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Incorporation of CdS nanoparticles formed in reverse micelles into silica matrices *via* a sol–gel process: preparation of nano-CdS-containing silica colloids and silica glass

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The incorporation of CdS nanoparticles, as prepared in reverse micellar systems, into silica matrices, *via* a sol–gel process, was investigated. The silica colloids containing CdS nanoparticles, CdS–COL, were prepared *via* the surface modification of CdS nanoparticles using 3-mercaptopropyltrimethoxysilane in reverse micelles. The recovery and dispersion of the nanoparticles was performed in an appropriate organic solvent, followed by a sol–gel process, using TMOS (tetramethyl orthosilicate) or TEOS (tetraethyl orthosilicate) in MeOH or EtOH solution. The size and morphology of the resulting CdS–COL was able to be controlled by changes in the silica source and the organic solvents. A CdS–COL stable against photoirradiation and heat treatment was able to be prepared which could be utilized as a photocatalyst for the generation of H_2 from propan-2-ol aqueous solution. The silica bulk glass containing the CdS nanoparticles, CdS–GLA, was also prepared, such that the cut off wavelength of the glass could be precisely controlled by regulating the water content (W_o) for the reverse micellar system, during CdS preparation.

Introduction

There has been much recent interest in the preparation and processing of nanoparticles, when using reverse micellar systems, with materials including metals, metal sulfides and oxides. One of the most attractive methodologies for the recovery and immobilization of nanoparticles, when formed in reverse micelles, is *via* the *in-situ* preparation of the supports, *via* hydrolysis. This has been realized for silica supports *via in-situ* hydrolysis of tetraethyl orthosilicate (TEOS)[1] and for polyurea supports *via in-situ* diisocyanate polymerization.[2,3] These methods can produce silica and polyurea (PUA) nanoparticle composites very easily, such that the products can be utilized as catalysts and photocatalysts. A further attractive methodology is to immobilize the nanoparticles into silica or polymer supports *via* chemical bonding. CdS semiconductor nanoparticles may be prepared size-selectively in reverse micellar systems[4,5] and the size-selective incorporation of the CdS nanoparticles into the thiol-modified mesopores of mesoporous silica has also been achieved.[6,7] The CdS nanoparticles, when prepared in reverse micelles, can also be recovered by surface modification, using thiol molecules such as thiophenol, followed by dispersion into non-micellar organic solvents.[8,9] The redispersed CdS nanoparticles can then be immobilized into polythiourethane (PTU)[10,11] or polyurethane (PU),[12] *via* polymerization of the appropriate monomer molecules in organic solvent. The resulting CdS–mesoporous silica, CdS–PTU, and CdS–PU composites, were utilized as photocatalysts for H_2 generation from propan-2-ol aqueous solutions.

The present study has been carried out, as an extension of the latter methodology, in order to develop a method for the preparation of CdS nanoparticle–silica matrix composite materials. Several investigators have reported the sol–gel preparation of CdS–silica composites, mainly with the aim of preparing materials for optical and optoelectronic applications, such as luminescence materials. In most studies, an *in-situ* preparation of the CdS nanoparticles, in the presence of a silica network, silica sol, or silica matrices, has been employed.[13–20] On the other hand, Rajh *et al.*,[21] Boilot *et al.*,[22–24] and Correa-Duarte *et al.*[25] have reported methods in which the preparation of the CdS nanoparticles is completely separated from the sol–gel procedure. As pointed out by Boilot *et al.*,[23] the latter method, in appropriate reaction media, allows the preparation of nanoparticles of well-controlled chemical and physical properties. Reverse micellar systems have advantages in controlling the chemical composition, size, and size distribution of the nanoparticles. In the present work, the preparation of CdS nanoparticles in reverse micellar systems, followed by recovery of the particles by surface modification and the immobilization of the particles into silica matrices *via* an appropriate sol–gel process, has been investigated. In this work nano-CdS-incorporating silica colloids (CdS–COL) suitable for use as photocatalysts have been prepared. Nano-CdS containing bulk glasses (CdS–GLA) have also been prepared.

