presence of EDTA anions; this indicates the participation of these anions in the structure of the ultrasmall CdS particles [10].

The optical spectra of CuS_x, PbS and ZnS particles formed in the same manner do not reveal a sensitivity to the presence of NaDS inside the DML membrane (Figs. 4–6).

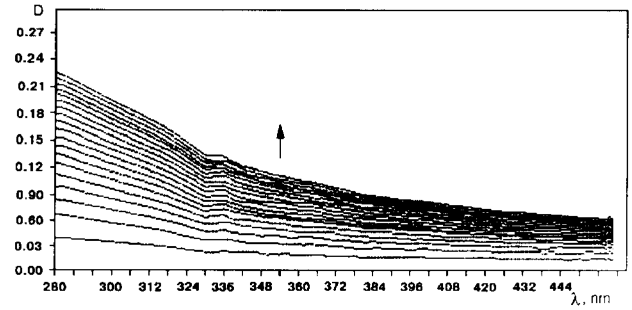

Fig. 6. Changes in the absorption spectrum of a suspension of NaDS-modified DML vesicles, containing initially 0.3 M $Na_2[ZnEDTA]$ in the cavities, on addition of 0.5 M Na_2S. The other conditions are the same as in Fig. 5.

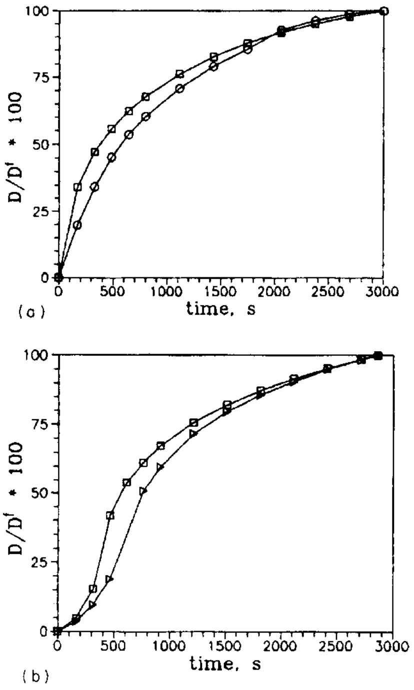

Fig. 7. Kinetics of metal sulphide particle growth inside the DML vesicles containing 0.3 M $K_2[CdEDTA]$ (a) and 0.3 M $K_2[CuEDTA]$ (b) in the cavities at 20 °C. The kinetics were monitored by the change in optical density at 362 nm (CdS) and 315 nm (CuS); the cell length was 10 mm. D^f is the optical density of the final registered state. The molar fraction of NaDS in the membrane was 0.2; pH of the outer solution: □, 8.2; △, 8.5; ○, 8.8.

3.2. Factors affecting the initial rate of metal sulphide particle formation inside the vesicles

In homogeneous solutions, reaction (1) proceeds rapidly. Thus the slower changes in the optical spectra of the vesicular systems during the growth of transition metal sulphides indicate that the rate-limiting stage in these systems is the permeation of sulphide anions through the membrane. The kinetic curves of CdS and CuS growth inside the vesicles at different pH values are given in Figs. 7(a) and 7(b). It can be seen that the rate of transition metal sulphide growth increases with increasing pH. The only sulphide-based particles whose concentration increases with a decrease in the solution pH are the non-charged H_2S molecules. Therefore, as in Ref. [1], we propose that, in NaDS-modified lecithin membranes, water-soluble non-charged H_2S molecules permeate through the lipid membrane leading to the formation of transition metal sulphides.

A kink is observed in the kinetic curves of CuS particle growth inside DML vesicles containing NaDS in the lipid membrane. A possible explanation for this observation is the formation of compounds such as CuS_x (with $x<1$) rather than CuS, resulting from redox processes between initial copper(II) cations and sulphide anions which have a sufficiently strong reducing ability.

