

**A NOVEL METHOD FOR STABILIZATION OF CdS
NANOPARTICLES IN AQUEOUS MEDIUM**

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**CdS NANOTANECİKLERİNİN SULU
ORTAMDA KARARLI KILINMASI İÇİN YENİ BİR
YÖNTEM**

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LIST of ABBREVIATIONS

NVP	: N-vinyl pyrrolidinone
DADMAC	: N,N-Dimethyl, N,N-Diallyl ammonium chloride
XRD	: X-Ray Diffraction
DLS	: Dynamic Light Scattering
TEM	: Transmission Electron Microscopy
CVD	: Chemical Vapor Deposition
CVC	: Chemical Vapor Condensation
IR	: Infra-red
DC	: Direct Current
RF	: Radio-Frequency
HOMO	: Highest Occupied Molecular Orbital
LUMO	: Lowest Unoccupied Molecular Orbital
DNA	: Deoxyribo Nucleic Acid
QD-LED	: Quantum Dot Light-Emitting Diodes
CTAB	: Cetyl Trimethylammonium Bromide
AOT	: Sodium Dioctyl Sulfosuccinate
GPC	: Gel Permeation Chromatography
NMR	: Nuclear Magnetic Resonance Spectroscopy
FTIR	: Fourier Transforms Infra-Red

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LIST of SYMBOLS

f_1	: Reactivity ratio of DADMAC monomer
f_2	: Reactivity ratio of NVP monomer
E_g	: Band gap energy
r	: radius of the sphere
ϵ	: dielectric constant of the semiconductor
h	: dielectric constant of the semiconductor
e	: elementary charge
m_r	: reduced mass of the electron-hole pair
$\Delta E(d)$	: the ground state energy of the semiconductor
d	: particle diameter
m_e^*	: effective masses of the electron
m_h^*	: effective masses of the hole
π	: pie number
F_1	: molar ratios of the first monomer (DADMAC) in the copolymer
F_2	: molar ratios of the second monomer (NVP) in the copolymer
η_{sp}	: specific viscosity
C	: concentration in g/dL
A	: intrinsic viscosity
B	: factor associated with electrostatic interaction of polymer with the solvent.
CdS	: Cadmium sulfide
Pt	: Platinum
SiO_2	: Silica
TiO_2	: Titanium dioxide
$TiCl_4$	: Titanium tetra chloride
$SiCl_4$	: silicon tetra chloride
Fe_3O_4	: iron oxide
Ag	: Silver
Ga	: Gallium
PbS	: Lead sulfide.
Ar	: Argon
Kr	: Krypton
λ	: wavelength

A NOVEL METHOD FOR STABILIZATION OF CdS NANOPARTICLES IN AQUAEUS MEDIUM

SUMMARY

Preparation of nanosize particles of semiconductor materials and pigments has found great attention in the last decade due to their wide range applications in various areas such as microelectronics catalyst coatings etc. These materials exhibit unusual physicochemical behaviors different from those of the bulk materials. Such differences have been ascribed to their large surface to volume ratio and “quantum confinement effects”. When size of a particle approaches to atomic dimensions optical and electrical behavior of the particle differ from those of the bulk material. This phenomenon has been referred to as “the quantum confinement effect”.

Among the semiconducting nanoparticles CdS is of special attention due to its large band-gap (2.41 eV). In the excited state the electron hole acts as oxidant while excited electron acting as reductant. Having those peculiarities CdS nanoparticles are excellent candidates as catalyst for photolysis of water.

There appear enormous reports dealing with preparation of CdS nanoparticles. Conventional methods for their preparation involve the use of thiol capping agents or precipitations of CdS in presence of surfactants or amphiphilic copolymers as stabilizing agents. Those reports reveal that current procedures allow preparing highly stable oil dispersions of CdS nanoparticles.

However stability of CdS nanoparticles in water is still challenging problem. Homogenous aqueous dispersion of CdS nanoparticles is essential to produce hydrogen by photolysis of water. Making stable CdS nanoparticles in water is still in its infancy and the subject needs further development.

In this thesis, we report a very efficient procedure for synthesis and stabilization of CdS nanoparticles in water. The resulting homogenous dispersions were employed for photo catalytic hydrogen generation from water. In this work we have used water soluble copolymers of N,N-diallyl, N,N- dimethyl ammonium chloride (DADMAC)-with N-vinyl 2-pyrrolidinone (NVP) for the stabilization of CdS dispersions in water. There appears only one paper dealing with copolymerization of these two monomers. Therefore we have reinvestigated first copolymerizability of the monomers in aqueous solution. It was found that copolymerization reactivity ratios are concentration dependent. For 30 % of the total monomer concentration the reactivity ratios were found to be; $r_1 = 0.32$ and $r_2 = 0.84$ for DADMAC and NVP respectively, by Finemann-Ross method. For 40 % of the total monomer concentration the reactivity ratios were; $r_1 = 0.32$ and $r_2 = 0.84$, indicating nearly alternating copolymerization. In the second part of the study these copolymers were employed for stabilization of CdS nanoparticles in water.

