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Surface photochemistry: efficient photocatalysis by CdS supported on a solid surface

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The photocatalytic efficiency of a series of CdS samples: (i) a colloidal solution in aqueous CH_3CN; (ii) suspensions of (a) supported colloidal particles, (b) bulk CdS, and (c) commercial powders, was compared with respect to stilbene *c–t* isomerization. The samples of type (ii a), prepared from cadmium chloride and H_2S showed a high photocatalytic activity, attributable to the combined effects of the catalyst particle size and the presence of chloride ions. Increased activity over the commercial sample was also shown in the conversion of hexamethyl(dewar)benzene to hexamethylbenzene, and in the cleavage of anthracene dimer. It has been found that bulk CdS is activated by grinding with $<10\%$ of certain metal chlorides and bromides.

Keywords: Semiconductor photocatalysis; colloidal CdS; CdS on solid supports; isomerization; halide ion effect

1. Introduction

With the exception of oxidation and reduction [1], the application of semiconductor photocatalysis for more general organic transformations is an area yet to be explored [2]. Our primary interest in the study of semiconductor-mediated-photoassisted organic reactions stems from the expectation that, subsequent to the initial interfacial electron transfer, surface-controlled processes could lead to behaviour different from that observed using other modes of effecting the electron transfer, as has been shown for the oxidation of 1,1-diphenylethylene with TiO_2/O_2 by Fox and coworkers [3]. Also, the semiconductor-mediated process could provide a superior synthetic procedure, since, aside from the facile separation of the catalyst from the reaction mixture, the catalyst itself, unlike homogeneous redox photocatalysts [4], is not found combined chemically in any of the products. However, these advantages are as yet outweighed by the frequently very poor efficiency of the semiconductor-mediated reactions as compared to homogeneous processes. For example, in the valence isomerization of hexamethyl(dewar)benzene (HMDB) to hexamethylbenzene (HMB), quantum yields of up to 213 have been reported with organic photosensitizers [5], while low quantum yields (0.68 for CdS and 1.23 for both ZnO and TiO_2) were obtained for reaction initiated on the semiconductor surface [6]. The limited efficacity of the semiconductor-mediated process has been largely attributed to the rapid recombination of the holes with electrons; a process which is, for colloidal particles, on the ps-ns time domain. [7]. This recombination rate is of paramount importance in heterogeneous photocatalysis if organic transformations of practical interest are to be achieved.

A considerable amount of research, mainly concerned with the light-induced solar energy storage, has been focussed during the past decade on developing strategies to impede this electron-hole recombination [8,9]. These include the use of very small semiconductor particles which may possess intrinsically high photocatalytic activity. These particles, though prepared easily in low concentrations (10^{-3} M), require additives as stabilizers in some organic solvents [10], the presence of which as well as photoinstability of the small particles may make it difficult to employ for preparative purposes. The same is true, so far, for particles confined within the restricted spaces provided by reversed micelles [11], vesicles [12], glasses [13,14]; more encouraging reports have been made for polymer films [15], clays [14] and zeolites [14,16].

Another approach has been to avoid the energy wasteful recombination by scavenging the conduction band electron (or hole) by suitable sacrificial electron acceptors (or donors). For instance, surface modification of the semiconductor with suitable dopants, such as noble metals, which can act as a sink for the photogenerated conduction band electrons, permits the obtention of hydrogen from water [9]. Mixed semiconductor [17] and cofabricated colloidal sandwich structures [18], which can act as electron relays have also been employed. Surface adsorbed molecular oxygen [2], and, very recently CBr_4 [19], have been shown to enhance the rate of semiconductor-mediated photoreactions, the electron being trapped as superoxide and CBr_4^{-} respectively. While undesired oxygenation may accompany the product formation when oxygen is present [20], the rapid dissociation of CBr_4^{-} radical anion into reactive CBr_3 and bromide ion [21] limits the general applicablity of the latter acceptor. We report here our results on the preparation, and application to three organic reactions, of an efficient CdS photocatalyst which can be stored easily under normal laboratory conditions without losing its photocatalytic activity.

2. Experimental

MATERIALS

Chemicals were of reagent quality. Tlc grade silica gel (SG) and alumina (AL), both from CAMAG and without binder, were washed with CH_3CN and dried at 90°C. TiO_2 was obtained from Degussa; CdS from Strem Chemicals (99%; lot. no. NATL)-*here termed bulk-B CdS*. The source and purification of *cis*-stilbene, HMDB and dianthracene is described elsewhere [19].