The dependence of the initial rate W_o of CdS formation inside the vesicles containing NaDS on the calculated H_2S concentration in the bulk solution is shown in Fig. 8. As shown in Fig. 8, the rectilinear part of the curve at low H_2S concentrations makes it possible to define the H_2S transmembrane penetration rate constant under the following assumptions: (1) the rate of H_2S penetration is proportional to the $[H_2S]$ transmembrane gradient, i.e. to the difference between $[H_2S]$ inside and outside the vesicle cavities; (2) at time zero, the H_2S concentration inside the vesicles is equal to zero:

$$W_o = \left.\frac{dC_{CdS}}{dt}\right|_{t=0} = k[H_2S]_{out}$$

$$k_{CdS} = \frac{W_o}{C_{CdS}{}^f}$$

$$= \left.\frac{d(C_{CdS}/C_{CdS}{}^f)}{dt}\right|_{t=0} = \frac{k}{C_{CdS}{}^f}[H_2S]_{out} = k'[H_2S]_{out}$$

where $C_{CdS}{}^f$ is the final registered concentration of CdS in the solution and k_{CdS} is the pseudomonomolecular rate constant of CdS particle growth with respect to the CdS concentration. The subscript "out" corresponds to the outer (with regard to the vesicular cavity) solution. The effective second-order penetration rate constant k', calculated under these assumptions for DML vesicles with a molar fraction of NaDS of 0.2,

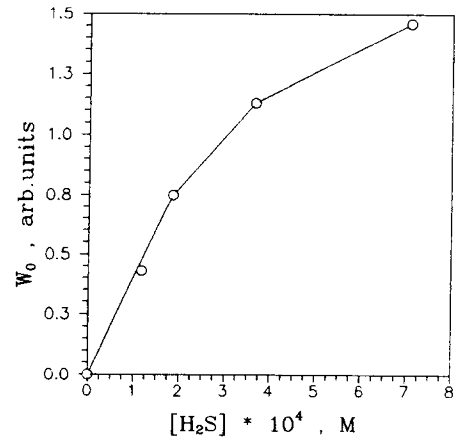

Fig. 8. Dependence of the initial rate W_o of CdS formation in the cavities of DML vesicles on the calculated concentration of non-dissociated H_2S at 20 °C. The molar fraction of NaDS in the membrane was 0.2.

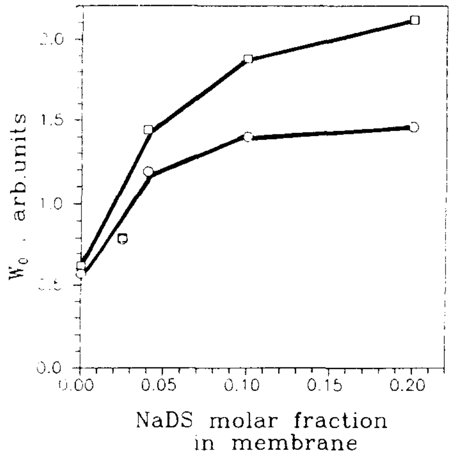

Fig. 9. Dependence of the initial rate W_0 of CdS formation in the cavities of DML vesicles on the NaDS concentration in the membrane at 20 °C. The initial rate was calculated at two different wavelengths: □, 362 nm; ○, 320 nm. The conditions are the same as in Fig. 3.

was found to be approximately 4 M^{-1} s^{-1} at room temperature. This value of k' should be considered as rather high even when it includes direct diffusional collisions of H_2S molecules with the large lipid vesicles as a preliminary step for H_2S transmembrane transfer.

The dependence of the initial rate of H_2S penetration on the concentration of NaDS in the membrane is shown in Fig. 9. As the concentration of NaDS in the DML membrane increases up to a molar fraction of 0.2, the initial rate increases by a factor of four in comparison with DML vesicles without NaDS. This observation can be explained by the existence of a "crumbling" membrane effect generated by the insertion of NaDS into the uniform lipid bilayer: the hydrophobic part of the NaDS molecule contains 12 carbon atoms, while the lipid molecule contains 36 atoms (Fig. 1).