In order to investigate copolymerization tendency of the monomers a series of mixtures with different monomer ratios were polymerized and DADMAC contents of the resulting copolymers were determined by chlorine analysis and the resulting data were evaluated by Finemann-Ross method.

This method indicated the reactivity ratios, $r_1 = 0.79$ and $r_2 = 0.82$, for 40 % (w/w) monomer concentrations. For 30 % of the total monomer concentration the reactivity ratios found were; $r_1 = 0.32$ and $r_2 = 0.84$. Such an unusual result implies

Concentration dependency of the reactivity ratio of DADMAC component is not surprising, because copolymerization of this monomer with acrylamide was also determined to be concentration dependent. This must be due to Coulombic repulsion between quaternary ammonium groups of DADMAC segments in the copolymers.

Experiments showed that, increasing DADMAC content induces greater stabilization. UV-visible spectroscopy, fluorescence spectroscopy, X-ray diffraction (XRD), dynamic light scattering (DLS) and transmission electron microscopy (TEM) were employed to characterize dispersions obtained this way. TEM images and XRD patterns of the samples revealed snake-like CdS nanoclusters constituting with cubic phase crystal structure. Fluorescence spectra of the samples showed a red-shift with a broad emission band in 550-800 nm range by excitation at 390 nm. The observed emission characteristics are in accordance with lengths of the nanoclusters (190-280 nm).

Colloidal CdS and TiO_2 particles are known to be efficient catalysts for photodecomposition of water to give hydrogen.

Therefore the CdS dispersions obtained were used as catalysts for the photo induced decomposition of water. The photo catalytic activities were tested by measuring volume of the evolved hydrogen in the absence and presence of noble metals, Pd and Pt. The results showed that, except the sample stabilized with the copolymer having 25 % DADMAC the homogenous dispersions showed good stabilities and excellent hydrogen generation rates. The highest hydrogen evolution rate, $0.264 \text{ mmol g}^{-1} \text{ min}^{-1}$ (5.9 mL per gram of CdS in min) was detected in the presence of Pt metal, while illuminating with mercury lamp. The amounts of hydrogen generated from all the samples were found to be far greater than those of CdS based photo-catalysts reported so far.

CdS NANOTANECİKLERİNİN SULU ORTAMDA KARARLI KILINMASI İÇİN YENİ BİR YÖNTEM

ÖZET

Yarıiletken maddelerin ve pigmentlerin nanometre büyüklükteki taneciklerinin hazırlanması, son on yılda mikroelektronik katalizör kaplamaları vb. gibi çeşitli alanlarda geniş çaptaki uygulamalarıyla büyük dikkat çekmiştir. Bu maddeler mikro ya da daha büyük boyutlu maddelerinkinden farklı fizikokimyasal davranış gösterirler. Bu farklı davranışın, bu maddelerin büyük yüzey/hacim oranından ve “quantum hapsetme etkileri”nden ileri geldiği anlaşılmıştır.

Bunlar arasında CdS, geniş band aralığı (2.41 eV) nedeniyle daha fazla dikkat çekicidir. Uyarılmış durumda elektron boşluğu yükseltgen olarak davranırken uyarılmış seviyedeki elektron indirgen özellik taşır. Bu özellikleri nedeniyle CdS nanoparçacıkları, suyun fotolizinin katalizlenmesi için mükemmel adaylardır.

CdS nanoparçacıklarının hazırlanması için pek çok yayın bulunmaktadır. Bunların hazırlanmasında uygulanan alışılagelmiş işlemler, tiol kapping ajanlarının ya da yüzey aktif maddeler veya amfifilik kopolimerler gibi maddelerin varlığında kadmiyum sülfürün çöktürülmesini içerir. Bu yayınlar göstermiştir ki bilinen yöntemler CdS nanoparçacıklarının yüksek kararlılıkta yağlı dispersiyonlarının hazırlanmasına imkân verir.

Buna rağmen sulu dispersiyonda kararlı CdS nanoparçacıklarının hazırlanması hala çözümlenmesi gereken bir problem olarak durmaktadır. CdS nanopartiküllerinin sulu homojen dispersiyonları, suyun fotolizi ile hidrojen üretmek için gereklidir. Suda kararlı CdS nanoparçacıkları üretmek konusu henüz gelişim aşamasında olup daha ileri geliştirmeleri gerektirmektedir.

