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Control of the size and photochemical properties of Q-CdS particles attached to the inner and/or outer surface of the lecithin vesicle bilayer membrane by the nature of its precursors

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Abstract

Cadmium sulfide nanoparticles have been generated in situ on the inner and/or outer surfaces of monolamellar lecithin vesicles. Chemical agents, strongly chelating or bounding the Cd^{2+} cations, are shown to influence dramatically the size of CdS nanoparticles as well as their optical, luminescence and photochemical properties. The more stable is a Cd^{2+}-containing complex created by these chelating agents, the smaller are the CdS particles formed. In case of $CdCl_2$ and $Cd(NO_3)_2$ as the CdS precursors inside the vesicles, a steady rise in the size of growing CdS nanoparticles is observed, while in case of K_2[CdEDTA] the accumulation of mass of growing CdS occurs without a change in the nanoparticles size. The size of CdS particles and their initial growth rate depend also on pH of the vesicle suspension, modification of the lipid membrane, being, however, independent of the $CdCl_2$ concentration, if $CdCl_2$ is the CdS precursor. In the presence of a sacrificial electron donor (S^{2-} or EDTA), the bandgap irradiation of the lipid-vesicle-supported CdS particles yields charge separation and electron transfer to lipophilic cetylviologen bications, $C_{16}V^{2+}$, embedded into the lipid bilayer. The initial quantum yield of $C_{16}V^{\bullet+}$ formation depends on the topology of vesicular systems and CdS localization on the inner or outer surface of the lecithin membrane. Presence of EDTA anions enhances sufficiently the initial quantum yield of vectorial electron phototransfer from CdS nanoparticles to cetylviologen.

Keywords: Cadmium sulfide; Photochemical properties; Lecithin vesicle

1. Introduction

Nanosized semiconductor particles (''Q-particles'') meet various applications, including photochemical solar energy conversion. Their size-dependent physical and chemical properties are somewhat different from those of the corresponding bulk materials. A favorite example is the well-established relationship between the optical absorption and the size of small CdS particles: as their radius decreases the absorption onset shifts to higher energies (the size quantization effect). Other examples exhibit their nonlinear optical properties, unusual fluorescence behavior, chemistry and so on [1].

Since nanosized particles are inherently liable to aggregate or grow in order to reduce their surface energy, careful and well-controlled synthetic methods are required for their preparation. The methodology applied so far can be classified into three categories: (i) an arrested precipitation from solutions by controlling solvents, reagents concentration and temperature or by using some stabilizers and growth-terminating reagents; (ii) stabilization of small particles in or by aggregation-preventing matrices such as polymers, glasses, monolayers over the air/water interface and bilayer lipid membranes; (iii) in situ synthesis in the confined spaces of zeolites, clay, organized surfactant aggregates (reverse micelles, vesicles and bilayer membranes), LB films. The latter matrices play an aggregation-preventing role as well.

Surfactant vesicles constitute a very flexible medium for supporting semiconductor nanoparticles: the particles can be localized at the outer, inner, or both surfaces of vesicles. Each arrangement has certain advantages. Semiconductor particles on outer vesicle surfaces are more accessible to reagents from the solution bulk, and can therefore, undergo, e.g., a more efficient photosensitized electron transfer [1]. On the contrary, smaller and more monodispersed semiconductor nanoparticles can be prepared and maintained for

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longer periods of time in the interior of vesicles than in any other arrangement.

Reagents, which are able to bound or coordinate constituents of semiconductor particles, play a crucial role in controlling the process of the nanoparticle growth, stabilizing the resulting colloidal dispersion, as well as ''passivating'' the semiconductor surface from redox processes.

Nanoparticles of sulfide semiconductors in suspensions of surfactant vesicles are usually prepared by the controlled precipitation of appropriate aqueous metal ions by adding gaseous H_2S. The size of these particles can be controlled by adjusting the number of precursor ions either encapsulated in, or bound to the external surface of the vesicles, and/or by managing the amount and rate of H_2S addition. At this procedure semiconductor nanoparticles of different sizes were shown to form at both inner and outer surfaces of the DHP vesicles [2]. A more precise control over the size of synthesized Q-CdS was obtained in DODAC vesicles [3]. Note, however, that adding a gaseous reagent, H_2S, during the nanoparticle preparation may create sufficient difficulties in reproducibility of the particle growth, that is well known in the synthesis of conventional heterogeneous catalysts.

Another more mild approach to synthesize nanosized transition metal sulfides in the surfactant vesicles suspension is to add sulfide anions as a component of solution of sulfide salts subsequent to preparing the suspended lecithin vesicles with a metal-containing precursor inside their cavities [4–6]. Appropriate outer solution pH helps to control the concentration of various forms of sulfide anions, and thus can provide the required or diminished rate of the sulfide particles growth. Alkali added to the outer water solution can stop this growth at any required stage [4]. This synthesis procedure was expected to be promising in preparing the sulfide semiconductor particles of a controlled size. However, thus formed CdS particles were found to behave quite strangely. Indeed, with K_2[CdEDTA] as the CdS nanoparticles precursor, the shape of the Q-CdS spectra unexpectedly remained constant during the particles growth [4,5]. This evidences in, probably, either a sort of a planar or very crumbly structure of the CdS nanoparticles formed under these mild conditions or dissolution of the growing CdS particles with sizes below some selected values [4,5].