On incorporation of dodecylsulphate anions into the membrane, the inner and outer membrane surfaces become negatively charged. Consequently, there should exist an electrostatic repulsion between the membrane and HS^- and S^{2-} particles. For this reason, the dependence displayed in Fig. 9 can also be regarded as additional proof that the sulphide particles penetrating through the lipid membrane are the non-charged H_2S molecules.

Thus we may conclude that the ionogenic surface-active compound NaDS, incorporated into the lipid membrane, serves a dual function as a "crumbling" and structuring component.

3.3. Direct determination of the CdS particle size

Standard TEM and SAXS methods were used for the direct determination of the CdS particle size. Unfortunately, the TEM measurements did not give satisfactory results, because a higher concentration of transition metal sulphide particles was needed on the TEM substrate surface.

In contrast, according to the SAXS data for the pure DPL vesicles, the average and most probable sizes of the CdS particles were found to be 38.3 Å and 30 Å respectively. This is slightly smaller than the diameter of 41 Å, calculated by assuming that all the cadmium localized in the vesicular cavity participates in the formation of one spherical CdS particle: the local concentration of the initial metal complex inside the vesicle cavities is 0.3 M, the vesicle cavity diameter is 200 Å and the CdS density is approximately 5 g cm^{-3} [1]. For the DML vesicles modified with NaDS, the most probable size of CdS particles (assuming a spherical shape) was determined to be 30 Å for the freshly prepared sample and 45 Å for a 1-day-old sample. Fig. 10 depicts the particle size distribution for the last two samples.

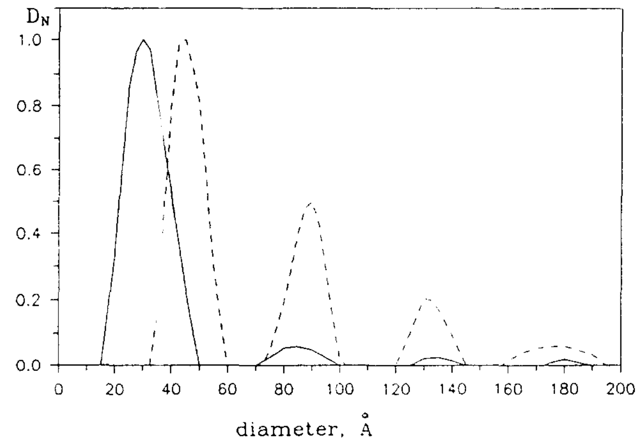

Fig. 10. Distribution of CdS particle size inside the inner cavities of NaDS-modified DML vesicles according to SAXS measurements; the conditions of particle growth are the same as in Fig. 3. The full and broken curves correspond to the freshly prepared sample and the 1-day-old sample respectively.

Unfortunately, no data on the shape of the particles were extracted from the above measurements. Thus, because the CdS aggregates in the NaDS-containing vesicles are expected to be planar, the above sizes should be considered as the largest or effective dimensions.

3.4. Influence of temperature on the initial rate of CdS particle formation and on the shape of the UV–visible absorption spectra

The effect of temperature on the lipid-membrane-supported semiconductor nanoparticle growth is of considerable interest since most of the lipid membranes experience a "gel–liquid crystal" phase transition in the temperature interval 20–50 °C (23 °C for pure synthetic DML [11]).

We have varied the temperature of CdS particle growth inside the NaDS-modified DML vesicles in the range 20–45 °C. The initial rate of particle growth increases with increasing temperature (Fig. 11), the observed increase corresponding to the apparent activation energy (19.5 kJ mol^{-1}) for H_2S transmembrane diffusion.