Bu tezde, suda uzun süre kararlı olan CdS nanoparçacıklarının elde edilmesi için çok etkin bir yöntem ortaya konmaktadır. Bu yolla elde edilen homojen dispersiyonlar, sudan fotokatalitik hidrojen üretimi için kullanılmıştır. Bu çalışmada N,N-diallil N,N-dimetil amonyum klorürü(DADMAC)-N-vinil 2-pirolidinon(NVP)la oluşturduğu suda çözünebilen kopolimerleri kararlı CdS dispersiyonları elde etmek için kullanılmıştır. Bu iki monomerin kopolimerleşmesi ile ilgili olarak literatürde bir tek makale bulunmaktadır. Bu nedenle öncelikle bu monomerlerin suda kopolimerleşmesini yeniden ele aldık. Bu kopolimerleşmede reaktivite oranlarının konsantrasyona bağlı olduğu bulunmuştur. Toplam monomer konsantrasyonunun 30% olması halinde reaktivite oranları Finemann-Ross yöntemiyle; $r_1=0.32$ ve $r_2=0.84$ bulunmuştur. Yine aynı yöntemle toplam monomer konsantrasyonunun 40 % olması halinde ise DADMAV ve NVP reaktivite oranları sırasıyla; $r_1=0.32$ ve $r_2=0.84$ bulunmuştur ki bu sonuç ele geçen kopolimerin hemen hemen alternatif olduğunu işaret eder. Çalışmanın ikinci bölümünde bu kopolimerler CdS nanopartiküllerinin suda stabilizasyonu için kullanılmışlardır.

Monomerlerin kopolimerizasyon eğilimlerini incelemek için farklı monomer oranlarında bir dizi farklı oranda monomer karışımı hazırlanarak polimerleştirilmiş ve oluşan kopolimerlerin DADMAC içerikleri klor analiziyle saptanmış, elde edilen veriler Finemann-Ross yöntemiyle değerlendirilmiştir.

Bu yöntem 40% (ağırlıkça) monomer konsantrasyonu için reaktivite oranlarının sırasıyla $r_1=0.79$ ve $r_2=0.82$ olduğunu göstermiştir. Toplam monomer konsantrasyonunun 30%'u için bulunan reaktivite oranları ise; $r_1=0.32$ ve $r_2=0.84$ 'tür. Alışılmışın dışındaki bu sonuç DADMAC bileşeninin reaktivite oranının konsantrasyona bağlı olduğunu göstermiştir. Bu sonuç şaşırtıcı değildir çünkü bu monomerin akrilamidle kopolimerizasyonunun da aynı şekilde konsantrasyona bağlı olduğu rapor edilmiştir. Bu, kopolimerizasyondaki DADMAC bölümlerinin quaterner amonyum grupları arasındaki Coulombic itmeden kaynaklanıyor olmalıdır.

Deneyler göstermiştir ki artan DADMAC içeriği daha yüksek kararlılığa neden olmaktadır. Bu yöntemle elde edilen dispersiyonları karakterize etmek için UV-görünür spektroskopi, floresans spektroskopi, X-ray sapması(XRD), dinamik ışık saçınımı (DLS) ve geçirimli elektron mikroskopi(TEM) uygulanmıştır. TEM görüntüleri ve XRD örnekleri, kübik faz kristal yapılardan oluşan yilansı CdS nanokümelerini açığa çıkarmıştır. Örneklerin floresans spektrumları, 390 nm'lik bir uyarmayla 550-800 nm aralığında geniş emisyon bandı ile kırmızı-kayma göstermiştir. Gözlenen emisyon karakteristikleri yilansı nanokümelerin uzunluğu ile uyumludur (190-280 nm).

Kolloidal haldeki CdS ve TiO₂ taneciklerinin suyun ışık etkisiyle bozunarak hidrojen çıkarılmasında etkin kataliz oldukları bilinmektedir.

Bu nedenle elde edilen dispersiyonlar, suyun ışık etkisiyle bozunmasında katalizör olarak kullanılmışlardır. Foto katalitik aktiviteler Pd, Pt gibi soy-metallerin varlığında hidrojen gazının çıkışının hacimce ölçülmesi ile test edilmiştir. Sonuçlar göstermiştir ki; %25DADMAC kopolimeri ile stabilize edilmiş örnek hariç tüm homojen dispersiyonlar iyi stabilizasyon ve mükemmel hidrojen çıkış hızları göstermişlerdir. En hızlı hidrojen çıkış hızı Pt metali varlığında cıva lambası ile aydınlatıldığında, 0.265 mmol g⁻¹ min⁻¹ (5.9 mL dakikada gram başına) olarak tespit edilmiştir. Tüm örneklerle elde edilen hidrojen miktarı; bugüne kadar CdS fotokatalizör olarak kullanıldığında ulaşılan rakamların oldukça üstündedir.

1. INTRODUCTION

Nanoparticles and nanostructured materials have found great interest in recent years. These have found extensive use in various fields such as high-density memory devices, high-efficiency lasers and transistors, and other optoelectronic devices [1, 2].

When dimensions of the particles approach to the nanometers some properties of the materials change dramatically. For example, the electrical conductivity exhibit non-Ohmic behaviour and staircase-like current-voltage curves are observed and the material has conduction properties between superconductors and insulators. And the relevant excitonic peak shifts to higher energy (blue shift) [3-4]. This property allows tuning of the band gap by adjusting the particle sizes [5]. Due to this fact these materials have potential applications in various areas such as optical switching, non-linear optic materials [6–7]. This electronic transition behavior has been coined as quantum confinement effect.

Those physical properties have been observed in various semiconductor nanoparticles.