The present work demonstrates that the driving force for stabilizing the CdS nanoparticles size is indeed their dissolving by the strongly chelating agents which can present even in precursors of CdS. Thus, by choosing an appropriate nature of the CdS precursors and lecithin membrane modifiers, as well as amounts of in situ formed H_2S to precipitate CdS, one can provide a simple, efficient and highly reproducible way to vary the size of CdS colloids in the cavities of lecithin vesicles. Moreover, lecithin vesicles are shown to generate different populations of CdS nanoparticles, whether they form on the inner or outer vesicle surface. Optical, fluorescence and photochemical properties of CdS nanoparticles, attached to the inner and/or outer surface of the bilayer membrane of lecithin vesicles are under discussion too.

2. Experimental

2.1. Chemicals

Sodium sulfide, Na_2S, sodium ethylendiaminetetraacetate, Na_2H_2EDTA were of ''pure'' grade from Reakhim. Ethanol and toluene were of ''chemical pure'' grade and were used without further purification. Distilled water was used to prepare all water solutions. pH of the outer (regarding the vesicular cavity) solution was maintained by the phosphate (pH=5.0–7.0) and borate (pH=8.0–10.0) buffers [4]. Compounds used for preparing buffers were of ''pure for analysis'' and ''chemical pure'' grades.

Potassium salt of cadmium ethylendiaminetetraacetate, K_2[CdEDTA], was synthesized as described in [4]. $CdCl_2$ and $Cd(NO_3)_2$ were of ''pure'' grade from Reakhim.

Lipid vesicles were prepared using synthetic lecithin DL-α-phosphatidylcholine dipalmitoyl, DPL (99%, Sigma). Membrane modifiers: thioglycerol, TG (Sigma), cetyltrimethylammonium bromide, CTAB (''pure'' grade, Reakhim), sodium dodecylsulfate, SDS (''pure'' grade, Reakhim) and alkylphenylpolyaethylenglykol (Triton X-100, Ferak Berlin) were used as received. *N*,*N*′-dihexadecyl-4,4′-dipyridinium dibromide (cetylviologen, $C_{16}VBr_2$) was previously synthesized and purified at the Boreskov Institute of Catalysis.

2.2. Methods

2.2.1. Preparation of vesicles

Lecithin monolamellar vesicles were prepared by sonification with ultrasound (35 kHz) of about 20 mg of lecithin or dried mixture of lecithin with an appropriate membrane modifiers or/and cetylviologen (in ethanol and toluene) in 1 ml of an appropriate water solution for 20 min at 52°C. After vesicles cooling to ambient temperature, they were centrifuged for 10 min at 3000 rpm and then passed through a gel-filtration column filled with Sephadex G-50 medium. 0.45 M KCl water solution was used as the eluent.

Four different preparation methods were used to arrange Q-CdS on the lecithin vesicle surfaces. In the first method, ''preparation A'', lecithin and water solution of a metal precursor ($CdCl_2$ or K_2[CdEDTA], for example) were cosonificated to give a 10^{-5} M lecithin vesicles suspension, which after gel-filtration contained ca. 2×10^{-3} M water solution of cadmium ions in the cavities of the vesicles (since the surface of unmodified lecithin vesicles is uncharged, it is assumed not to adsorb the charged Cd-containing species). In the second method, ''preparation B'', instead of pure lecithin, a dried mixture of lecithin with an appropriate membrane modifier was used to attach cadmium ions on both inner and outer surfaces of the vesicles. For

example, in the case of CTAB as the modifier, the surface of vesicles becomes positively charged and expected to adsorb the $CdEDTA^{2-}$ anions. Preparations "C" and "D" involved the addition of $CdCl_2$ to suspensions of empty vesicles ("C"), or to vesicles with cadmium ions in the cavities ("D").

2.2.2. Optical measurements

The UV–Vis optical absorption spectra were registered in single or cyclic modes with a scan rate of 10 nm/s and processed by a Specord M400 spectrophotometer (Karl Zeiss Jena, GDR). During the measurements vesicle suspensions were stirred with a small magnetic stirrer. The optical measurements during the CdS particle growth were carried out at room temperature in standard 1 cm quartz cells using a thermoregulated two-channel cellholder. Nanocrystal spectra were measured immediately following the sulfide incubation. Absorption spectra were corrected for light scattering by the vesicle suspension for some samples as follows. Prior to data acquisition the suspension was passed through an anion exchange column to remove any unreacted sulfide. It was necessary to add 20 μl of the detergent Triton X-100 dissolved in 200 μl of H_2O to the CdS/vesicle suspension to eliminate light scattering by the vesicles, which affected nanocrystal absorbances. No nanocrystal agglomeration was observed immediately after micellization, although aging of dispersion for several hours yielded broadening in the size distribution.