Unexpectedly, at temperatures above 30 °C in modified DML vesicles, the spectral shape of the synthesized CdS aggregates exhibits a dramatic metamorphosis. The changes

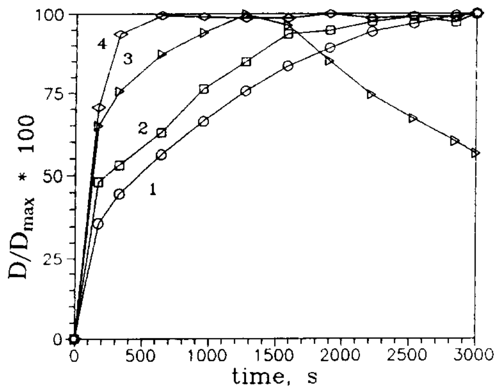

Fig. 11. Ratio D/D_{max} for CdS particle growth inside the DML vesicles, containing initially 0.3 M $K_2[CdEDTA]$ in the cavities, at different growth temperatures. D_{max} is the maximum observed optical density of the sample for each temperature. The change in optical density was monitored at 330 nm; the cell length was 10 mm. Temperature: 1, 20 °C; 2, 25 °C; 3, 30 °C; 4, 45 °C.

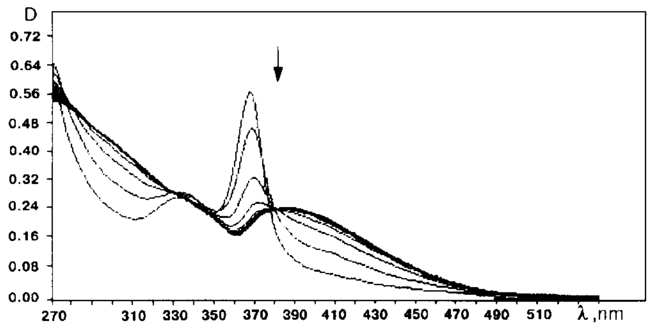

Fig. 12. Changes in the absorption spectrum of a suspension of NaDS-modified DML vesicles, containing initially 0.3 M $K_2[CdEDTA]$ in the cavities, on addition of 0.5 M Na_2S at 45 °C. The other conditions of particle growth are the same as in Fig. 3.

observed in the optical absorption spectrum of the CdS aggregates during particle growth inside the modified DML vesicles at 45 °C are shown in Fig. 12. We can see that, under these conditions, at time zero, the spectral shape is similar to that observed at room temperature (see Fig. 3); however, the final spectrum is not typical of a semiconductor CdS particle and resembles that of a metallocomplex with Cd^{2+} cations. It is interesting to note that the transformation of the semiconductor CdS aggregates (after growth) into the new type of structure is accompanied by the existence of two isobestic points (at approximately 328 and 381 nm, see Fig. 12). We can assume that this indicates a transition from one well-defined structure to another. The explanation of this observation is the object of future investigations.

3.5. *Photophysical and photocatalytic properties of the synthesized Q-sized CdS and CuS_x aggregates*

A preliminary study of the photophysical and photocatalytic properties of Q-sized CdS and CuS_x particles incorporated into the inner cavities of DML vesicles was performed.

3.5.1. *CdS aggregates*

No detectable luminescence of the synthesized CdS particles was observed for the systems synthesized at room temperature. A possible explanation could be the efficient quenching of the luminescence by residual sulphide anions, electron-donating nitrogen-containing groups of the neighbouring phospholipid molecules, etc.

3.5.1.1. *Photostimulated electron transfer across the "vesicular cavity–membrane" border*

To carry out interfacial electron transfer across the lipid membrane, sensitized by the CdS nanoparticles, a photochemical system with cetylviologen ($C_{16}VBr_2$) as the lipophilic electron carrier was prepared. A schematic view of such a system is shown in Fig. 13. Cetylviologen is the most typical representative of a large class of lipophilic reversible molecular electron carriers (relays), which are widely used for the creation of photochemical systems based on lipid vesicles [1,12].

