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Preparation of stable CdS nanoparticles in aqueous medium and their hydrogen generation efficiencies in photolysis of water

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ABSTRACT

Diallyl dimethyl ammonium chloride (DADMAC)-N-vinyl 2-pyrrolidinone (NVP) copolymers were demonstrated to provide excellent stabilities for *in situ* generated CdS nanoparticles in aqueous medium. Nearly transparent and stable CdS dispersions (up to 0.1 M concentrations) were produced in 1% copolymer solutions. Experiments showed that, increasing DADMAC content induces greater stabilization. UV-visible spectroscopy, fluorescence spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used for characterization of the stable nanoparticles. TEM images showed snake-like alignment of nonspherical CdS nanoparticles with 50–70 nm of size, due to template effect of the cationically charged polymer.

The CdS nanoparticles in aqueous medium showed reasonably high catalytic activities in photolysis of water, as inferred from hydrogen evolution measurements carried out in the absence and presence of noble metals, Pd and Pt. The highest hydrogen evolution rate (5.6 mL per gram of CdS in min) was detected in the presence of Pt metal, while illuminating with mercury lamp (160 W).

1. Introduction

Synthesis of nanometer size of semiconductor and metal particles has found great interest, in recent years, due to their size dependent optoelectronic and catalytic properties [1–3]. Those properties are associated with their high surface area-to-volume ratio and quantum confinement effects. Having unusual properties these nanomaterials have found wide application in various fields such as in light-emitting diodes [4,5], electrosensors [6], photocatalysis [7] and so forth.

Of many semiconductor materials CdS is of special interest because of its high band gap between the valence and conduction bands (2.41 eV). There appear many significant reports in the literature dealing with preparation of CdS nanoparticles dispersible in organic media. *In situ* formation of CdS in presence of thiols or dithiocarbamates has been demonstrated to be successful for producing stable nanoparticles. Various thiols with different chain lengths have been studied as capping and stabilizing agents.

Sastry et al. [8] obtained stable nanoparticles of CdS by coordinating with octadecanethiol in water–petroleum ether mixtures, based on ‘‘two-phase approach’’ developed by Brust and his coworkers [9]. Various sulfur compounds such as mercaptoacetic acid [10], 2-mercapto-ethanol [11], thiourea [12], long chain alkyl xanthates [13] and thioglycerol [14] have been used as capping or stabilizing agents for preparing CdS

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nanoparticles. Bunker and Harruff [15] were able to obtain stable nanoparticles in reverse-micelle system (water in hexane) by using only sodium dioctyl sulfosuccinate (AOT) as stabilizing agent.

Polymers such as poly (N-vinyl 2-pyrrolidinone) [16] and poly (oxyethylene)$_{10}$-nonyl phenol ether [17] have been employed in stabilization of CdS nanoparticles.

Block copolymers forming micelles in selective solvents have also been used to produce CdS nanoparticles. In such system the micelle cores behave as nanoreactors in which the particles grow up to a limited size confined by the micelle core.

Douglas et al. [18] described preparation of CdS nanoparticles with controllable size by reaction with H_2S in micellar solution of styrene-2-vinyl pyridine block copolymers using tetrahydrofurane as solvent. Also amphyphilic block copolymer, poly (styrene-b-ethylene oxide) [19] has been used in stabilization of CdS nanoparticles by hydrogen bonding with the polyethylene oxide block.

Agostiano and coworkers [20] reported a useful procedure yielding relatively narrow size of CdS nanoparticles (35–40 nm) by cetyl trimethyl ammonium bromide (CTAB) forming reverse micelles in water–*n*–hexane mixture. Presumably the stabilization in this case is provided by double salt formation between the quaternary group and CdS. Also styrene-based diblock ionomers have been demonstrated to form spherical CdS particles in nanosizes [21]. Interestingly Moffitt and Eisenberg showed that CdS nanoclusters are obtained in the same reaction conditions in presence of random ionene–styrene copolymers [22].

Despite tremendous reports dealing with oil-soluble CdS nanoparticles, there appear only few reports on the preparation of water-soluble CdS nanoparticles [23–25]. However stability of CdS is of special interest due to its well-known catalytic activity in photodecomposition of water to generate hydrogen.

Hydrogen generation by photolysis of water using solar energy has been one of the most popular area of research, since the first World Hydrogen Energy Conference in 1976 [26]. Various biological [27] and chemical photocatalysts such as TiO_2, CdS and tantalates [28,29] have been described and compared with each other. Considerable efforts have also been devoted to combination of those semiconductors to improve light absorption and carrier generation for better hydrogen generation from water [30].