METHOD OF CdS PREPARATION

(i) *Colloidal CdS* was prepared by a method similar to that described [22]. H_2S was bubbled slowly for 30 min through an Ar saturated solution of the Cd salt (1.0×10^{-3} M; 250 mL) in CH_3CN containing 2% water. Excess H_2S was removed by outgassing under reduced pressure, the sol was saturated with Ar, and stored at 5°C in the dark.

(ii) *Supported CdS*: A steady stream of H_2S was passed through a deoxygenated (Ar) stirred solution of the Cd salt (3.8×10^{-3} M to 3.3×10^{-2} M; 100 mL) in a 9:1 CH_3CN–H_2O solvent mixture for 4 min. After 10 min additional stirring, a weighed amount (2–3 g) of support material (SG, AL or TiO_2) was added and Ar passed through for 10 min. The CdS-loaded support material was filtered using a sintered crucible, washed with 100 mL CH_3CN, and dried (90°C; 72 hr). Alternatively, either if required or when Na_2S was used, the support material was added before introducing the sulphide reagent. Both preparations yielded equally active CdS samples. The supported catalysts thus obtained are referred in the text as SG–CdS, AL–CdS or TiO_2–CdS respectively.

(iii) *Bulk-A CdS*: Either, (a) a steady stream of H_2S was bubbled for about 4 min through an Ar saturated aqueous solution of the Cd salt (3.3×10^{-2} M; 100 mL), or (b) to an aqueous solution of Cd salt (Ar saturated) (3.7×10^{-2} M; 90 mL) was added, dropwise, an aqueous sodium sulfide solution (0.33 M; 10 mL). The precipitated CdS in both cases was filtered, washed with 200 mL water, and dried (90°C; 72 hr). Fine powders were obtained by grinding with a pestle & mortar.

(iv) *Physical Mixtures*: Weighed amounts of commercial CdS and metal salts (MS) or SG were ground together and dried (100°C) before use.

CHARACTERIZATION OF CdS PARTICLES

Photoluminescence data were collected on a Perkin-Elmer MPF-4 fluorescence spectrophotometer using a triangular cell for the colloidal sols and a 1 mm path flat cell, held at 45 °, in the front-face fluorescence of supported CdS. Particle size determinations utilized transmission electron microscopy (TEM), on a Philips EM 201, and scanning electron microscopy (SEM), on an ISI DS-130 instrument. Samples for TEM analyses were prepared as described by Ramsden and Grätzel [22]. SEM analyses were performed using the upper sample stage and the sample, a thin layer of the supported CdS on an aluminium block, was coated with a very thin conducting film of gold before analysis. The X-ray diffraction (XRD) analyses were obtained with a Rigaku diffractometer using Cu [K_α] radiation. The diffractograms were compared with those reported for standard CdS samples [23]. Diffractograms having broad and diffuse peaks as well as having some extra or missing some standard peaks were identified as polytypes. The average crystallite size was estimated from the XRD line width. Cadmium analyses were obtained by atomic absorption spectroscopy.

IRRADIATION PROCEDURE

A solution of organic substrate (dianthracene 0.002 M, *cis*-stilbene 0.015 M, HMDB 0.05 M; 4 mL) in dichloromethane in the presence of a weighed amount of CdS or supported CdS was sonicated for 10 min, then irradiated ($\lambda > 400$ nm) using a 1-kW PTI xenon lamp run at 840 W. IR radiation was removed by passage through 10 cm of water. Reduced light intensities, measured with a Scientech 364 power meter, were obtained by interposing wire mesh. The mixture was constantly stirred during the irradiation: the quantitative reproducibility of the reactions was *critically dependent on the manner of stirring*. Samples were deoxygenated by bubbling Ar through the solution and then sealed (Teflon tape). Anthracene formation was followed spectrophotometrically and *t*-stilbene and HMB formation by glc.