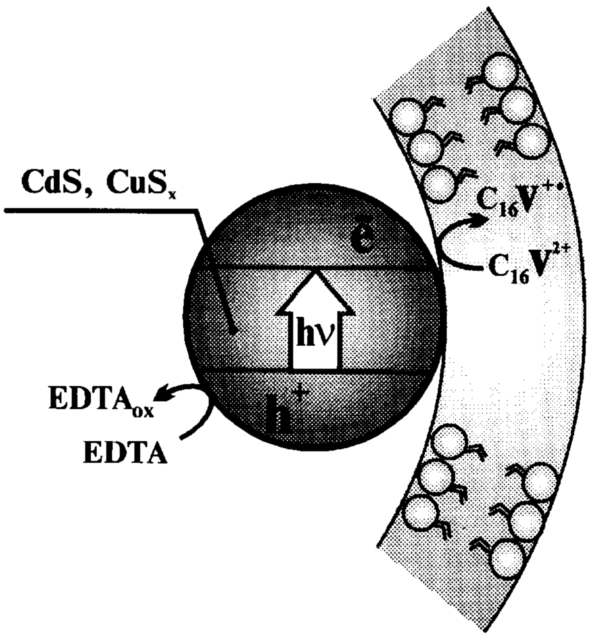

Fig. 13. Schematic view of photostimulated interfacial electron transfer across the "vesicular cavity–membrane" border. $EDTA_{ox}$ denotes the products of EDTA anion oxidation.

The samples for photochemical measurements were prepared in the following manner. Before sonification, dry lecithin was dissolved in an ethanol–toluene (2.3 : 1) solution of cetylviologen with subsequent removal of the solute by evaporation in vacuo by heating at approximately 50 °C. Further details are given in Section 2.2.1. Preliminary experiments have shown that the amounts of S^{2-} and H_2EDTA^{2-} released as a result of CdS particle formation, which function as sacrificial electron donors, are insufficient for photoelectron transfer with a noticeable quantum yield. Therfore, together with the metal complex, an additional electron donor was placed inside the vesicle cavity: Na_2H_2EDTA or cysteine with a local concentration of 10^{-2} M.

On irradiation of the deoxygenated vesicle suspension, containing CdS and Na_2H_2EDTA in the inner cavities and $C_{16}V^{2+}$ in the lipid membrane, by a continuous light source ($\lambda = 365$ nm), the accumulation of cation radicals of cetylviologen in the membrane was observed. This process was registered by a change in the optical density at the cation radical absorption maximum ($\lambda = 602$ nm) and can be schematically represented as

$$\mathrm{EDTA} + C_{16}V^{2+} \xrightarrow{\mathrm{CdS},\ h\nu} \mathrm{EDTA_{ox}} + C_{16}V^{\cdot +}$$

For the molecular ratio $C_{16}V^{2+}$ to lipid of 1 : 100, the value of the quantum yield was found to be approximately 1%. This value is typical for the systems under investigation (see Ref. [1]).

An attempt was made to create a photochemical system based on vesicles, containing sodium dodecylsulphate and cetylviologen in the membrane at the same time. However, during sonification, the formation of a water-insoluble compound was observed as a result of the interaction between dodecylsulphate anion and cetylviologen bication. After removal of this residue, the samples for photochemical measurements were prepared in the usual manner. The quantum yield in this system was found to be 0.18%. Because of the small concentration of $C_{16}V^{2+}$ and the absence of NaDS in the membrane (due to leakage as the non- soluble residue), this value is not representative of such systems.

3.5.2. CuS_x aggregates

It is well known that suspensions of CuS_x do not exhibit photocatalytic activity in the light-stimulated production of dihydrogen from sulphide-containing aqueous solutions [13]. Consequently, we expect a low photochemical activity of CuS_x nanoparticles in the reduction of $C_{16}V^{2+}$ due to the negative redox potential of the pair $C_{16}V^{2+}/C_{16}V^{\cdot +}$, which is close to that needed for the evolution of dihydrogen from water.

However, in the $C_{16}V^{2+}$-modified vesicular system, the presence of CuS_x leads to the efficient reduction of $C_{16}V^{2+}$ even during the growth of CuS_x. The method of preparation of the samples for the photochemical measurements was similar to that for CdS.