In this article, we report preparation of CdS nanoparticles stable in aqueous solutions by using copolymers of *N*,*N*-diallyl *N*,*N*-dimethyl ammonium chloride (DADMAC) with *N*-vinyl 2-pyrrolidinone (NVP) as stabilizer. To the best of our knowledge this is the first report dealing with stabilization of nanosize CdS by quaternary ammonium polymers in water. The procedure presented herein yielded nearly transparent and stable dispersions. UV-vis spectroscopy, X-ray diffraction (XRD), light scattering (LS), and transmission electron microscopy (TEM) were employed to examine physical characteristics of the CdS dispersions. TEM images of these solutions revealed aligned clusters consisting of 50–70 nm size of nonspherical CdS particles.

Photocatalytic activities of the solutions were investigated by measurement of evolved hydrogen under illumination with mercury lamp (160 W). Effects of Pt and Pd metals on hydrogen evolution were also studied.

2. Experimental

2.1. *Materials*

N-vinyl pyrrolidinone (NVP) (Alrich) was distilled before use. All the chemicals used were analytical grade products; 2,2′-azobis-(2-methyl propionamidine) dihydrochloride (AMP) (Alrich), *N*,*N*-dimethyl *N*,*N*-diallyl ammonium chloride (DADMAC) (65% aqueous solution) (Alrich), $Na_2S \cdot H_2O$ (E. Merck), $Cd(NO_3)_2 \cdot 4H_2O$ (E. Merck). They were used as purchased.

2.2. *Preparation of DADMAC–NVP copolymers*

The copolymers were prepared according to the procedure described before [31]. In a typical procedure, 24.9 g (0.1 mol) commercial *N*,*N*-diallyl *N*,*N*-dimethyl ammonium chloride solution (65%), 11.2 g (0.1 mol) 1-vinyl 2-pyrrolidinone (99.5%) and 32.4 mL distilled water were charged to 100 mL volume of three-necked flask equipped with a reflux condenser. To the mixture with 40% of total monomer concentration 0.562 g (2×10^{-3} mol) 2,2′-azobis-(2-methyl propionamidine) dihydrochloride (AMP) was added and nitrogen was flushed for 5 min. Then the mixture was stirred for 1 h at 65 °C. The mixture was cooled to room temperature and poured into 150 mL of isopropanol. The solvent was decanted and the residue was dissolved in 60 mL methanol and reprecipitated in acetone (100 mL). The polymer was isolated by decanting the solvent and dried at 70 °C under vacuum for 24 h.

By the same procedure homopolymer of DADMAC and the monomer mixtures with 1/3 and 3/1 molar ratios of DADMAC/NVP were polymerized to obtain copolymers in different compositions.

2.3. *Preparation of CdS nanoparticles*

The aqueous dispersions of CdS nanoparticles were prepared by gradual addition of cadmium nitrate solution to the copolymer solutions in presence of sodium sulfide. In a typical procedure one gram of dry copolymer with 1/1 DADMAC/NVP ratio was dissolved in 20 mL water in a beaker. In another beaker 2.4 g (0.01 mol) $Na_2S \cdot 9H_2O$ was dissolved in 60 mL water. The solutions were combined and a solution of $Cd(NO_3)_2 \cdot 4H_2O$ (3.08 g, 0.01 mol) in 100 mL water was added dropwise to the above solution within 5 min, while sonicating with a Bandelin sonopuls HD 3200 homogenizer at 20 KHz (using MS 72 probe at 30% power out). A faintly yellow and nearly transparent solution was obtained.

2.4. *The characterizations*

Characterization of the copolymers and CdS dispersions was performed by the following instruments. Gel Permeation Chromatography (GPC) traces of the copolymer samples were taken by Hewlett Packard 1050 A series instrument, in water with a flow rate of 0.5 mL/min using aqueous polyethylene glycols as standards. ^1H-NMR spectra of the polymers were obtained in D_2O by a Bruker AC (250 MHz) spectrometer. FT–IR spectra were recorded on a Perkin Elmer FT–IR Spectrum One B spectrometer. The fluorescence emission measurements were carried out using Varian Cary Eclipse Fluorescence Spectrophotometer at 90° position. UV-visible spectra were obtained a Chebios Optimum-One UV-Visible Spectrophotometer. The transmission electron microscopy (TEM) images were recorded with a JEOL-JEM 100SX microscope, working at a 100 kV accelerating voltage. Samples for TEM were prepared by drip-drying of the aqueous dispersions on a copper grid (400 meshes) coated with carbon film.