Experimental

Chemicals

3-Mercaptopropyltrimethoxysilane (MPTMS), sodium bis(2-ethylhexyl)sulfosuccinate (Aerosol OT; AOT), tetraethyl orthosilicate (TEOS), and tetramethyl orthosilicate (TMOS) were supplied by the Tokyo Chemical Industry, Ltd. (TCI). Isooctane (2,2,4-trimethylpentane) was obtained from Ishizu Seiyaku Ltd. $Cd(NO_3)_2\cdot 4H_2O$, $Na_2S\cdot 9H_2O$, and all other chemicals were obtained from Wako Pure Chemical Industries, Ltd. All reagents were used without further purification. The preparation and filtration of the reverse micellar solutions were as described in previous papers.[4,8]

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Preparation and recovery of CdS nanoparticles

CdS nanoparticles were prepared in a reverse micellar system consisting of 0.1 mol l^{-1} AOT, water and isooctane. Here the molar ratio of water to AOT (= $[H_2O]/[AOT]$; water content) is denoted as W_o. A 50 ml AOT–isooctane reverse micellar solution of the required W_o value (normally $W_o = 6$) containing 0.8 mmol l^{-1} $Cd(NO_3)_2$ was added rapidly to a second micellar solution (50 ml) of the same W_o containing 0.4 mmol l^{-1} Na_2S, and stirred by magnetic stirrer at 298 K in a glass vessel. 0.025 ml of MPTMS was added to the reverse micellar solution, three minutes after the formation of the CdS nanoparticles, without dilution. The CdS nanoparticles, surface-modified with MPTMS, were then collected *via* centrifugation and were washed twice with hexane, and then dispersed again in the required organic solvent (5 ml), such as DMF, dichloromethane, chloroform, or TMOS. The resulting CdS-dispersed DMF and CdS-dispersed TMOS are abbreviated henceforth as CdS–DMF and CdS–TMOS, respectively.

Incorporation of CdS nanoparticles into silica matrices

The CdS-incorporating silica colloids (CdS–COL) were normally prepared in 10 ml MeOH or EtOH, with the required quantities of CdS–DMF (0.8 ml in most cases) or CdS–TMOS, and TMOS or TEOS. The hydrolysis (silica sol formation) was initiated *via* the addition of 1.2 ml of 28% NH_3 aqueous solution (NH_3/H_2O hereafter) under vigorous stirring by magnetic stirrer. Following 15 min stirring for the case using TMOS or 12 h stirring for the case using TEOS, the CdS–COL particles were collected *via* centrifugation and were washed with MeOH or EtOH and then with acetone and finally dried *in vacuo*.

The CdS-containing bulk glass (CdS–GLA) was prepared in 10 ml MeOH, with 0.8 ml CdS–DMF and 1.2 ml of NH_3/H_2O, with the hydrolysis being initiated by the addition of 0.8 ml TMOS. Following mild stirring, the solution temperature was raised gradually to 323 K over a period of 2 days, and then maintained at 323 K for 3 days in order to remove MeOH from the silica gel. The solution temperature was then raised again to 353 K over 2 days and maintained at 353 K for 1 day, raised to 423 K over 2 days, and finally kept at 423 K for 1 further day, in order to remove DMF and NH_3/H_2O.

Analysis

The water content of the reverse micellar solution (W_o) was determined using a Karl-Fischer moisture meter (Kyoto Electronics MKS-1s). The absorption spectra for the CdS nanoparticles in micellar solution and in silica glass were recorded on a diode-array UV-vis spectrophotometer (Hewlett-Packard 8452A). The diffuse reflectance spectra for the CdS nanoparticles, incorporated in silica colloid, following dispersion of the CdS–COL in water, were recorded on a UV-vis spectrophotometer (Japan Spectroscopy V-550) equipped with an integrating sphere attachment (ISV-469). The diameters of the respective CdS nanoparticles were estimated on the basis of their absorption onsets, according to the Brus equation,[26] as shown in previous papers.[4,8] SEM measurements were carried out on a Hitachi S-5000L. The mean CdS–COL diameter was measured *via* a laser scattering particle-size distribution analyser (Horiba LA-910W). The specific surface area for CdS–COL was measured by the BET method, using N_2 adsorption at 77 K (Shimadzu Flowsorb II 2300). The quantity of CdS in CdS–COL was calculated on the assumption of a quantitative formation and recovery of the CdS nanoparticles in the reverse micellar systems.