During deoxygenation, i.e. during the passage of Ar over the surface of the sample for 1 h with vigorous stirring, the sample changes to a blue colour due to the accumulation of $C_{16}V^{\cdot +}$ even in the dark. In our opinion, this dark process can be attributed to the oxidation of S^{2-} anions by $C_{16}V^{2+}$, catalysed by Cu^{2+}/Cu^{+} cations (or by CuS_x itself), which can take place on the "vesicular cavity–membrane" border. Indeed, the sulphide and bisulphide anions can behave as strong two-electron reducing agents [13]

$$2S^{2-} - 2e \longrightarrow 2S_2^{2-} \qquad E_{S_2^{2-}/S^{2-}} = -0.524 \text{ V vs. NHE}$$

$$S_2^{2-} - 2e \longrightarrow S \qquad E_{S/S_2^{2-}} = -0.476 \text{ V vs. NHE}$$

and thus can serve as reductants for the one-electron acceptor $C_{16}V^{2+}$ embedded into the membrane (in the lipid membrane $E_{C_{16}V^{2+}}{}^0 = -0.20$ V vs. normal hydrogen electrode (NHE) [14]). We should note that, in the case of CdS nanoparticles, this dark process was not observed during particle growth inside the vesicle cavities; during CdS particle growth outside the vesicles, a very small amount of $C_{16}V^{\cdot +}$ was detected. This is because the Cd^{2+} cations are much less active in "one-/two- electron" redox processes in comparison with Cu^{2+} cations.

The $C_{16}V^{\cdot +}$ formed can be further oxidized by O_2 from the air. After the removal of O_2 by Ar, the accumulation of $C_{16}V^{\cdot +}$ occurs only if residual sulphide anions remain in the system.

To confirm the above suggestion, additional pretreatment of the sample for photochemical measurements was performed. Before the measurements, pure dioxygen was passed for a certain period of time over the surface of the synthesized sample with vigorous stirring at ambient temperature in order to remove residual sulphide anions by oxidation. The sample consisted of a vesicle suspension with a $C_{16}V^{2+}$-modified membrane and CuS_x in the inner cavities. It should be noted that O_2 molecules penetrate easily through the lipid membrane.

It was found that after the replacement of dioxygen by Ar, following more than 2–10 min of dioxygen pretreatment, the formation of $C_{16}V^{\cdot +}$ in the membrane does not occur, confirming the "dark" catalytic nature of the reduction of $C_{16}V^{2+}$. The samples obtained showed a remarkable photochemical activity on irradiation by a continuous laser source (458 nm), although the quantum yield of $C_{16}V^{\cdot +}$ formation was much smaller than for CdS, being of the order of 0.04% after 2 min of pretreatment.

Thus the more sophisticated (compared with CdS) methods of preparation of the CuS_x-based vesicular systems allow the generation of photochemically active systems of the type shown in Fig. 13 with remarkable quantum yields of CuS_x-assisted vectorial electron transfer through the "water–lipid" interface. The influence of the modification of the lipid bilayers with NaDS on the photochemical properties of the CuS_x system seems to be the same as in the CdS-based system.

4. Factors controlling the size of the CdS nanoparticles

An extremely interesting problem is the constant shape of the absorption spectra of the transition metal sulphide aggregates during growth inside the cavities (spectra typical of Q-sized semiconductors) (see Fig. 3). This constant shape should indicate a constant sulphide nanoparticle size during total mass accumulation, which is not expected for a spherical shape or free growth. For this reason, the two most plausible explanations are a constant spectrum-defining size of the growing nanoparticles or the existence of factors preventing the creation of nanoparticles with a wide distribution of sizes.

The first situation corresponds to a planar-like lamellar structure of transition metal sulphides synthesized inside the vesicular cavities; the spectrum-defining parameter in this case would be the thickness of the lamellar aggregate, which remains constant during the growth of the lamellar structure along the lipid bilayer.