The initial rate of the CdS particle growth was determined as the change of total CdS concentration at the initial time moment (extinction coefficients at 320, 360, 400, 440 nm were measured as ca. 2978, 2191, 1646, 1208 $M^{-1}\,cm^{-1}$). Cadmium ion conversion into CdS was calculated as the ratio of current optical density of the sample, D, to that at a total conversion of the precursor to CdS, D_{max}, at certain wavelengths. The sizes of CdS particles were determined from the absorption spectra of CdS using the well-known correlation of the absorption inflection point – particle size data by Henglein [7].

Fluorescence measurements were carried out using luminescence spectrophotometer SFL-2 (USSR) in a 1.0 cm optical path quartz cell at room temperature.

2.2.3. Steady photolysis

Before photochemical measurements, oxygen was removed from the samples by a 1 h argon passing over the surface of vesicle suspensions on stirring. The samples were irradiated in standard 1 cm quartz cells. All measurements were carried out at 20°C.

Continuous argon laser ILA-120 (Karl Zeiss Jena, GDR) was used as a source of illumination with λ=458 nm. Standard glass filter OS-11 was used for cutting the scattered light with $\lambda \leq 600$ nm. The intensity of the incident light was measured with a bolometer LM2 (Karl Zeiss Jena, GDR).

The samples were irradiated in the cell compartment of spectrocolorimeter Specol-20 (Karl Zeiss Jena, GDR). The change of optical density caused by the accumulation of cation-radicals $C_{16}V^{\bullet+}$ was monitored at λ=602 nm ($\varepsilon^{602}_{C_{16}V^{\bullet+}} = 12400\,M^{-1}\,cm^{-1}$ [4]). The process quantum yield was calculated using the equation $\phi = w_0/I_{abs}$, where w_0 is the initial rate of the $C_{16}V^{\bullet+}$ accumulation (molecules/s), I_{abs} is the intensity of absorbed light, quanta/s. In the case of CdS, $I_{abs} = I_0(1 - 10^{-D^{458}_{CdS}})$, where D^{458}_{CdS} is the optical density of CdS at λ=458 nm, I_0 is the incident light intensity.

2.2.4. Transition electron microscopy (TEM)

Direct measurements of particle size were done at the Boreskov Institute of Catalysis using JEM-100CX (JEOL, Japan) electron microscope with 10 Å resolution. The samples were deposited on carbon-coated copper grids. Typically, a droplet of CdS nanocrystals in vesicles was placed on the grid and stained by 0.5% uranyl acetate. Magnification was 200 000 and 500 000.

3. Results and discussion

3.1. Generation of CdS nanoparticles

3.1.1. Size of CdS nanoparticles

CdS nanoparticles inside lecithin vesicles were produced by adding Na_2S to the vesicle suspension containing different precursors of CdS.

K_2[CdEDTA] is known to be widely used as the CdS precursor, since it imposes minor pH and ionic strength changes during the CdS formation inside the vesicles [4,5,8]. Moreover, EDTA anions serve as an efficient electron donor in many photochemical experiments, which is convenient for studying, e.g., transmembrane electron transfer. However, the presence of EDTA has been shown to restrict the possibility of varying the size of CdS nanoparticles [4,5]. These restrictions seem to originate from either dissolving the finest CdS aggregates due to exponentially increasing solubility of these aggregates at diminishing their size (see [5,9]) or, in the case of lecithin vesicles, from formation of a thin lamellar sulfide structure covering the inner vesicle surface [4,5].

Fig. 1(a) shows a set of absorption spectra recorded during the growth of CdS particles inside the lecithin vesicles with K_2[CdEDTA] as the precursor with the initial local concentration 0.3 M. In Fig. 1(b) and (c) the CdS precursors are $CdCl_2$ and $Cd(NO_3)_2$, respectively at the same initial concentrations. It is clear from Fig. 1, that the shape of the spectra of growing CdS nanoparticles differs essentially for precursors of different nature.

With K_2[CdEDTA] as the precursor, the absorption onset is in a range of 502±2 nm. According to the absorption inflection point-particle size data of [7], this onset should correspond to "large" CdS particles with diameter (under assumption of their spherical shape) lying between 6.8 and 7.4 nm. The most striking features here are as follows. First,