3. Results and discussion

Controlled introduction of H_2S into an aqueous CH_3CN solution (10^{-3} M) of cadmium chloride or perchlorate gave a comparatively stable CdS sol. When cadmium nitrate was used the CdS precipitated immediately. More concentrated solutions of cadmium chloride or perchlorate gave colloidal suspensions in 90% CH_3CN-H_2O which appeared turbid and the turbidity disappeared upon centrifugation. Addition of a support material such as silica gel to the colloids with stirring resulted in adsorption of the CdS particles. The supported CdS can be filtered, washed both with organic solvents and water, and dried. By varying the starting cadmium salt, sulphide reagent, initial Cd^{2+} concentration, and the type of support we were able to prepare a variety of supported CdS photocatalysts which could be compared with the bulk-A and bulk-B CdS.

The colloids were characterized by their absorption and emission spectra, particle size measurements; SEM, XRD and fluorescence analyses were used for the bulk and supported CdS samples. The absorption spectra recorded for the dilute colloidal suspensions are similar to spectra reported for larger particles (> 10 nm) [24]. The absorption rises steeply from the onset at 515 nm, towards short wavelength corresponding to the bulk bandgap excitation of 2.4 eV. The colloidal solutions from cadmium chloride and perchlorate gave fluorescence spectra different from each other and the emission maximum and intensity depended on the starting material. Thus, when the sol was prepared from $CdCl_2$, a relatively strong red emission (λ_{max} 700 and 760 nm) was observed in contrast to the green emission (λ_{max} 522 nm) reported for the aqueous colloidal suspension [25]. The CdS colloid derived from the perchlorate salt, however, showed a very weak emission with maximum centered at 580 nm. In both cases no green emission corresponding to direct electron-hole recombination was observed. The red emission has been attributed to sulphur vacancies acting as donors and reacting with photogenerated holes [22,25]. The 580 nm emission may have its origin in the recombination of the holes and electrons on the surface of the particles. This emission, found to be quenched by the presence of water [13a], is weak in intensity. The supported colloid prepared from dilute solutions of $CdCl_2$ showed fluorescence emission similar to that of the original sol: that is, the particles are largely unaffected by the transfer from the sol to the support. However, the supported CdS particles prepared from higher concentrations of $CdCl_2$ showed several emission maxima between 500 and 800 nm, the origin of which is unclear. TEM analyses of the sols prepared from $CdCl_2$ revealed the presence of large particles with average diameter of 13.5 nm; a similar particle size (~ 10 nm) has been reported for colloids prepared from $CdCl_2$ in the presence of polyphosphates [25]. Surface analyses (SEM) were carried out for the SG and AL supported CdS particles. While that of the SG–CdS catalysts showed the surface essentially unchanged, the AL–CdS catalyst revealed the presence of large sponge-type aggregates. SEM of deposited ZnS–CdS catalyst on Al_2O_3 has been reported to show particles with a diameter of 0.3 μm which in turn were aggregates of ~ 4 nm diameter particles [26]. XRD analysis gave the crystal morphology and the average crystallite size for bulk-A, bulk-B CdS powders and for the supported CdS particles (table 1). The XRD data suggests that the hexagonal (α) form is favoured by H_2S addition and that the cubic (β) crystals are formed with sodium sulphide. The XRD lines for the bulk-A CdS and the supported CdS catalysts were much broader [27] than those in the bulk-B CdS, and the estimated average crystallite size ranged from 4–16 nm. This broadening, presumably deriving from the small microcrystallites, indicates that the catalysts either consist of small particles or large clusters which contain small crystallites; the latter possibility seems to be more reasonable for the bulk-A CdS powders with small average crystallite size.

The bulk-A CdS samples, found to contain very small crystallites, were tested as photocatalysts in inducing stilbene *c–t* isomerization and the results, together for bulk-B CdS, are included in table 1. The commercial powder, chosen here for comparison, indeed had a large surface area (32.4 $m^2\ g^{-1}$) and a demonstrated high photocatalytic activity for N-vinylcarbazole dimerization [28]. The CdS-mediated stilbene isomerization is known to proceed in one direction (*cis* to *trans*) [2] and in the present study the disappeared *cis*-stilbene was converted to *trans* isomer quantitatively. The bulk-A CdS samples prepared from various cadmium salts, showed higher photoactivity than bulk-B CdS, but the increase

Table 1
Relative rates of *c–t* photoisomerization of *cis*-stilbene catalyzed by bulk-A CdS and SG-supported CdS samples prepared from various cadmium salts