DADMAC contents of the copolymers were assigned by chlorine analysis using mercuric thiocyanate method [32]. X-ray diffraction (XRD) patterns of the CdS samples were recorded using a SHIMADZU XD-D1 diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). Powder samples were prepared as follows: to 10 mL of the aqueous dispersion there was added 0.5 g NaCl and heated to 90 °C for 30 min. The yellow precipitate was filtered, washed with alcohol and dried at 50 °C for 6 h under atmospheric pressure.

2.5. *The hydrogen generation measurement*

Amounts of hydrogen evolved the aqueous dispersions were measured by gasometrically while illuminating with 160 W Hg lamp. The samples (50 mL) containing 0.1 g CdS were prepared by appropriate dilution of above dispersions. Then, 1.9 g (15 mmol) Na_2SO_3 and 2.4 g (10 mmol) $Na_2S\cdot 9H_2O$ were dissolved in it. The resulting transparent solution was charged to a 100 mL volume of flat-bottom flask mounted on a magnetic stirrer. The flask was connected with a gas outlet tube, end of which was connected to the top of an inverted gas burette partially immersing in water. The solution was irradiated with a mercury lamp (160 W, OSRAM HWL, E27) while stirring and volume of the evolved gas was monitored by displacement of water level inside the burette. To investigate effects of noble metals on the hydrogen evolution experiments were repeated in the presence of elemental Pt and Pd. K_2PtCl_6 and Pd $(CH_3COO)_2$ were used respectively as source of these metals. These metals were generated *in situ* from their dilute solutions mixed with mother liquor and following addition of 0.1 mL hydrazinium hydroxide solution (60%) while stirring. Concentrations of the noble metals were chosen as 1 mg per 50 mL of CdS solution.

2.6. *Measurement of the quantum yield*

Quantum yield of the hydrogen generation was estimated by ferrous oxalate ($K_3Fe\ (C_2O_4)_3\cdot H_2O$) actinometer system ($Ø_o = 0.605$). Three minutes of illumination of 50 mL standard solution (6.47×10^{-5} M) with the mercury lamb indicated a 3.26 μmol Fe (II) formation. Comparing with the hydrogen evolution (≈70 μmol per 3 min) from Pt activated sample (stabilized with poly (DADMAC)), this value implies a quantum yield of 1.3%. The quantum yields for the other samples would be proportional to their hydrogen evolution rates.

3. Results and discussion

To stabilize CdS nanoparticles in aqueous medium DADMAC–NVP copolymers were chosen. Quaternary amino group the DADMAC component was considered as binding sites for nanosize CdS particles via ionic bond formation, while the NVP component was expected to provide steric stabilization. CdS was *in situ* formed in aqueous solutions of the polymers under sonication.

3.1. *Preparation and characterization of the copolymers*

DADMAC–NVP copolymers used for stabilization CdS nanoparticles were prepared as described by us [31] and Tophichev et al. [33]. It was demonstrated that radically initiated copolymerization of DADMAC with NVP in concentrated aqueous solution (40% w/w) yields mostly alternating copolymers (Scheme 1) as inferred from the reactivity ratios, $r_1 = 0.79$ and $r_2 = 0.82$ (by Finemann–Ross method for DADMAC and NVP respectively).

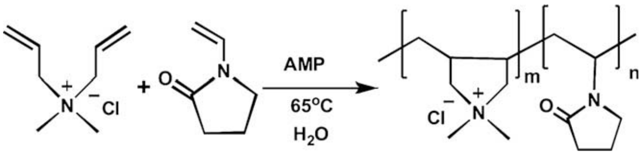
The alternating tendency was ascribed to partial charge transfer interaction between the two monomers.

It was also found that the reactivity ratios are concentration dependent due to strong electrostatic repulsion of the quaternary ammonium groups of the DADMAC component, as in the case for its copolymerization with acryl amide [34]. Molecular weights and compositions of the copolymers employed in stabilization of CdS are given in Table 1. The numbers of repeating units of the comonomers were simply estimated by correlation of the molecular weights with the chlorine analysis data.

3.2. *Preparation and characterization of CdS nanoclusters*

The CdS nanoparticles were generated by gradual addition of cadmium nitrate solution (1 M) to the solution of sodium sulfide–copolymer mixture in water under sonication. This procedure gave nearly transparent and light yellow solutions. In order to inspect stabilization limits of the copolymers, to their solution (1 g polymer in 40 mL water) there was added cadmium nitrate solution (0.25 M) until persisting clouding of the solutions, in presence of excess sodium sulfide (20 mmol). The molar ratio of cadmium nitrate to DADMAC segment was used as a measure of the stability limit for the copolymers. This ratio was found to be around 0.8 for the case of copolymers with higher DADMAC units (Table 2).