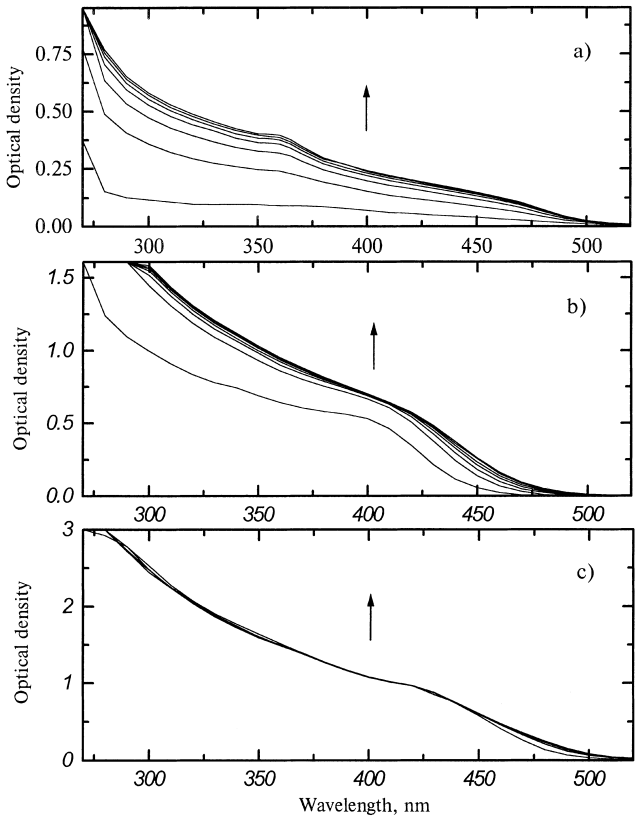

Fig. 1. Absorption spectra of Q-CdS in the process of their growth after addition of 0.5 M Na_2S to the suspension of pure DPL vesicles, containing initially 0.3 M K_2[CdEDTA] (a), $CdCl_2$ (b) or $Cd(NO_3)_2$ (c) in the cavities and borate buffer with pH=8.0 in the outer solution ("preparation A"). The spectra were recorded at 150 (a), 100 (b) and 60 s (c) intervals at room temperature; arrows show consistency in the changes. Absorption spectra are corrected for the light scattering by the vesicle suspension.

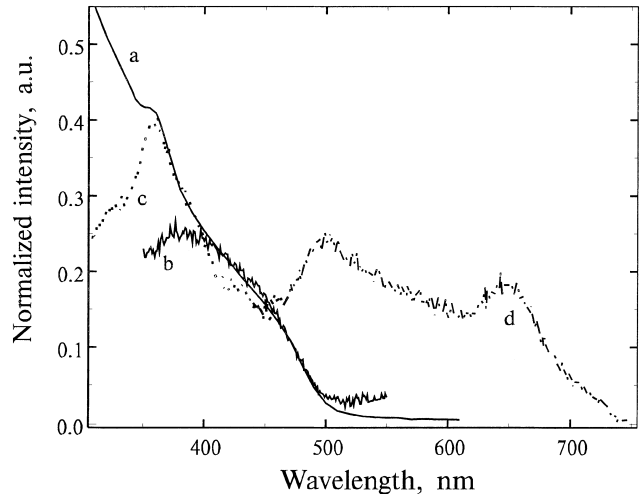

Fig. 2. Absorption (a), as well as uncorrected luminescence excitation ((b) λ_{em}=650, (c) λ_{em}=500 nm) and emission ((d) λ_{ex}=390 nm) spectra of CdS particles obtained from K_2[CdEDTA] and incorporated in the inner cavities of the DPL vesicles. Emission and excitation spectra have been normalized to the absorption scale. The vesicles were prepared by cosonication of 20 mg of lecithin with 0.3 M K_2[CdEDTA] water solution in 1 ml of water, followed by gel-filtration ("preparation A"). CdS particles were generated by the subsequent addition of 0.5 M Na_2S at pH=8.0.

an additional absorption band at 360 nm is clearly observed only in presence of EDTA and corresponds to 2.1 nm particles. Second, the absorption edge as well as the absorption maximum practically does not shift with time. So, the size of the CdS particles remains constant on the formation [4,5]. As seen with negative stain electron microscopy, the average diameter of the original sonicated monolamellar liposomes is ca. 35 nm. The maximum calculated particle diameter, allowed for the formation of CdS from the quantity of Cd^{2+} ions trapped in the vesicle cavity ca. 28 nm in diameter, is 6.0 nm, see, e.g. [6]. The immediately observed CdS particle size lies in a region of 2–8 nm (with K_2[CdEDTA] as the precursor), according to TEM. One should note also, that the final optical density of the synthesized CdS, and hence, its integral volume in the case of K_2[CdEDTA] is lower, than in the case of $CdCl_2$ or $Cd(NO_3)_2$ (provided for that the initial cadmium ion concentration is the same in all cases). Apparently, during the CdS synthesis in the presence of EDTA the number of the CdS particles formed increases, but their diameter (or the spectrum shape determining size) does not change. When the vesicles (with CdS from K_2[CdEDTA] inside) were destroyed by the detergent Triton X-100 in the excess of sulfide-ions, the conversion degree of cadmium ions into CdS increased, and maximum at 360 nm disappeared.

Excitation and emission luminescence spectra of CdS originated from K_2[CdEDTA] are shown in Fig. 2. The emission spectrum has two distinct maxima at 500 and 640 nm. The broad lower-energy band (at ca. 640–670 nm) is usually attributable to emission from very shallow traps in CdS [10–12]. In contrast, the spectrum attributed typically to excitonic fluorescence appears as a sharp band at 500 nm, i.e. near the absorption onset and is considered to arise from detrapping of the trapped electrons [10–12]. So, the observed emission spectrum reflects contributions of both excitonic and trapped fluorescence of the CdS particles inside the lecithin vesicle cavities.