Cd salt	Sulphide	Crystallite size (A)	Crystal type	Percent isomerization [a,b]
Bulk-A CdS				
chloride	H_2S	162	$\alpha+\beta$	55.4
perchlorate	H_2S	129	α	33.6
nitrate	H_2S	119	α	27.2
chloride	Na_2S	50	β	46.3
perchlorate	Na_2S	38	β	44.6
nitrate	Na_2S	43	β	39.9
Bulk-B CdS	–	255	polytype	23.5
SG-supported CdS [c]				
chloride	H_2S	99	α	89.2
perchlorate	H_2S	50	α	10.6
nitrate	H_2S	50	α	5.6
chloride	Na_2S	–	–	5.9
perchlorate	Na_2S	–	–	16.3

[a] The solutions of *cis*-stilbene (0.015 M; 4 mL) were irradiated ($\lambda > 400$ nm; Corning Filter 3.74) under comparable conditions for 2 min in the presence of 40 mg of bulk CdS or 40 mg (total weight) of SG-CdS catalysts.

[b] Amount of *cis*-stilbene disappearance; error: within 10%.

[c] Catalyst preparation employed 1.5 mmole cadmium salt per gram of SG support.

had no direct correlation with either the crystal type or the average crystallite size. Similar observations have been noted previously [6,28].

Dilute CdS sols (7.5×10^{-4} M) in 2% aqueous acetonitrile, prepared from $CdCl_2$ induced *c–t* isomerization of *cis*-stilbene (0.01 M), when irradiated ($\lambda > 400$ nm). While the initial efficiency of *trans*-stilbene formation was high, the CdS sol was unstable and was bleached readily under the irradiation conditions. This instability in the colloids limits their applicability as photocatalysts.

On the other hand supported CdS catalysts appeared to be stable and irradiation of a suspension of SG-CdS in CH_2Cl^2 also catalyzed the *c–t* isomerization of *cis*-stilbene. These SG-CdS catalysts, however, showed remarkable variation in their catalytic activity (table 1). Both starting cadmium salt and sulphide reagent appeared to affect the catalyst efficiency. The SG-CdS catalysts prepared using H_2S and cadmium salts such as perchlorate or nitrate showed photoactivity considerably less than the catalyst made from the chloride. Surprisingly, substituting Na_2S for H_2S, the chloride gave the less active catalyst. It should be noted that the supported CdS catalysts contained relatively small amounts of CdS. Nonetheless, in 2 min irradiation nearly 90% of *cis*-stilbene (0.015 M; 4 mL) was found to be isomerized. Under comparable conditions, a 40

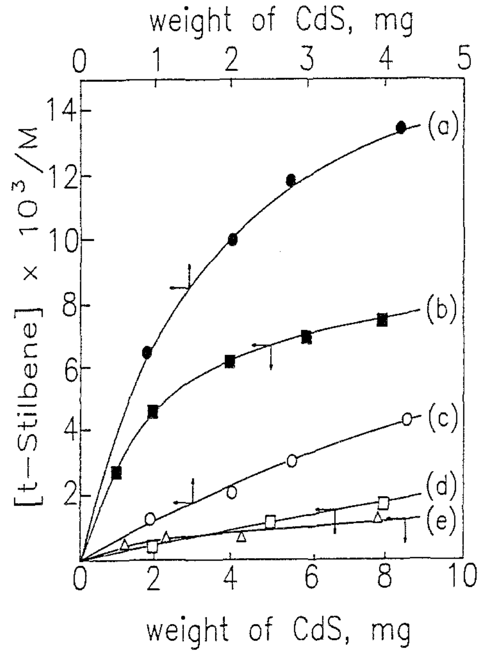

Fig. 1. Photoisomerization of *cis*-stilbene catalyzed by various CdS samples: (a) SG-supported CdS; (b) bulk-B CdS mixed with 8 mol% $CdCl_2$; (c) SG-CdS after washed with water; (d) bulk-B CdS; (e) physical mixture of bulk-B CdS and SG. In experiments with catalysts (a), (c), and (e), a 40 mg total weight of catalyst was employed.