Photoirradiation experiments

0.05 g CdS–COL was dispersed in 20 ml of 15 vol% propan-2-ol aqueous solution. In this, the propan-2-ol is employed as a sacrificial electron donor for the photogenerated positive hole in the CdS nanoparticles. The solution was purged with argon for 1.5 h in a test tube, sealed with a septum, and then photoirradiated with a 2 kW xenon lamp (Ushio UXL-2003D-O) for 12–120 h. Irradiation light of wavelengths (λ) <300 nm and light in the IR range were cut off by the Pyrex glass of the tube and by the water filter, respectively. The quantity of H_2 formed in the gas phase was measured by gas chromatography (Shimadzu GC-14B), as described previously.[4]

Results and discussion

Incorporation of CdS nanoparticles in silica colloids

CdS nanoparticles, prepared in reverse micellar systems of $W_o = 3$ or 6, surface-modified with MPTMS and dispersed in DMF, were incorporated in silica colloids. As shown in Fig. 1, the diffuse reflectance spectra for the resulting CdS–COL, measured following dispersion in water, demonstrate the characteristic absorption of size-quantized CdS. Thus, the dispersion and incorporation of the CdS nanoparticles was carried out successfully, as they retained their quantum-size effect.

Typical SEM images for CdS–COL prepared using TEOS and TMOS are shown in Fig. 2. The CdS–COL particles prepared using TEOS are much larger than those prepared using TMOS, and this is attributable to the slower sol–gel reaction with TEOS compared to TMOS. Thus each CdS–COL particle, prepared from TEOS, can contain several CdS nanoparticles. This feature of the structure may allow the photo-induced aggregation of the CdS nanoparticles in the silica matrices. As shown in Fig. 3(a), a red shift for the absorption onset of the CdS nanoparticles was observed for CdS–COL, prepared using TEOS. The onset wavelength following 120 h of photoirradiation is, however, still less

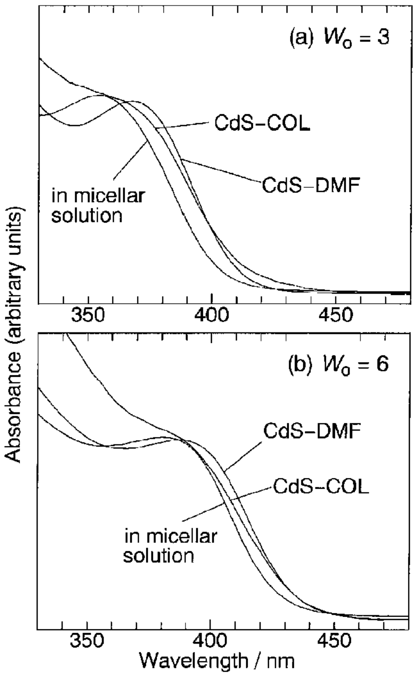

Fig. 1 Absorption spectra for CdS nanoparticles in reverse micellar solution (3 min after formation), in DMF following surface modification and dispersion, and diffuse reflectance spectra for CdS nanoparticles in CdS–COL. The CdS nanoparticles were prepared at (a) $W_o = 3$ or (b) $W_o = 6$, and CdS–COL was prepared in EtOH using CdS–DMF and TEOS.

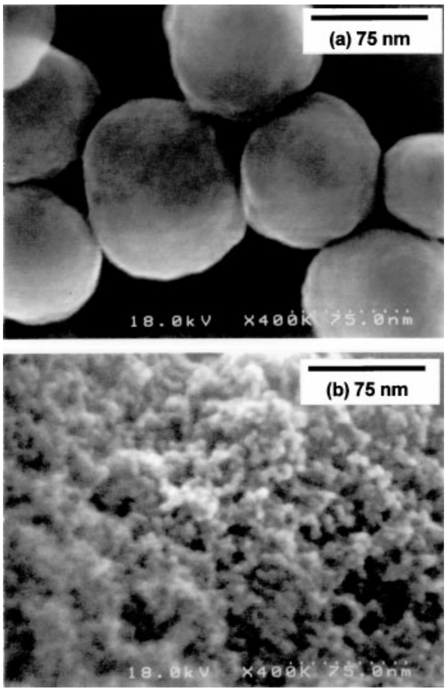

Fig. 2 SEM images for CdS–COL, prepared in (a) EtOH using CdS–DMF and TEOS, and (b) MeOH using CdS–DMF and TMOS.

than that for bulk CdS (*ca.* 500 nm), thus indicating that the CdS in silica colloids retain their quantum size effect. As shown in Fig. 3(b), when thiophenol, in place of MPTMS, is used for CdS surface modification, the absorption onset wavelength for CdS reaches 500 nm. Thus, the CdS–silica bond effected by MPTMS is essential for the effective incorporation and stabilization of CdS nanoparticles in silica matrices. On the other hand, when the sol–gel process, using TMOS, is carried out in MeOH, the size of the silica colloids is comparable to that of the CdS nanoparticles, as shown in Fig. 2(b). Thus, in this case, the CdS nanoparticles are probably surrounded by silica nanoparticles, to form roughly aggregated composite clusters, which, as shown in Fig. 3(c), are unstable under photoirradiation.