This means that remaining 20% of DADMAC repeating units involves in stabilization of the particles for the case of poly (DADMAC). The same CdS/DADMAC ratio for the case of P3 implies that the charged segments provide much higher stabilization, comparing with non-charged NVP units. Although this ratio is slightly greater for the case of P1 (see first column of Table 2) upper limit of CdS concentration in this case is low (0.05 M).



Scheme 1 – Copolymerization of DADMAC with NVP.

Table 1 – Physical characteristics of the poly (DADMAC) and its copolymers employed in stabilization of CdS nanoparticles ([Initiator]/[Monomers]: 1/100, total monomer concentrations: 40.0% (w/w), at 60 °C).

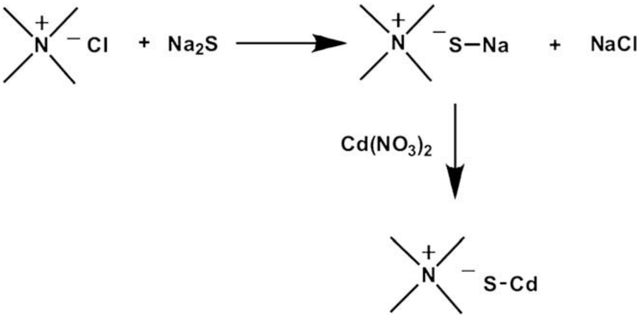
Initial DADMAC/NVP molar ratio	Polym.	Chlorine content (mmol g^{-1})	Molar ratio of DADMAC		GPC[a]		The copolymer composition
			(by chlorine analysis)	(by NMR)	M_w	M_n	
1/3	P1	2.00	24.7%	24.2%	16000	13900	$(DADMAC)_{32}$-co-$(NVP)_{97.5}$
1/1	P2	3.70	50.6%	48.9%	14700	11000	$(DADMAC)_{54.5}$-co-$(NVP)_{53}$
3/1	P3	5.04	75.1%	73.2%	11500	9600	$(DADMAC)_{58}$-co-$(NVP)_{19}$
1/0	P4	–	–	–	11200	10100	Poly (DADMAC)

a GPC traces were taken in aqueous solutions, using polyethylene glycol standards.

Table 2 – Comparison of stabilization limits and hydrogen evolution rates of the CdS nanoparticles in aqueous solution of DADMAC–NVP copolymers.

Copolymer	Limit conc. of CdS[a]	[CdS]/[DADMAC]	Stability under irradiation	Hydrogen evolution rate (μmol/0.1 g min)
$(DADMAC)_{32}$-co-$(NVP)_{97.5}$	0.05 M	1.0	Fair	6.7
$(DADMAC)_{54.5}$-co-$(NVP)_{53}$	0.071 M	0.82	Good	6.8
$(DADMAC)_{58}$-co-$(NVP)_{19}$	0.088 M	0.80	Excellent	6.9
Poly (DADMAC)	0.104 M	0.81	Excellent	7.0

a Determined by gradual addition of 0.1 M Cd(II) to a 80 mL solution containing 1 g polymer and 0.01 mol sodium sulfide.



Scheme 2 – Stabilization of CdS nanoclusters by quaternary ammonium groups of the polymers in water.

The solutions showed no evidence of precipitation upon standing for over 3–4 days at room temperature. The yellow solutions stabilized with P3 and P4 did not show any precipitation for over 20 days at the same conditions.

Most probably stabilization by the copolymers is being maintained by double salt formation between CdS^- and the quaternary ammonium group as depicted in Scheme 2. The ionic interaction with some percent of the cationic groups makes the copolymer a good binder for CdS particles and rest portion of charged groups, together with NVP segments, impart solvation effect to hold the polymer–CdS complex stable.

UV absorption spectrum of the CdS dispersion (Fig. 1) stabilized with 1/1 DADMAC–NVP (P2) copolymer shows one maximum at 340 nm and a shoulder around 460 nm. The shoulder can be ascribed to the surface plasmon absorption of

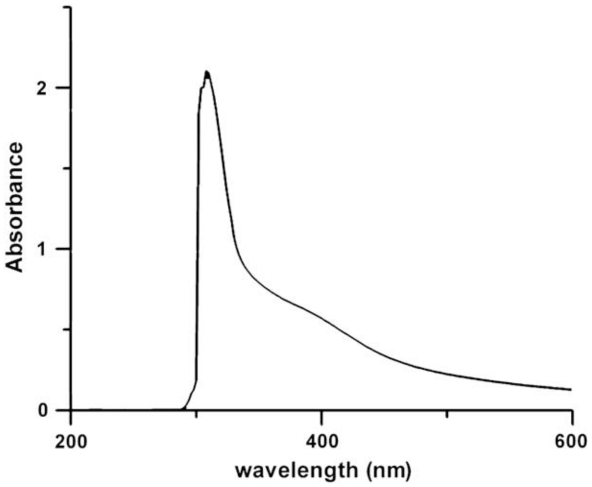


Fig. 1 – UV-Visible spectrum of aqueous CdS nanoparticle dispersion stabilized with $(DADMAC)_{54.5}$-co-$(NVP)_{53}$.