Among semiconductor nanoparticles, CdS is the most interesting due to its high photosensitivity and attractive application in the photocatalysis and photoconducting cells, in particular in the observation of the dependence of these properties on size. Consequently, much effort has been extended in the synthesis of these small quantum size particles. CdS particles were successfully synthesized in a variety of media, such as aqueous and non-aqueous solvents, reversed micelles, vesicles, zeolites and other methods [8-10].

This work is devoted to preparing CdS nanoparticles or nanoclusters for photo splitting of water. The work consists of three subtitles; i) preparation of N,N-diallyl N,N-dimethyl ammonium chloride (DADMAC)-N-vinyl 2-pyrrolidinone (NVP) random copolymers as stabilizer, ii) *in situ* formation of stable CdS nanoclusters in aqueous solution of the copolymer, iii) investigation of the photocatalytic activities of the resulting solutions in hydrogen generation.

The copolymer compositions were assigned by chlorine analysis and ^1H -NMR spectra. The copolymerization reactivity ratios were estimated based on Finemann-Ross method. Four copolymers with 25 %, 50 %, 75 % and 100 % DADMAC (in mol /mol) were employed as stabilizing agent to obtain homogenously dispersed CdS nanoclusters. CdS nanoclusters were characterized by Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Particle Size Analyzer, UV-Visible Spectroscopy and Fluorescence Emission Spectroscopy (FES) techniques. The photo-catalytic activities of the resulting CdS nanoclusters were investigated by measurement of hydrogen evolution rates while illuminating with mercury lamp (160W).

2. THEORETICAL PART

2.1. Preparation of Nanoparticles

Nanoparticles can be synthesized by utilizing a variety of methods.

Different methods are used in order to optimize specific properties of the materials. These methods can be classified into physical and chemical methods although many preparation methods involve combination of both methods. General principles of nanoparticle generations have been listed in Table 2.1.

Table 2.1: Preparation of nanostructured materials.

Method	Variation	Mechanism
Gas-phase condensation	In inert gas or vacuum	Physical
	In reactive gas (CVD)	Chemical
Sputtering	Plasma	Physical
Mechanosynthesis	High-energy milling	Physical
	Mechanical alloying	Physical
Laser pyrolysis		Chemical
Sol-gel process		Chemical
Preceramic polymer		Chemical
Thermal decomposition	Reactive precursors	Chemical
	Gaseous precursors	Chemical
Sonochemical decomposition		Chemical

The methods such as gas-phase condensation, sputtering deposition, laser ablation [11], and plasma synthesis [12], can be classified into the physical methods. Chemical synthetic methods allow cost-effective production of many nanoparticles with desired surface functionalities. The most common chemical methods include

sol-gel process[13], pyrolysis of prepolymers [14], thermal decomposition of organometallics [15], chemical vapor deposition [16], and laser assisted pyrolysis [17], recently sonochemical methods have been demonstrated very useful for generation of various nanoparticles [18].

The properties of the nanostructured materials obtained by those methods are quite different from those generated by conventional grinding processes [19-26]. The major goal in preparing nanosize materials is to explore advanced materials with tailored properties.

2.1.1. Physical Methods

Many physical methods have been used to produce nanostructured materials as given in Table 2.1. The most important physical method is described as follows.

2.1.1.1 Gas Phase Method

Among those gas phase methods seems to have a widespread use in preparation of nanosize pigment particles. The gas phase process involves condensation of supersaturated vapor. The resulting particles coagulated are collected at the bottom of the reservoir.

This method has been most widely used in synthesis of single-phase metals and ceramic oxides by evaporation of an inert-gas. Various approaches have been used to generate the supersaturated vapor depending on the precursor materials.

Generally, the formation of the vapor is achieved within an aerosol reactor at elevated temperatures. The most straight forward method of successful super saturation is to heat a solid and evaporate it into a background gas. This method is particularly useful for the production of metal nanoparticles. In the presence of a reactive gas such as oxygen, oxides or other compounds can be produced from the evaporated material. This method has also been used to prepare composite nanoparticles with controlled the morphology. In another variation of this method, the precursor material is introduced into the reactor as solids, powders, liquids or gases and the nanoparticles, produced by a separate process.

In some cases, the supersaturated vapor is produced by cooling or by chemical reaction with a suitable reagent. Chemical decomposition reactions can also be used to create nanosize powders.

The supersaturated vapor nucleation process is initiated by the formation of very small particle seeds from the molecular phase. These nuclei subsequently grow up by further collisions and coagulation takes place.

Schematic lay out the process is depicted Fig 2.1.