With $CdCl_2$ or $Cd(NO_3)_2$ as the precursor (i.e. without strongly chelating EDTA), the absorption onset is seen to increase during the Q-CdS growth from 440 to 480 nm for $CdCl_2$ and from 470 to 495 nm for $Cd(NO_3)_2$ (see Fig. 1(b) and (c)). This corresponds to the growth of the particle size, subsequent to CdS nucleation, from a mean diameter of ca. 3.3 to 4.9 nm and from 4.3 to 6.1 nm for $CdCl_2$ and $Cd(NO_3)_2$, respectively.

With $CdCl_2$ as the precursor, at the beginning of the CdS growth the optical spectrum has also a maximum at 400 nm, corresponding to the initial particle diameter of 2.6 nm. The luminescence spectra of Q-CdS particles in case of $CdCl_2$ as the precursor show broad emission maxima at 600 and 640 nm, the wavelengths corresponding to the electron-hole recombination in traps lying below the CdS conduction band edge.

The average diameter of the final CdS particles formed according to the "preparation A" method is less for K_2[CdEDTA] than for $CdCl_2$ and even for $Cd(NO_3)_2$ (4.5, 4.9, and 6.1 nm, respectively). Evidently, agents, strongly chelating or bounding the Cd^{2+} cations, influence dramatically the size of CdS nanoparticles [9]. The less is the stability constant of the complex created by these chelating agents, the larger is the CdS particle diameter. EDTA, a strong chelating ligand with the stability constant $K=5\times10^{16}$ M^{-1} for $CdEDTA^{2-}$ [13], shifts the equilibrium between the CdS and $CdEDTA^{2-}$ complex, yielding a lower degree of the cadmium ions conversion into CdS. Our results agree well with those of work [9]: the stability constant for $CdCl_2$ is equal to 4×10^2 M^{-2}, while that for $Cd(NO_3)_2$ is 2.5 M^{-2} [12].

The effect of pH was investigated in detail for the in situ formation of CdS. At any given amount of H_2S formed from Na_2S, the wavelength of the prompt absorption edge, and hence, the size of the nascent and final CdS particles, decreased with increasing pH values. Sulfide particles, formed in situ by adding Na_2S to the metal-ion-precursor-containing lecithin vesicles, continue to grow until they reach thermodynamically stable size. At pH 7.0, 8.0, 9.0, 10.0, the final particle size was 5.1, 4.8, 4.7 and 4.3 nm, respectively with the 0.3 M $CdCl_2$ as the precursor (the reaction time was 1000 s).

Membrane modification also changes the average diameter of Q-CdS particle formed from 0.3 M $CdCl_2$. This diameter is ca. 4.8, 4.4, 4.0 and 3.4 nm in cases of: unmodified membrane, membrane modified with SDS (SDS molar fraction in the membrane 0.1) and CTAB (CTAB molar fraction in the membrane 0.003), unmodified membrane with a subsequent addition of thioglycerol ([TG]:[Cd^{2+}]=17), respectively.

Assuming that the Cd^{2+} ions did not diffuse through the membrane during the vesicle preparation, one should expect an increase in the particle size at higher $CdCl_2$ concentration inside the vesicle cavities. Indeed, with nonmodified DPL vesicles, the average diameter increases from 4.2 to 4.8 nm for the initial $CdCl_2$ concentrations 0.1 and 0.3 M.

With the CTAB modified membrane at $CdCl_2$ concentrations 0.1, 0.2, 0.3 M the average diameter is equal to 5.0, 4.4, 4.0 nm (CTAB molar fraction in the membrane 0.003). Apparently, exposure of such systems to H_2S formed from Na_2S yields nucleation at several sites.

3.1.2. The rate of the Q-CdS particle growth in the cavities of lecithin vesicles

On Fig. 1 one can see some evident difference in the kinetics of the CdS nanoparticles growth for three different CdS precursors inside the lecithin vesicles (provided that for initial cadmium ion concentration is the same in all cases 0.3 M).

So, the conversion of the captured Cd^{2+} ions into CdS for K_2[CdEDTA] is only 0.2 (the reaction time is 1000 s), the initial rate of Q-CdS growth being estimated as 7.1×10^{-7} M s^{-1}. With $CdCl_2$ the initial rate is much higher: 3.5×10^{-5} M s^{-1}, the conversion degree being 1. Note, in this case particles grow through two stages: a very rapid one at the beginning, and smoother one after major particles formed (Fig. 1). This two-phase kinetics may evidence in a sort of some particles' rearrangement after their initial nucleation. For $Cd(NO_3)_2$, which is also a weak complexating agent, the initial rate was found to be 4.6×10^{-5} M s^{-1}, the conversion degree being less than 1.

The $CdCl_2$ concentration appears not to influence the Q-CdS initial growth rate in a concentration range of 0.1–0.3 M.