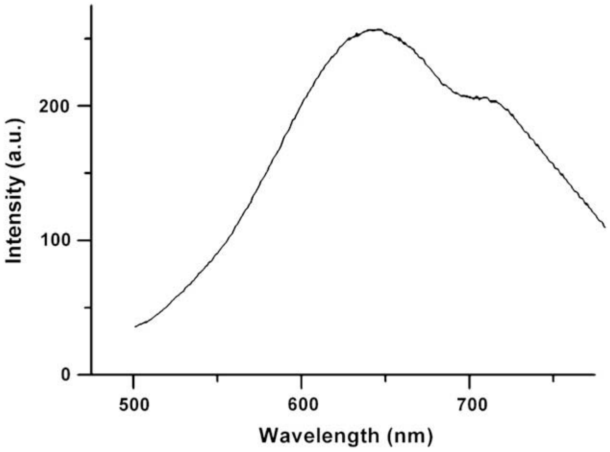


Fig. 2 – Fluorescence emission spectrum of aqueous CdS nanoparticle dispersions stabilized with $(DADMAC)_{97}$-co-$(NVP)_{34}$ (excitation wavelength, 390 nm).

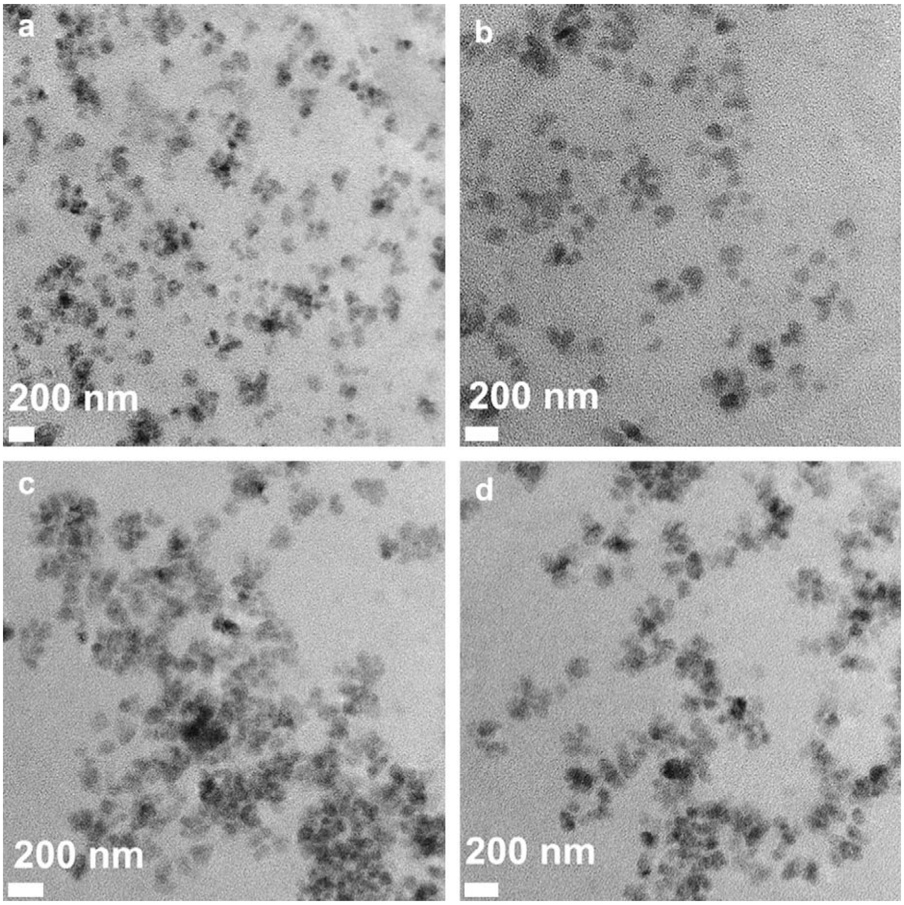


Fig. 3 – TEM images of stable CdS particles stabilized with P1 (a), P2 (b), P3 (c) and poly (DADMAC).

the CdS particles. In the spectrum the absorption edge is observed at 520 nm of wavelength which is relatively longer than those for the nanoparticles with diameters below 20–30 nm.