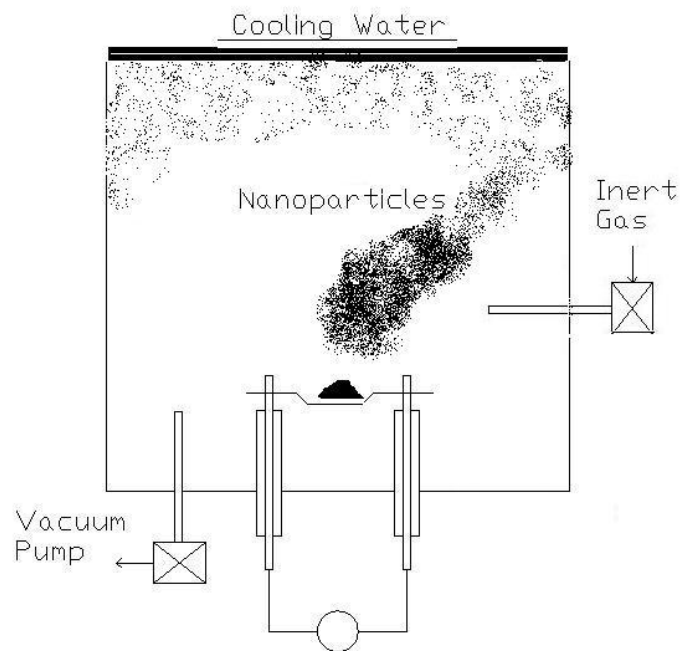


Figure 2.1: An experimental device for gas-phase condensation using a vacuum evaporator.

The evaporation process may varied. These can be summarized as follows [27]:

- Flame pyrolysis
- Furnace flow reactors
- Laser induced pyrolysis
- Laser vaporization
- Thermal plasma
- microwave plasma
- sputtering
- Laser ablation
- Droplet evaporation

Flame pyrolysis process is one of the most common techniques and it has great application to generate bulk quantities of nanomaterials such as carbon black and

fumed silica. In flame pyrolysis, nanoparticles form by the flame heat to initiate the chemical reactions. This is a relatively inexpensive, which is used in large scale production of the fumed silica (SiO_2) and ultra fine TiO_2 . The precursor materials are titanium tetra chloride (TiCl_4) or silicon tetra chloride (SiCl_4) respectively for TiO_2 the flame source is generally a mixture of methane-oxygen. This process also allows preparing complex products. For example, Zachariah *et al* described the production of iron oxide (Fe_3O_4) particles embedded in SiO_2 host particles [28].

Furnace flow reactors are the simplest systems used to produce saturated vapor for substances having a large vapor pressure at moderate temperatures. In these systems a crucible containing the base material is placed in a heated flow of inert carrier gas. Materials such as metal carbonyls with low vapor pressure are fed into the furnace. This method has been used to produce nanoparticles such as silver (Ag), gallium (Ga), and PbS [29].

In the laser pyrolysis technique, a flowing reagent gas is heated rapidly with an IR laser. The starting molecules are heated selectively by absorption of the laser energy whereas the carrier gas does not absorb the laser energy. Decomposition of the precursor takes place due to increasing temperature. The super saturation results in formation of the nanoparticle. This process has been used to produce Si nanoparticles from silane (SiH_4) [30] and Fe nanoparticles from iron pentacarbonyl (FeCo_5) [31].

Plasma reactors can also be used to evaporate or initiate the chemical reactions. The temperature may reach up to $10,000^\circ\text{C}$. Powder feeds can also be decomposed by the plasma. The main types of plasma used are Direct Current (DC) plasma jet, DC arc plasma and Radio-Frequency (RF) induction plasma [32]. This method finds commercial use in producing metal and metal oxide nanoparticles.

In sputtering method materials are bombarded with high velocity ions of an inert gas e.g. Argon (Ar) or Krypton (Kr) on a solid surface. The atoms or ions are ejected from the surface. Ion guns or hollow cathode plasma sputters are normally used in the vacuum systems. Urban *et al* demonstrated formation of nanoparticles of different metals by magnetron sputtering of metal targets. This process requires low pressure which deters extensive use of the method to produce nanoparticles in aerosol form [33].

Gas phase synthesis methods have advantage of controlling of particle size, crystallinity, porosity, degree of agglomeration, and chemical homogeneity [34].

2.1. 2 Chemical Methods

2.1.2.1. Chemical Vapor Condensation (CVC)

Chemical synthesis of nanostructured materials has been extensively studied [31-33]. The simple variation of the chemical methods is chemical vapor condensation (CVC) (or so called chemical vapor deposition, CVD). Chemical Vapor Deposition (CVD) methods have been employed for the manufacturing of semiconductors [34] which are used to deposit thin films of silicon and other semiconductors.

In this technique the vapor is formed in a reaction chamber by pyrolysis or by a chemical reaction such as oxidation, reduction, and nitridation. The nanopowders are deposited on the surface and surface growth begins by nucleation. Few nuclei on the surface serve as seed points for further deposition. The deposition patterns are obtained by using masks.

Several factors such as uniform heating of the reactor and rapid quenching of the gas phase- nanoparticles affect success of the process. Fig 2.2 shows a typical CVD reactor.