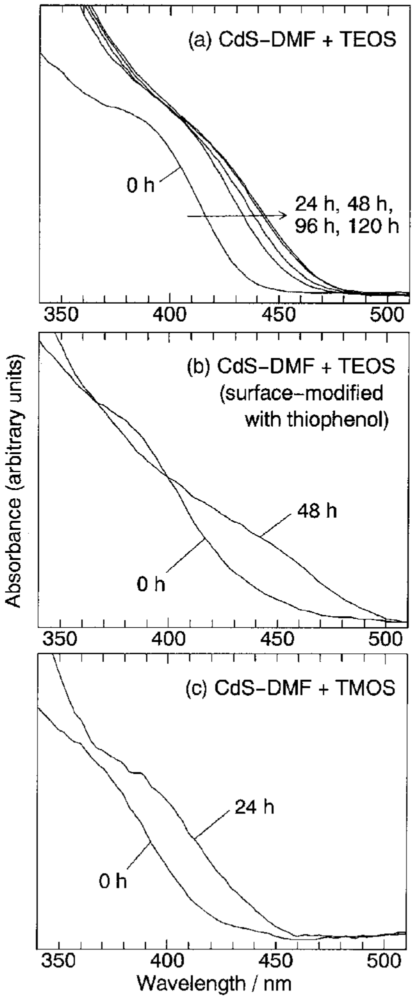

Fig. 3 Diffuse reflectance spectra for CdS nanoparticles in CdS–COL as prepared and following photoirradiation in 15 vol% propan-2-ol aqueous solution. (a) CdS–COL prepared in EtOH by using CdS–DMF and TEOS, (b) as (a) above but with CdS–DMF prepared *via* surface modification with thiophenol, and (c) CdS–COL prepared in MeOH using CdS–DMF and TMOS.

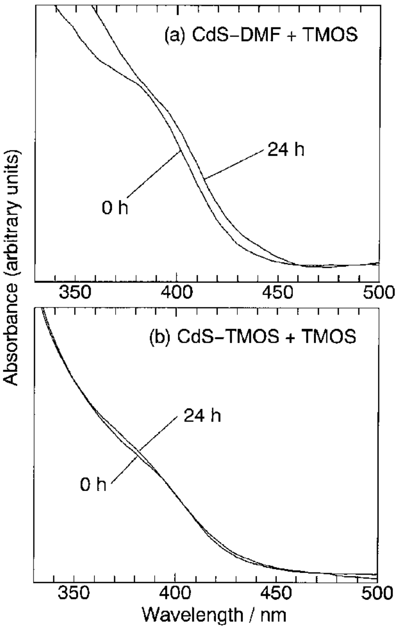

Fig. 4 Diffuse reflectance spectra for CdS nanoparticles in CdS–COL as prepared and following 24 h of photoirradiation in 15 vol% propan-2-ol aqueous solution. CdS–COL was prepared in MeOH by sequential addition of TMOS with (a) CdS–DMF and (b) CdS–TMOS.

Improvement of the stability of CdS–COL against photoirradiation

A sequential addition of TEOS or TMOS was employed, with first 0.08 ml and then later 0.72 ml being added after a 15 min interval, giving a total addition of 0.8 ml TEOS or TMOS. In the TEOS procedure, the CdS–COL particles were found to be further coated by a silica shell, such that the resulting CdS–COL lost photocatalytic activity. With TMOS, the second addition of TMOS caused the roughly aggregated composite clusters to become attached to one another. This obviously improves the stability of CdS–COL, in respect of maintaining their photocatalytic activity, as shown in Fig. 4(a).

The effect of the organic solvent used for the dispersion of the surface-modified CdS nanoparticles was then examined. Using chloroform or dichloromethane in place of DMF, the stability of CdS–COL prepared by the sequential addition of TMOS was found to be reduced, thus indicating that the stability of CdS–COL is seriously affected by the solvent. In order to improve the contact between the CdS nanoparticles and the TMOS molecules, TMOS itself was used as the dispersion solvent. The CdS–COL prepared in MeOH using CdS–TMOS (0.3 ml) and subsequent addition of TMOS (0.5 ml) has a morphology similar to that for CdS–COL prepared by using CdS–DMF. The stability *versus* photoirradiation is however, as shown in Fig. 4(b), improved by using CdS–TMOS, since almost no change is observed in the diffuse reflectance spectrum, following 24 h photoirradiation. The CdS nanoparticle size is estimated from the absorption onset wavelength as 3.7 nm. The photocatalytic property experiments were therefore carried out using CdS–COL prepared according to the procedure, in which CdS–TMOS and the subsequent addition of TMOS were employed.