Photoluminescence (PL) spectra of the aqueous dispersions were obtained by excitation at 390 nm. PL spectra of the sample with 0.3 g/L of CdS show a broad emission band in 550–800 nm range as shown in Fig. 2. Position of emission maxima and bandwidths is known to be related to the shape and size of the particles [35,36]. So the fluorescence at longer wavelength must be associated with the dimensions of CdS particles.

Presence of two emission maxima at 650 and 720 nm in the spectrum is somewhat unusual. The reason for the second maximum is unclear yet. Most probably this maximum might be due to fluorescence emission of peripheral CdS^- ions contacting with the quaternary ammonium groups of the stabilizing copolymer. Net charge on CdS may causes reduction of energy of the excited triplet level to give an additional emission maximum at longer wavelengths.

Interestingly TEM images of the dispersions in Fig. 3 show nonspherical CdS particles. There are no significant differences in the particle sizes of the samples with different stabilizing copolymers. In all samples the particle sizes are in 50–70 nm range. Marked difference in Fig. 3d is that, the CdS particles stabilized with poly (DADMAC) exhibit snake-like orientation. Although some partial orientations are also observed in the other samples, such alignment seems to be increasing by increasing DADMAC content in the stabilizing copolymer. This assembling might be due to the template effect induced by cationic groups on the stretched copolymer chains.

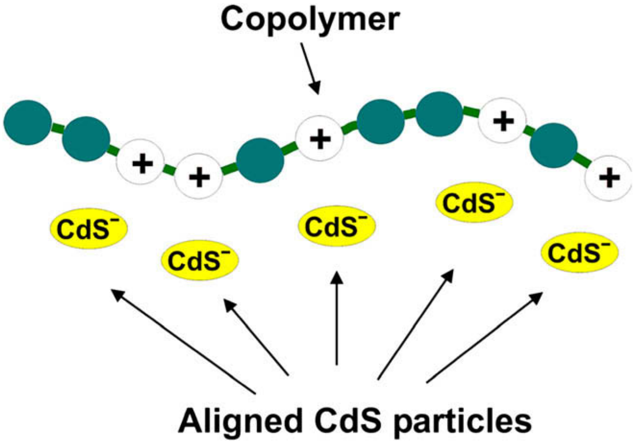


Fig. 4 – Schematic illustration for stabilization and alignment of CdS nanoparticles by template effect of the cationic copolymer.

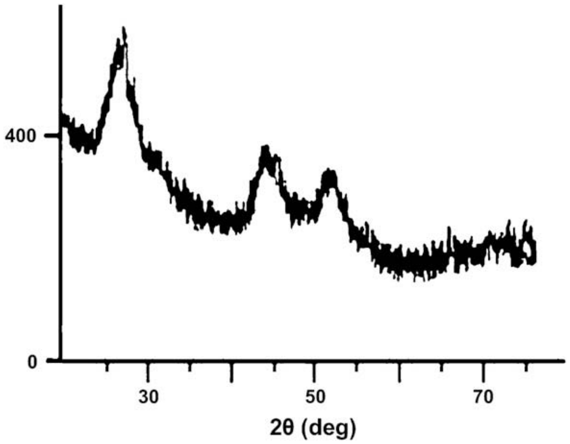


Fig. 5 – XRD pattern of CdS nanoparticles stabilized with DADMAC–NVP (1/1) copolymer (P1).

Having fully ionized quaternary ammonium groups, poly (DADMAC) chains are expected to take stranded form in the solution normally. The CdS particles *in situ* generated accumulate along side with polymer chains in the aqueous solution. Most probably this assembling is being disturbed while agitation. Upon standing, oriented form is restored to give snake-like figures, as seen in the simplified picture in Fig. 4.

XRD patterns of CdS powders (Fig. 5) obtained by precipitation from the disperse samples show three peaks with 2θ values of 26.507°, 43.917° and 51.911° corresponding to the (111), (220) and (311) planes respectively for the cubic phase [37] of β-CdS (JCPDS01-0647). The crystalline dimensions were found to be $a = b = c = 5.82$ Å.

3.3. *Hydrogen generation efficiencies of the dispersions*

The aqueous dispersions (50 mL) containing 0.1 CdS were used for hydrogen generation in presence of NaS and Na_2SO_3 as sacrificial reagents. This was performed by monitoring volume of evolved hydrogen while illuminating with a mercury lamp (160 W) for 4 h. One of the common problems in the hydrogen generation is photocorrosion of CdS. To avoid this problem a mixture of sodium sulfide and sodium sulfite was used as suggested in the literature [38].