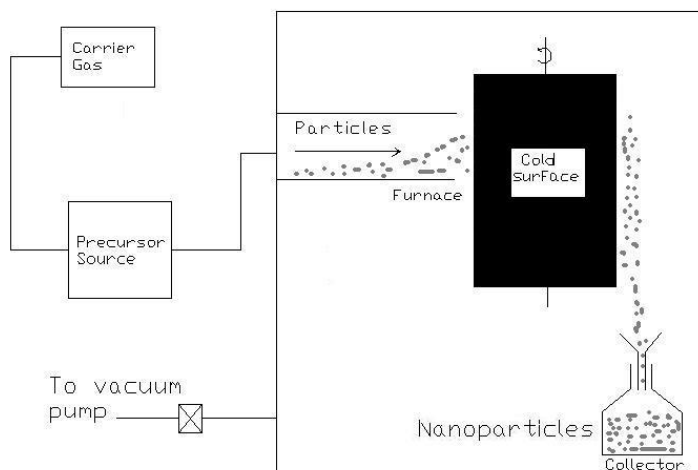


Figure 2.2: Schematical representation of chemical vapor deposition apparatus.

CVD methods have been used to produce nanostructured powders of oxides, carbides, nitrides, borides, or their composites. For instance ceramic nanocomposites have been prepared from organometallic precursors by laser-induced pyrolysis [17]. In another example nanophase Si–N–C-containing ceramic particles have been obtained by the ultrasonic injection of liquid silazane precursors into the beam of a

high-powered CO₂ laser. In a similar study liquid silazanes have been prepared by ammonolysis of methyldichlorosilane using anhydrous ammonia. The resulting material [CH₃SiH₂NH]_x, has been demonstrated to be in cyclic form with 3 or 4 repeating units. In laser pyrolysis reactions, self-crosslinking occurs by nucleophilic displacement the –SiH–NH– group with neighboring silicon atoms. Fig 2.3 shows a schematic diagram of the laser processing system.

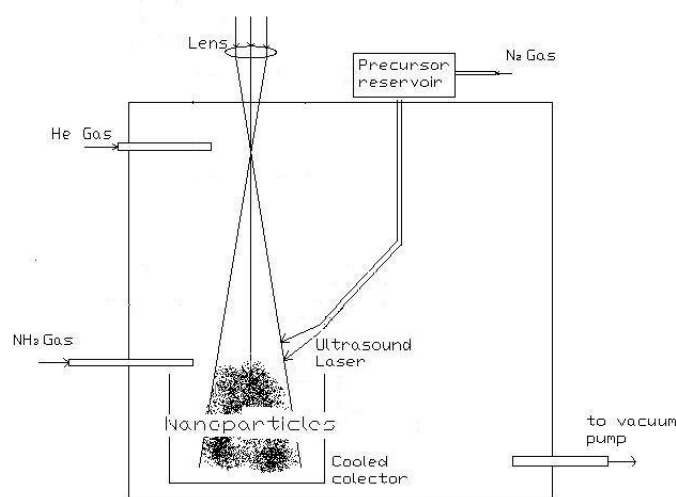


Figure 2.3: Experimental setup for nanostructured Silicon nitride and carbide by laser processing.

The preceramic powders obtained by this method have been converted into Si₃N₄/SiC nanocomposites by thermal treatment at 1100 °C in NH₃ or N₂ gas.

Direct conversion of the silazane into Si(C, N) nanoparticles was also obtained via the ultrasonic injection of the precursor into a hot-wall reactor [17].

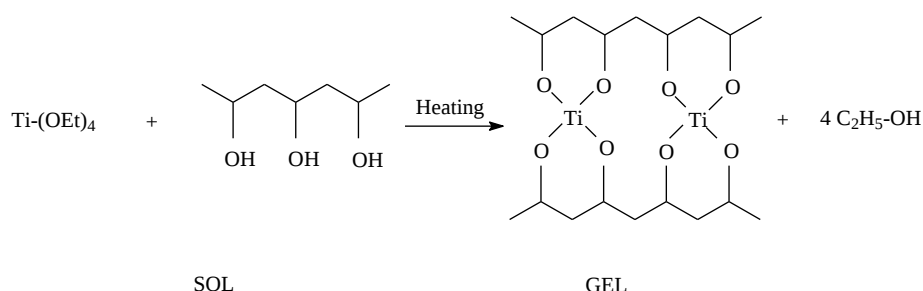
This method has been extensively used for the production of metals, metal borides, and composites for use in magnetic, electronic, and catalytic applications.

2.1.2.2 Sol–Gel Process

The sol–gel process has a particular attention for the fabrication of inorganic nanostructured materials, and the process is expected to be effective for ceramic materials [35]. The process allows the development of new materials with good homogeneity.

The sol–gel process is solidification of a mixture so called “sol” by removal of a low molecular weight component by exchanging with high molecular weight reagent

such as polymer. The method allows preparing various nanohybrids in different shapes.



Scheme 2.1: Formation of titana sol by poly (vinyl alcohol)

Scheme 2.1 shows a typical sol-gel process from titanium tetra alkoxide.

The main disadvantage of the method is the high porosity of the gel. The high porosity of the gel, however, might be useful in some cases, such as the fabrication of inorganic membranes and thermal insulation of aerogels [35-36].

Nonshrinking organic-inorganic glass/polymer nanocomposites with polymer contents have been reported. For example, tetraalkyl orthosilicates have been hydrolyzed in presence of preformed polymers [37] to form glassy films consisting of nanostructured SiO_2 .