mg sample of bulk-B CdS required about 30 min to attain about 80% reaction. Appropriate control experiments showed that both CdS catalyst and light were necessary for the reaction and no isomerization occurred in the presence of the support, $CdCl_2$, or both, either in the dark or under illumination. The effect of CdS mass (percent loading) on the photoisomerization efficiency was obtained using supported CdS (prepared from $CdCl_2$ and H_2S (see fig. 1(a)). The reaction yield increased nonlinearly with increased CdS loading and at high loading (about 12% based on Cd analysis) a plateau was reached indicating surface saturation. The catalytic efficiency of the SG–CdS catalyst was not much affected when washed with acetonitrile or methanol. However, after washing with water (and drying at 90°C) the photoreactivity decreased considerably (fig. 1(c)). Addition of $CdCl_2$ (~ 20% by wt.) to a previously washed SG-CdS catalyst or to a catalyst prepared from perchlorate salt resulted in a reaction efficiency increase (2–4 times). This suggested that the supported CdS catalyst prepared from cadmium chloride was very active not only because of the small CdS particles present but also because of the presence of chloride ions. Washing the supported catalysts with water appears to remove the adsorbed cadmium and chloride ions more effectively than the organic solvents ($CdCl_2$ solubility in acetonitrile: $\sim 10^{-3}$ mol L^{-1}).

Table 2
Effect of added metal salts (MS) on the bulk-B CdS catalyzed *c–t* photoisomerization of stilbene [a]

Added metal salt	Molar ratio of MS/CdS	Amount of CdS+MS used [b], mg	Percent isomerization [c]
none	–	40	22.2
effect of chloride ions			
$CdCl_2$	0.08	44	85.8
$BaCl_2 \cdot 2H_2O$	0.08	45	89.3
$SrCl_2 \cdot 6H_2O$	0.08	46	80.6
$PbCl_2$	0.08	46	80.7
NaCl	0.25	44	72.3
$ZnCl_2$	0.16	46	1.7
$InCl_3$	0.16	50	0.5
$SnCl_2 \cdot 2H_2O$	0.08	45	2.0
effect of bromide ions			
$CdBr_2$	0.16	52	87.1
NaBr	0.25	47	74.2
$PbBr_2$	0.08	48	89.4
effect of fluoride ions			
NaF	0.26	43	12.3
KF	0.12	42	4.8
effect of other cadmium salts			
$Cd(OAc)_2 \cdot 2H_2O$	0.16	46	< 0.1
$Cd(NO_3)_2 \cdot 4H_2O$	0.16	53	< 0.2

[a] The solutions of *cis*-stilbene (0.015 m; 4 mL) were irradiated ($\lambda > 410$ nm; Corning Filter 3.73) under comparable conditions for 2 min.
[b] All samples contained about 40 mg of bulk CdS.
[c] Amount of *cis*-stilbene disappearance; error: within 10%.

We have attempted to define the scope of the chloride ion effect. The bulk-B CdS powder was ground together with a number of metal chlorides and dried. The results obtained for the *c–t* isomerization are given in table 2 and compared in fig. 1(b) and 1(d)) where the amount of CdS with and without added $CdCl_2$ was varied. The reaction efficiency increases dramatically in the presence of added chlorides of cadmium, barium, strontium, and lead. Sodium chloride at high concentration was found to increase the rate moderately. However, the chlorides of zinc, indium, and tin appeared to quench the isomerization. Decrease in the reaction efficiency can be understood as resulting from the covering of the active sites on the catalyst surface by the added dopants, thus limiting the available active surface for the reaction. Bromides also increased the catalyst efficiency as effectively as chlorides. Fluoride ions and other cadmium salts, however, were not effective and, indeed, reaction was apparently quenched. The metal chlorides ($CdCl_2$ and $BaCl_2$) and bromides ($CdBr_2$ and $PbBr_2$) are transparent ($\lambda > 400$ nm) and did not themselves initiate any significant dark or light induced isomerization. The presence of silica gel per se was not responsible for the increased efficiency; addition of SG slightly decreased the activity of the bulk-B CdS (see fig. 1(e)).

That the reaction was catalytic, at least on the supported CdS, was indicated by the irradiation of a 40 mg sample of SG-CdS catalyst containing 6.4 mmoles CdS for 1 hour in the presence of *cis*-stilbene (7.5×10^{-2} M; 4 mL) which produced 195 mmoles of *trans*-stilbene. Also, the catalyst, when recycled, catalyzed the reaction with nearly equal efficiency.

A supported catalyst was also prepared using alumina or TiO_2 as support materials. The TiO_2–CdS catalyst was found to be about 50% more photoactive than SG–CdS while AL–CdS showed catalytic activity closer to that of SG-supported CdS. Like SG, the TiO_2 and alumina supports did not themselves initiate stilbene isomerization when irradiated with visible light (> 400 nm). The higher activity of the TiO_2–CdS catalyst was found, at least partly, to originate from the increased amount of CdS loading (about 16% based on Cd analysis) on the TiO_2 surface (33% more Cd in TiO_2–CdS compared to SG-CdS).