However the use of more than 1 g of sodium sulfite per 50 mL of solution resulted in sudden precipitation of CdS.

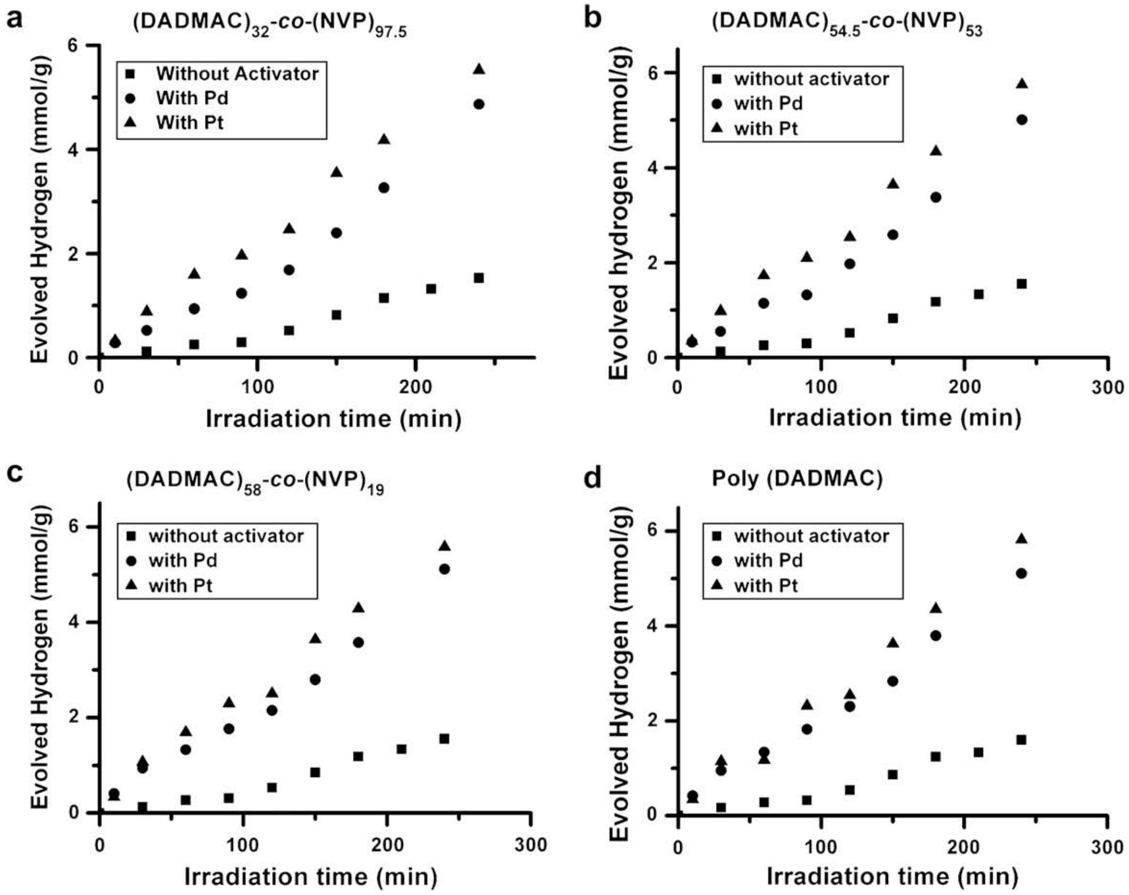


Fig. 6 – a): Hydrogen generation by irradiation of CdS nanoparticles (0.1 g/50 mL) stabilized with P1 in the absence and presence of the noble metal actuators. b): Hydrogen generation by irradiation of CdS nanoparticles (0.1 g/50 mL) stabilized with P2 in the absence and presence of the noble metal actuators. c): Hydrogen generation by irradiation of CdS nanoparticles (0.1 g/50 mL) stabilized with P3 in the absence and presence of the noble metal actuators. d): Hydrogen generation by irradiation of CdS dispersions (0.1 g/50 mL) stabilized with poly (DADMAC) in the absence and presence of the noble metal actuators.

Table 3 – Effects of noble metals on the hydrogen evolution rates of the dispersions stabilized by DADMAC–NVP copolymers.

Copolymer	Hydrogen[a] evolution rate (μmol/0.1 g.min) (without activator)	Hydrogen[b] evolution rate (μmol/0.1 g.min) (activated with Pd)	Hydrogen[c] evolution rate (μmol/0.1 g.min) (activated with Pt)
$(DADMAC)_{32}$-co-$(NVP)_{97.5}$	6.7	19.0	22.8
$(DADMAC)_{54.5}$-co-$(NVP)_{53}$	6.8	19.5	22.9
$(DADMAC)_{58}$-co-$(NVP)_{19}$	6.9	19.5	23.0
Poly (DADMAC)	7.0	19.3	23.1

a With 0.1 g CdS in 50 mL water.
b With 0.1 g CdS plus 1 mg Pd.
c With 0.1 g CdS plus 1 mg Pt metals.