The sol-gel process have been employed to produce ceramic xerogel membranes constituting with TiO_2 and ZrO_2 having a mean pore diameter smaller than 2 nm and micro porosity is bigger than 50% [36]. These membranes can be used as catalytic or photo catalytic materials.

2.1.2.3. Precipitation In The Presence Of Stabilizing or Capping Agent

Another method of the chemical route is precipitation in the presence of stabilizing or capping agent. By using conventional “wet chemistry” procedures various nanoparticles have been prepared in solution or in precipitate forms. This method is relatively straightforward and provides simple route to the synthesis of many nanoparticles in acceptable costs. The preparation of metal nanoparticles by this method dates back to 19th century. On going studies since that time revealed

possible synthesis of various nanosize metals. Many comprehensive reviews are available on this subject. Pioneering studies of Brust *et al* and others have made great contribution in this area [38-39].

This method has been used to generate a wide range of nanoparticles including chalcogenides, metals and alloys including gold, cobalt and nickel as well as carbon and titania nanotubes.

Nanoparticles produced by these wet chemical methods can remain in well dispersed form which may be used as slurries. They can be isolated by precipitation in a nonsolvent.

The wet milling of larger particles in high shear media mills is another technique [40]. However the method gives particles in broad size distributions.

2.2. Semiconductor Nanoparticles

Semiconductor nanoparticles have been of major interest due to their interesting size-dependent photo physical properties. The electronic energy levels between the valence band and conduction band is very close in semiconductors. The energy difference between these levels is referred to as the band gap, E_g . This difference is analogous to the energy spacing between HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital) in the molecular orbital theory.

The band gap is the most fundamental property of the semiconducting materials. Insulators have band gaps up to 4 eV and almost zero band gap is present in metallic conductors. The semiconductors have band gaps ranging from -0.5 - 3.5 eV. This energy corresponds to electromagnetic radiation ranging from the near infrared through the visible light. Light absorption of semiconductors within this wavelength range causes to excitation of the valence electrons in the valence band to the conduction band creating an "electron hole". Recombination of the electron-hole pair, or "exciton," may lead to photoluminescence very similar to molecular fluorescence in ordinary materials (Figure 2.4).

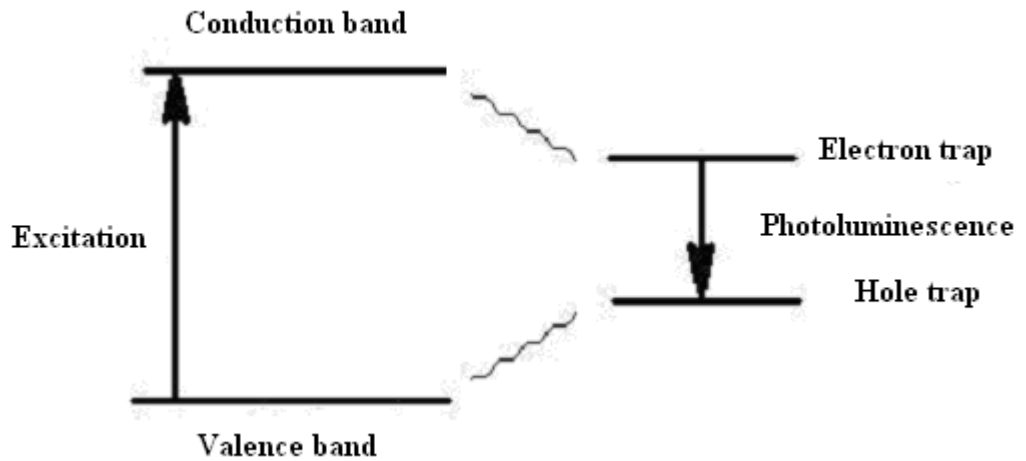


Figure 2.4: Simplified photoluminescence mechanism of a semiconductor.

Presence of impurities in the semiconductor may lead to luminescence with lower energy. For CdS nanoparticles, the photoluminescence can range from blue, green, yellow, orange and red depending on particle size and synthesis conditions.

The "hole" can be considered as a particle having mass and positive charge. The Bohr model can be used to calculate the energy difference between the electron and hole pair. The simple formula is,

$$r = \frac{\epsilon h^2}{\pi m_r e^2} \quad (2.1)$$

Where r is the radius of the sphere; ϵ is the dielectric constant of the semiconductor; h is Plank's constant, e is the electronic charge, and m_r is the reduced mass of the electron-hole pair. As the size of the semiconductor approaches to the Bohr radius ($0.59 \text{ \AA}$), the semiconductor shows the quantum effects. The particles with $1\text{--}100 \text{ \AA}$ size exhibits quantum confinement effect and are referred to as "quantum dots".

Since these nanocrystals are much smaller than the wavelength of the visible light, dispersions of these materials are almost transparent. Such an effect has been observed by Chester Berry at Kodak in the absorbance spectra of AgI colloids. They attributed this phenomenon to the quantum confinement effect. The experimental work of Berry was the basis of this hypothesis [41]. Brus and Rossetti noticed that CdS nanocrystals grown in glass shows unusually blue-shift in the absorbance spectra [42].