Photocatalytic properties of CdS–COL

The quantity of the CdS nanoparticles can be easily controlled by controlling the quantity of CdS–TMOS involved in the sol–gel process. The quantity of H_2 per unit quantity of CdS, formed *via* the photocatalytic reaction, as shown in Fig. 5, increases with an increasing quantity of CdS in CdS–COL. The apparent mean diameter of CdS–COL also increases with an increase in CdS content, thus indicating that the presence of CdS nanoparticles in the sol–gel process may affect the CdS–COL morphology. Actually, the specific surface area for CdS–COL is increased by increasing the CdS content, with values of 174 $m^2\ g^{-1}$ for CdS-free silica colloid and which increases almost monotonously from 208 $m^2\ g^{-1}$ at 0.51 μmol CdS (g CdS–COL)$^{-1}$ to 256 $m^2\ g^{-1}$ at 3.05 μmol CdS (g CdS–COL)$^{-1}$. The effective surface area of the CdS nanoparticles incorporated in silica matrices is thus also probably increased by a rougher morphology.

The effect of the W_0 value of the reverse micellar system for the CdS preparation on the diffuse reflectance spectra and photocatalytic properties of the CdS–COL was also investigated and the results are shown in Figs. 6 and 7. The CdS nanoparticle size can be controlled precisely in reverse micelles by controlling W_0[4,5] and at the same time, the absorption onset of the CdS–COL can also be precisely controlled, although the lack of the exciton peak may indicate the increase in polydispersity of the nanoparticles.[27] The estimated particle sizes for the CdS range from 3.0 nm at $W_0 = 2$ to 3.8 nm at $W_0 = 8$. Although a discussion of the photocatalytic activity of CdS–COLs having a different absorption onset is rather difficult, it does appear that the quantity of H_2 formed is likely to increase with a decrease in W_0, probably owing to the increase in the effective CdS surface area due to decreasing CdS particle size.

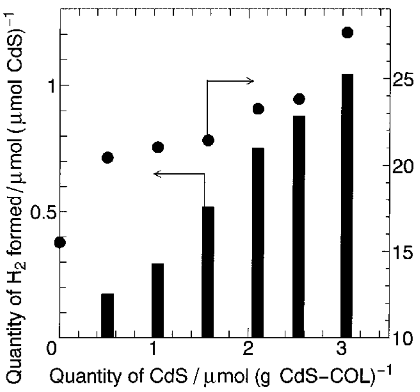

Fig. 5 Quantities of H_2 generated on CdS–COL *via* photocatalytic reaction for 12 h and the mean diameter of CdS–COL, as a function of the CdS content in CdS–COL.

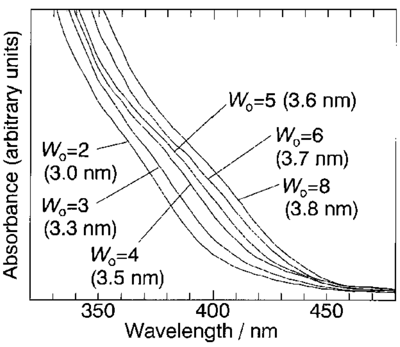

Fig. 6 Diffuse reflectance spectra and the estimated size of CdS nanoparticles in CdS–COL. Effect of the W_0 value of the reverse micellar systems used for CdS preparation.

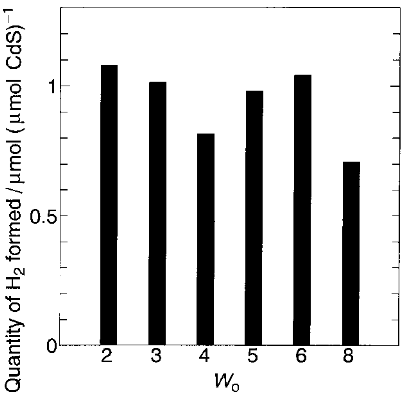

Fig. 7 Quantities of H_2 generated on CdS–COL *via* photocatalytic reaction for 12 h. Effect of the W_0 value of the reverse micellar systems used for CdS preparation.