To ascertain whether the supported catalysts had general applicablity, or whether an idiosyncratic behaviour of *cis*-stilbene was being observed, the SG–CdS catalyst was used to effect the cycloreversion of dianthracene to anthracene, and the valence isomerization of HMDB to HMB. The results, presented in table 3, show the relative efficiency with respect to the bulk-B CdS. Since the SG–CdS mediated reactions are extremely fast, the reaction rates could not be compared at low conversions. Instead, the comparison was made of the time taken to bring the samples to nearly equal conversions. Since the reactions studied here proceeded cleanly with no apparent side reactions, the amount of product formed was taken as the reactant conversion. The supported catalysts are at least 40–53 times more efficient than commercial powder and this represents a minimum value as efficiencies obtained were not corrected for the difference in light absorption.

The CdS-mediated reactions described here are all quenched by the addition of electron donors such as 1,2,4-trimethoxybenzene (E_{ox} 1.12 V vs SCE [29]) (table 3), indicating the intermediacy of a radical cation. The increased photoefficiency of the catalyst then reasonably derives from the implied longer lifetime of the hole. It has been suggested that doping of cadmium chalcogenides with chloride ions introduces donor level below (0.023 eV) the conduction band [30]. Recently, the same energy level has been associated with interstitial sulphur (I_s) formation in the CdS by substitutional doping by chloride ions [25]; see also ref. [31]. Since the photogenerated electrons can equilibrate between the conduction band and I_s (or be trapped as I_s^-), the process could cause delay in the electron-hole recombination. The effect of halide ions on semiconductor-mediated photoreactions is relatively unstudied. Very recently a retarding effect of

Table 3
Relative efficiency of various photoreactions catalyzed by bulk-B CdS vs SG–CdS [a] catalysts

Irradiation conditions			reaction conversion [c] (%)	relative efficiency [h]
Catalyst	[quencher [b]] (M)	(time) (sec)		
c–t isomerization of stilbene (0.015 M) [d]				
bulk CdS	–	900	49.6	
SG–CdS	–	20	45.3	41
SG–CdS	7.5×10^{-3}	20	<0.5	
valence isomerization of HMDB (0.05 M) [e,f]				
bulk CdS	–	1080	51.3	
SG–CdS	–	20	48.4	51
SG–CdS	2.1×10^{-2}	20	1.2	
cycloreversion of anthracene dimer (0.002 M) [d,f,g]				
bulk CdS	–	1800	17.5	
SG–CdS	–	30	15.4	53
SG–CdS	1.8×10^{-3}	30	4.8	

[a] The catalyst was prepared using 3.3 mmoles of $CdCl_2$ and 2 g SG.

[b] 1,2,4-trimethoxybenze.

[c] For each reaction, a set of irradiations were done under comparable conditions in the presence of 40 mg of bulk CdS or 40 mg (total weight) of SG–CdS catalyst; error: within 10%.

[d] Irradiation wavelength >410 nm (Corning filter 3.73).

[e] Irradiation wavelength >400 nm (Corning filter 3.74).

[f] Light intensity was reduced by placing four sheets of wire mesh before the sample.

[g] Reaction mixtures were purged with argon prior to irradiation.

[h] Ratio of the time required to effect equal amount of reaction catalyzed by SG-CdS vs bulk-B CdS and the values are not corrected for the difference in light absorption.

chloride ions on the TiO_2 mediated photo-oxidation of organic compounds in aqueous medium has been reported [32].

4. Conclusion

We have demonstrated that colloidal CdS particles possessing a high photocatalytic activity can be prepared and adsorbed onto various supports. Such supports provide convenient means of storage of the colloidal particles under normal laboratory conditions. The relatively high photocatalytic efficiency of adsorbed CdS particles (~ 50 times as compared with bulk CdS powder) prepared from cadmium chloride and H_2S is then tentatively rationalized on the basis of the small size of the CdS particles and the presence of chloride ions. The latter may function by the introduction of donor level (electron trap) lying close to the conduction band. We have also shown that the photocatalytic efficiency of commercial bulk CdS powder can be increased by addition of chloride and bromide ions.

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