The second situation corresponds to the behaviour of transition metal sulphide nanoparticles inside the vesicular cavities as labile colloidal particles affecting both the lipophilic equilibrium and interactions with strong chelating agents such as EDTA anions.

It is well known that, in bulk liophilic systems, a spontaneous dispersion of macrophase should occur, the size d of the thermodynamically stable colloidal particles being expressed via a Rebinder–Shchukin condition [15]

$$d \leqslant \beta \sqrt{\frac{kT}{\sigma}}$$

where β is a quasiconstant dimensionless parameter (equal to approximately 3–6), σ is the surface tension of the colloid–bulk solution interface and k and T are the Boltzmann constant and the temperature respectively. Thus if the Rebinder–Shchukin restriction takes place for the sulphide nanoparticles in the vesicular cavities, there are well-defined thermodynamic restrictions which do not allow the appearance of sulphide particles with a size greater than that following from the particular value of the parameter σ. At certain values of σ, this situation is equivalent to that of the growth of "crumbly" sulphide aggregates.

It is also well known [16] that very small CdS particles have a much higher solubility than bulk CdS, since the solubility product (SP) for CdS depends on the nanoparticle diameter d as

$$\mathrm{SP} = \mathrm{SP}_\infty \exp\left(- \frac{4\sigma V_{\mathrm{CdS}}}{dRT} \right)$$

where SP_∞ is the solubility product of bulk CdS, V_{CdS} is the molar volume of CdS and R is the universal gas constant [15]. For this reason, very small CdS particles (in Ref. [16] with d less than 25 Å) can undergo dissolution by EDTA anions to form a stable complex CdEDTA^{2-}. It should be noted that EDTA anions are present in the vesicular cavities since CdEDTA^{2-} was used as the precursor of CdS. Dissolution should occur when the concentration of free Cd^{2+} aquacations in equilibrium with CdEDTA^{2-} and free EDTA anions is smaller than that over the CdS particles; the latter concentration is controlled by the solubility product and S^{2-} concentration. In our case, this means that inside the vesicle cavities a certain minimum concentration of penetrated S^{2-} anions is needed to initiate the rapid creation of a CdS particle, which should have a size no smaller than the "critical" size, thus preventing particle dissolution. Thus in the presence of EDTA anions inside the vesicles, it is not possible to create or observe CdS particles with a size smaller than the "critical" size.

These phenomena are controlled by the value of the surface tension σ, and can lead to a very narrow, fixed distribution of CdS particle size, the latter undergoing a change through the variation of σ during modification of vesicles by the addition of selected surfactants.

Recently, a similar phenomenon of constant particle size in Q-sized CdS colloids during the dissolution of CdS particles by the addition of EDTA anions has been found [17].

5. Conclusions

The well-controlled preparation of ultrafine transition metal sulphide particles inside the cavities of lipid vesicles allows the synthesis of ultrasmall semiconductor particles of various photochemically active transition metals, e.g. PbS, ZnS, CdS and CuS_x. In the case of CdS, the modification of a bilayer lipid (DML) membrane with an ionogenic surface-active compound such as sodium dodecylsulphate can result in the formation of ultrasmall CdS aggregates with UV–visible spectra typical of Q-sized semiconductors of 10 Å. These CdS aggregates consist of either a very thin lamellar (two-dimensional) structure or a "crumbly" aggregation of ultrasmall cadmium sulphide clusters composed of approximately 100–1000 atoms of Cd. Of crucial importance in the formation of these nanoparticles is the presence of strongly chelating ligands such as EDTA anions which can both control the size of the particles and participate in the final structure of the metal sulphide aggregates.

The well-pronounced quantum nature of the synthesized sulphide structures makes them interesting objects for photocatalytic activity studies and for use as photocatalysts in various structurally organized photochemical systems based on lipid vesicles. Of great interest is the observed photochemical activity of CdS and CuS_x nanoparticles, which may allow the future design of much more complicated and, perhaps, more light-sensitive photocatalytic systems.

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