3.1.3. Rate-limiting stage in the CdS nanoparticles' growth

An increase in pH followed by a decrease of the equilibrium concentration of the molecular form of sulfide-ions, H_2S, has been shown to result in slowing-down Q-CdS growth rate, see also [4,5]. Considering a fast formation of CdS particles in homogeneous solutions and independence of this rate on $CdCl_2$ concentration in our case (in the $CdCl_2$ concentration range of 0.1–0.3 M), we expected the penetration of the uncharged H_2S molecules through the lipid membrane to be the limiting stage of CdS formation in the vesicle cavities [4,5].

Taking into account that with the DPL vesicles, the CdS formation rate is ca. 10^{-8} mol CdS/s·cm^3 of the vesicle suspension at room temperature and pH=8.0 ($CdCl_2$ is the precursor), one can estimate the rate of penetration as

$$P = \frac{W_0 \cdot V}{S}$$

for H_2S penetration through the lipid membrane. Here W_0 is the CdS initial growth rate; V the total volume of the vesicle suspension; and S is the total outer surface area of the membrane of the vesicles. Since for our samples V=2 cm^3 and $S\approx8.6\times10^4$ cm^2 (for 2×10^{-9} mol/cm^3 concentration of vesicles with outer diameter 35 nm), and so estimated P should be of the order of 10^{-13} mol/cm^2 s. Evidently, this value is very close to the rate of penetration of charged ions: $Cl^- - 10^{-13}$ mol/cm^2 s, $K^+ - 5\times10^{-15}$ mol/cm^2 s, and much smaller than that for an uncharged H_2O molecule (about 10^{-4} mol/cm^2 s) [14], even when taking into account much smaller concentration of water soluble sulfides in respect to that of water molecules.

Thus, a simple penetration of uncharged H_2S molecules, which are evidently similar to H_2O hardly is the rate-limiting stage of Q-CdS formation in the vesicle cavities. Diffusion of negatively charged HS^-, and indeed, S^{2-} anions is not the rate limiting step as well, because initial CdS growth rate decreases, when HS^- and S^{2-} concentrations increases (with increasing the solution pH).

For this reason one can expect that the actual limiting stage of the CdS nanoparticles formation has a more complicated origin. For example, one can assume that it could be the diffusional collisions of H_2S molecules with the surface of the vesicles in the suspension bulk. Indeed, it is easy to

estimate an effective rate constant k for such collisions:

$$k \approx 4\pi(R_{ves} + R_{H_2S})(D_{ves} + D_{H_2S}).$$

Here R and D are, respectively, the radia and diffusion coefficients of the colliding species. Evidently,

$$k \approx 4\pi R_{ves} D_{H_2S},$$

since the radius of the vesicles $R_{ves} \approx 10$ nm is much larger than that of H_2S molecules, while, on the contrary, diffusion coefficient D_{H_2S} for H_2S molecules is much higher than that of the vesicles. Taking $D_{H_2S} \approx 10^{-5}$ cm^2 s^{-1}, one can obtain $k \approx 10^{-10}$ cm^3 s^{-1}. It means, that each vesicle is exposed to ca. $k \cdot [H_2S]$ collisions with H_2S molecules per second. At pH=8.0 and $[Na_2S]=10^{-2}$ M, the value of $[H_2S]$ is ca. 10^{-3} M$\approx 10^{18}$ cm^{-3}. Thus, at this pH, each vesicle is exposed to ca. 10^8 collisions with H_2S molecules per second, that indeed is much higher than the observed rate of the CdS nanoparticle growth (the CdS initial growth rate inside one vesicle corresponds to bounding of ca. 10 S^{2-} ions per second). Thus, simple diffusional collisions of H_2S molecules (as well as those of charged sulfide anions) with the vesicles also are hardly determining the rate-limiting stage of the CdS nanoparticles formation.

So, the nature of the rate-limiting stage for formation of CdS nanoparticles inside lecithin vesicles seems to be very complicated and involves, probably, a preliminary complexation of S^{2-} with some species of either the lipid membrane or the CdS precursors. The latter conclusion results from sufficient slowing down the formation of CdS in the presence of EDTA, as is noted above.

The properties of the lipid membrane appear to affect the CdS particle growth rate too [5]. For two CdS precursors, K_2[CdEDTA] and $CdCl_2$, we have investigated this effect in detail. Fig. 3 shows that the influence of the tested membrane modifiers is similar for the both CdS precursors: SDS enhances the permeability (or reactivity of an intermediate), and hence, the initial rate of the CdS growth; CTAB provides an opposite effect.

For studying the vectorial electron phototransfer across the lipid/water interface we attempted also to synthesize systems of inverted topology with the externally "attached" CdS nanoparticles, as shown in Fig. 4(b) ("preparation C", see Section 2). As the vesicle suspension with obtained CdS in the outer solution passes through the gel-filtration column, the synthesized CdS particles adsorb on the CTAB, but not on SDS-modified membrane. Most likely this originates from an electrostatic repulsion of negatively charged Q-CdS particles and sulfate-anions on the negatively charged vesicle surface.