Improvement in the stability of CdS–COL against heat treatment

The CdS–COL, prepared in MeOH using CdS–TMOS and the subsequent addition of TMOS, turned a brownish color, following heat treatment at 373 K, and a red shift in the absorption onset was observed. In order to improve the thermal stability of CdS–COL, 0.5 ml TEOS, in place of TMOS, was added 15 min after the addition of 0.3 ml CdS–TMOS, with the expectation of forming a silica shell over the CdS–silica composite cluster. This is similar to the strategy employed by Correa-Duarte *et al.*,[25] in which they reported that the stability of CdS nanoparticles against photoirradiation in the presence of O_2 was improved by a silica shell coating obtained *via* a sol–gel process using TEOS. The morphology of the resulting CdS–COL was effectively changed by use of different solvents in the sol–gel process. The apparent size of the CdS–COL was increased by increasing the EtOH/MeOH volume ratio, but the largest CdS–COL (*ca.* 80 nm in diameter) was obtained in acetone. The thermal stability of CdS–COL was found to be improved, as compared with in (a) 10 ml MeOH, by the use of (b) 5 ml MeOH + 5 ml EtOH, (c) 10 ml EtOH, and (d) 10 ml acetone. These latter cases of CdS–COLs, prepared using CdS–TMOS and TEOS, are stable against heat treatment up to 573 K, and are also stable against photo-irradiation except for (d), in which photo-induced CdS nanoparticle growth is observed. The photocatalytic activity of the CdS–COL is, however, decreased with increasing colloid size, probably because the silica shell decreases the effective surface area of the CdS nanoparticles. The quantity of H_2 formed following 24 h photoirradiation was 5.0 μmol H_2 (μmol CdS)$^{-1}$ for case (a), 3.9 μmol H_2 (μmol CdS)$^{-1}$ for case (b), 0.5 μmol H_2 (μmol CdS)$^{-1}$ for case (c), and 1.7 μmol H_2 (μmol CdS)$^{-1}$ for case (d), while 6.0 μmol H_2 (μmol CdS)$^{-1}$ was obtained for CdS–COL prepared in MeOH, using 0.3 ml CdS–TMOS and subsequent addition of 0.5 ml TMOS.

Preparation of CdS–GLA

The CdS–GLA obtained are transparent, but become yellowish in color with increasing W_0 value of the reverse micellar system used for CdS preparation, as was also the case for CdS–COL. As shown in Fig. 8, the absorption onset for CdS–GLA shifts from *ca.* 430 nm at $W_0 = 2$ to *ca.* 460 nm at $W_0 = 8$, thus indicating that the CdS–GLA can be utilized as a cut off filter.

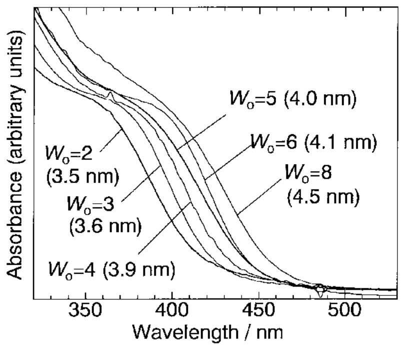

Fig. 8 Absorption spectra and the estimated size of CdS nanoparticles in CdS–GLA. Effect of the W_o value of the reverse micellar systems used for the CdS preparation.

The estimated particle sizes for CdS nanoparticles in CdS–GLA range from 3.5 nm at $W_o = 2$ to 4.5 nm at $W_o = 8$, and are larger in size than the corresponding particles for CdS–COL. The shrinkage of the silica gel during the course of CdS–GLA formation may cause some aggregation of the CdS nanoparticles.

Conclusions

The incorporation of CdS nanoparticles, prepared in reverse micellar systems, into silica matrices *via* a sol–gel process was investigated with the following results.

(1) CdS nanoparticle-containing silica colloids, CdS–COL, were prepared *via* surface modification of CdS nanoparticles in reverse micelles, recovery and dispersion of the nanoparticles, followed by a sol–gel process using TMOS and/or TEOS. The resulting CdS–COL was stable against both photoirradiation and heat treatment, and was utilized as a photocatalyst for H_2 generation from propan-2-ol aqueous solution.

(2) CdS nanoparticle-containing silica bulk glass, CdS–GLA, was also prepared, for which the cut off wavelength of the glass could be precisely controlled by controlling the W_o value of the reverse micellar systems used for the CdS preparation.

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