Excess Na_2SO_3 was especially detrimental for the sample stabilized with P1 and P2. This can be considered as evidence for the assumption of double salt formation between the quaternary ammonium groups of the copolymer and CdS^- anions, as discussed above. Addition of excess Na_2SO_3 causes to exchange of CdS^- counter anions of the polymer with sulfite ions and the coalescence takes place. Having less DADMAC contents the quaternary groups of P1 are blocked with sulfite anions in low concentrations. The other polymers with higher DADMAC segments are less prone to destabilization with Na_2SO_3. For this reason, in these experiments 0.5 g of Na_2SO_3 was employed per 50 mL solutions. Amount of hydrogen versus irradiation time plots is linear as shown in Fig. 6.

From the slopes of the curves hydrogen evolution rates of the samples were found to be in 6.7–7.0 μmol per 0.1 g CdS in minute (Table 2). This reveals almost equal activity of CdS nanoparticle dispersions. This might be due to nearly equal surface area of CdS particles in the samples. This makes approximately 1.7 mL/min of hydrogen gas per gram of CdS.

The nanoparticle dispersions did not show any precipitation while illuminating with the mercury lamp.

Moreover, we have also studied stabilities of the irradiated solutions against sunlight irradiation. The stability limits of the solutions were simply estimated by exposure of the samples to sunlight. It was observed that in the case for the samples stabilized with the copolymers, P1 and P2 possessing 25–50% of DADMAC precipitated within two and three days respectively. However the other samples constituting P3 and P4 did not show any sign of precipitation within 6 days.

3.4. *Effects of noble metals*

Presence of noble metals has been reported to enhance catalytic activity of CdS in hydrogen generation [39] from water. Ranjit et al. [40] reported that hydrogen evolution rates are closely related to redox potential, work function and hydrogen bond energies of the noble metals employed and those metals with more positive reduction potential and less hydrogen bond energy, provide better hydrogen evolution.

In order to inspect effect of noble metals on hydrogen evolution, those experiments were repeated in presence of Pd and Pt (1 mg per 50 mL solution) metals. Fig. 6 shows photogenerated hydrogen as a function of irradiation time in the presence and absence of the noble metals.

From Fig. 6 and from Table 3, it is clearly seen that, in the presence of Pd and Pt metals the hydrogen evolution rates increase almost by a factor of 3. For the case of Pd metal the hydrogen evolution rate is around 19.5 μmol/0.1 g min, which corresponds to 4.7 mL hydrogen per gram of CdS in minute. Even higher hydrogen evolutions were observed by activation with Pt. All the samples having minute amount (0.1 mg) of Pt showed substantially higher hydrogen evolutions. Overall quantum yield of the hydrogen generation from the Pt activated sample was determined to be 1.3% by ferric oxalate method. These results are inconsistent with those reported by Sathish et al. [2].

Twenty-three micromoles of average hydrogen evolution per 0.1 g in minute come to 337 mL of hydrogen per hour, per gram CdS. As far as we know, taking power of the mercury lamp (160 W) into consideration, these hydrogen evolution rates are higher than those reported so far, for the photocatalytic systems with CdS.

The high hydrogen evolution rates attained must be due to transparency of the dispersions which allow penetration of the light. Since the CdS particles are not thoroughly encapsulated by the copolymers, these particles must be in contact with water. This fact might be another factor for the high photocatalytic activities.

4. Conclusion

Generation of CdS in aqueous solutions of DADMAC–NVP copolymers yields highly stable and concentrated nanoparticles. This procedure yields 50–70 nm sizes of nonspherical CdS particles. These particles form snake-like assembling, due to template effect of the quaternary ammonium groups of the copolymer in the stranded form. The resulting transparent dispersions show excellent photocatalytic activities in hydrogen generation from water. Regarding with the commercial availability of the starting materials, the procedure presented in this work provides a means of easy access to stable CdS nanoparticles having high catalytic activities for photolysis of water. Although there remain many things, such as long-term stability and control of the nanoparticle sizes to be studied, the results attained in this work are promising and deserve detailed investigations.

The results also show that, even higher catalytic activities can be attained by using smaller and more stable CdS nanoparticles in water. This study also implies that, the idea of cost effective hydrogen generation by photocatalytic means is not unrealistic.

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