3.2. Photochemical properties of Q-CdS inside lipid vesicles

We have studied some features of photoelectron transfer across the water–lecithin bilayer interface, when the bilayer contains lipophilic $C_{16}V^{2+}$ cations as reversible electron acceptors. At irradiation of the CdS particles into their

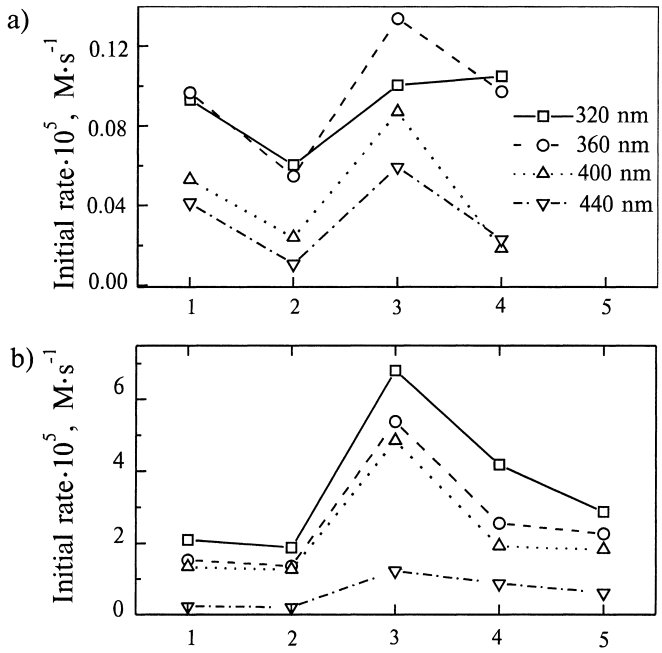

Fig. 3. Effect of the lipid membrane modification on the initial rate of the Q-CdS particle growth. The initial concentrations of K_2[CdEDTA] (a) and $CdCl_2$ (b) in the inner cavities of the vesicles are 0.3 M. The membrane composition is as follows: (1) without modificators; (2) the membrane is modified with CTAB (0.003 molar fraction of CTAB in the membrane); (3) the membrane is modified with SDS (0.1 molar fraction of SDS in the membrane); (4) the membrane is modified with CTAB and $C_{16}V^{2+}$ (0.003 molar fraction of CTAB and 0.01 molar fraction of $C_{16}V^{2+}$ in the membrane); (5) thioglycerol ([TG]:[Cd^{2+}]=17) is added subsequent to preparation of the vesicle suspension prior to Na_2S addition at pH=8.0. The initial rate is calculated at different wavelengths: 320, 360, 400, 440 nm.

absorption band, the electron transfer was detected by accumulation of the reduced form of cetylviologen. Under study were CdS nanoparticles, attached to either the inner and/or outer surface of the bilayer membrane of lecithin vesicles (Fig. 4). The S^{2-} anions served as a sacrificial electron donor.

For the systems' topology as in Fig. 4(a) the initial cadmium ion concentration being 0.3 M (other conditions being the same), the initial quantum yields of $C_{16}V^{\bullet+}$ formation in cases of K_2[CdEDTA], $CdCl_2$, $Cd(NO_3)_2$ appeared to be ca. 2.4%, 0.9%, 0.7%, respectively. One can suppose that a higher quantum yield in the first case is caused by the presence of a sufficient amount of EDTA anions, which serve as an efficient additional electron donor.

The quantum yield depends on the $C_{16}V^{2+}$ concentration in the lipid membrane. e.g., for the same topology of the system ($CdCl_2$ as the precursor) with molar fractions of $C_{16}V^{2+}$ 0.005 and 0.01, the quantum efficiency of $C_{16}V^{\bullet+}$ formation appeared to be 0.9%, while with molar fraction 0.02, the quantum yield increases to 1.4%.

Cetylviologen and its reduced forms are known to be reversible electron relays in the process of electron phototransfer across the lipid–water interface. Therefore, the quantum yield of the $C_{16}V^{\bullet+}$ formation depends probably

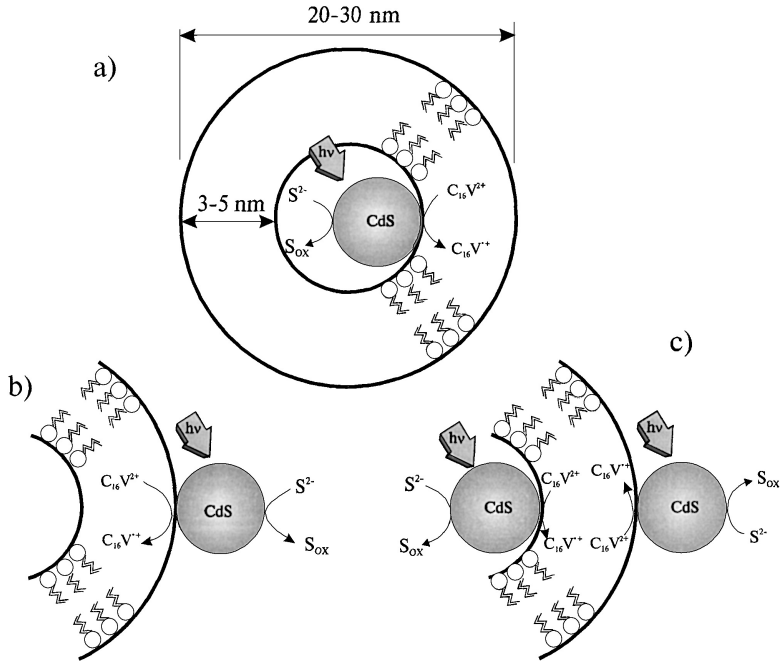

Fig. 4. Schematical view of the designed photocatalytic systems for the CdS/lipid membrane interface electron transfer. The vesicles were prepared by cosonication of 20 mg of lecithin with a dried mixture of lecithin with CTAB and $C_{16}V^{2+}$ (0.003 molar fraction of CTAB and 0.01 molar fraction of $C_{16}V^{2+}$ in the membrane) with: (a) 1 ml of 0.3 M water solution of a metal precursor ($CdCl_2$ or K_2[CdEDTA], for example) (''preparation A''); (b) 1 ml of KCl water solution with the addition of $CdCl_2$ subsequent to preparation of the vesicles (''preparation C''); (c) 1 ml of 0.3 M water solution of a metal precursor ($CdCl_2$ or K_2[CdEDTA], for example) with the addition of $CdCl_2$ subsequent to preparation of the vesicles with the CdS precursor inside the cavities (''preparation D''). CdS particles were generated by the further addition of 0.5 M Na_2S.

on the localization of CdS nanoparticles. We have found, that the quantum yield for CdS nanoparticles localized at the inner vesicle surface is lower than for those attached to the outer surface (the topology, corresponding to Fig. 4(b)): 0.9% and 3.2%, respectively ($C_{16}V^{2+}$ molar fraction in the membrane is 0.01, the initial $CdCl_2$ concentration in the vesicle cavities is 0.3 M – ''preparation A'', see Section 2; $CdCl_2$ added concentration is 2.5×10^{-4} M – ''preparation C''). Note, that the average diameter of the external CdS nanoparticles in this case was larger (the absorption onset is at ca. 510 nm, i.e. CdS particles formed are of ca. 9.0 nm in diameter according to [7]) than that of the particles inside the vesicle cavities (4.9 nm in diameter). Thus, at the same concentration of the poorly mobile electron carrier $C_{16}V^{2+}$, the quantum yield of its reduction seems to be larger if larger is the area of the contact of CdS particle with the membrane. The maximum $C_{16}V^{\bullet+}$ concentrations, accumulated during the irradiation of above systems (CdS nanoparticles inside or outside the vesicle cavities), appeared to be 24% and 45%, respectively (with regard to the total $C_{16}V^{2+}$ concentration). The quantum yield of $C_{16}V^{2+}$ reduction for CdS, attached to both inner and outer surfaces (the topology, corresponding to Fig. 4(c)) was 3.2%, the maximum conversion of $C_{16}V^{2+}$ being estimated as 45% ($C_{16}V^{2+}$ molar fraction in the membrane is 0.01, the initial K_2[CdEDTA] concentration in the vesicle cavities is 0.3 M; $CdCl_2$ added concentration is 2.5×10^{-4} M – ''preparation C''). The last observation seems to comply with the recently rationalized mechanism of cetylmethylviologen photoreduction, which involves the rate-determining disproportionation

$$2C_{16}MV^{\bullet+} \leftrightarrow C_{16}MV^{0} + C_{16}MV^{2+}$$

and subsequent diffusion of the uncharged $C_{16}MV^{0}$ molecules across the bilayer [15]. Therefore, the processes of $C_{16}MV^{2+}$ reduction in the outer and inner bilayers are not independent.

4. Conclusions

The data presented demonstrate that Cd^{2+} chelating agents can influence dramatically the size of CdS nanoparticle grown in the cavities of lecithin vesicles. Moreover, the presence of Cd^{2+}-bonding ligands as well as lipid membrane modifiers, and pH of the outer water solution affect the CdS particle diameter and the initial rate of their growth. Of all these manipulations, the shape of the semiconductor nanoparticles formed remains close to sphere.

Note that the presence of some organic ligands like EDTA anions can enhance the initial quantum yield of photoreduction processes, as it is seen in the case of $C_{16}V^{2+}$ reduction.

Diffusional collisions of H_2S molecules with the vesicles as well as the ''simple'' penetration of uncharged H_2S molecules across the lecithin membrane hardly are the rate-limiting stage of the CdS nanoparticles formation,

the rate of this stage being nevertheless proportional to the concentration of H_2S.

The quantum yield of the $C_{16}V^{\bullet+}$ formation depends on the topology of the vesicular system, on localization of CdS nanoparticles on the lipid membrane and on the area of the CdS-membrane contact.

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