The following formula given by Brus is very useful to make correlation between the adsorption edge and size of the particles.

$$\Delta E(d) = \frac{h^2 \pi}{d^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{3.572 e^2}{\epsilon d} - \frac{0.24 e^4 \pi^2}{h^2 \epsilon^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right]^{-1} \quad (2.2)$$

Where $\Delta E(d)$ is the ground state energy of the semiconductor, h is Planck's constant, e is the electronic charge, d is the particle diameter, ϵ is the dielectric constant, and m_e^* and m_h^* are the effective masses of the electron and hole, respectively [43].

The first term in this equation denotes the kinetic energy of the electron and the hole, which increases with decreasing particle size which is analogous to the particle-in-a-box model. The second term represents the Coulombic stabilization of the exciton. The third term correlates the electron and the hole. For CdS crystals of 50 Å diameters, these three terms are 0.42, 0.18 and 0.015 eV, respectively.

It was also shown that quantum-sized CdS nanocrystals exhibit size-dependent redox properties.

Table 2.2: Some bulk semiconductors with band gap energies

Semiconductor	Band gap Energy (eV) (at pH7)
SiC	3.0
GaAs	1.4
CdS	2.4
TiO ₂	3.0

The difference in band gap energies of bulk and semi conducting materials is given by [42]

$$E(d) = E(\text{bulk}) - \Delta E_c(d) \quad (2.3)$$

By using the effective mass model of Brus [42]

$$E^\circ(d) = E^\circ(\text{bulk}) - \frac{h^2 \pi}{d^2 m_e^*} \quad (2.4)$$

2.3. Stabilization of Nanoparticles

Stabilization of nanoparticles is a big problem and essential for their storage and transportation.

Various low-molecular weight organic compounds such as carboxylic acids, alcohols and amides have been used as stabilizers. Traditional surfactants have also been widely employed as stabilizer for the nanoparticles. At present amphiphilic block copolymers are preferred to attain higher stabilities.

One of the blocks in amphiphilic polymers is anchored by physical or chemical means on the particle surface and the other block provides homogenous dispersion in the medium. Many block and graft copolymers have been studied for perfect nanoparticle stabilization [44].

The chemistry and physics of various surfactant systems, has been subjected in various textbooks [45–48]. Self-assembly of surfactants and their micelle sizes provide size control of the nanoparticles [49–51].

Depending on concentration and temperature of their solutions the shapes of micelles may vary as sketched in Fig 2.5 of surfactants depends on their nature, concentration, type of solvent and production method. The most typical surfactant microstructures are shown in Fig 2.5. About 50–100 surfactant molecules are spontaneously joining into aggregates known as micelles when the micelle-forming concentration in water is above critical.

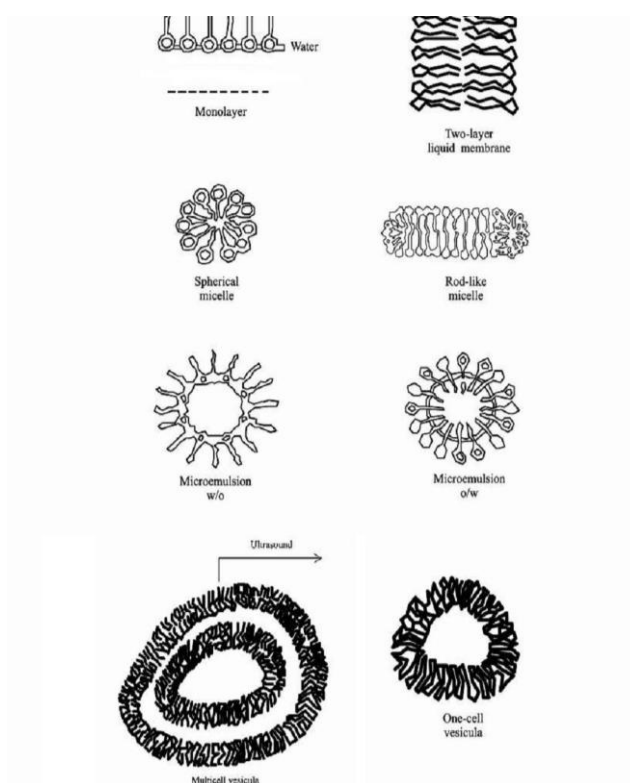


Fig 2.5: Typical microstructures of the micelles of surfactants

When water-soluble surfactants are transferred into a hydrocarbon solvent the micelles are transformed into inverted micelles [52].

Such transformations are influenced by the hydrophilic–lipophilic ratio of the block copolymers.

Inverted micelles show unique behavior that they may accomodate large volumes of water. Lamella vesicles are obtained in bulb form 100–800nm size while swelling of the liquid film in water.

Stabilization of nanoparticles occurs either by charge stailization or steric stabilization depending on chemical structure of the stabilizing molecule or polymer. Low-molecular surfactants are less efficient than their polymer analogs.

In contrast to low-molecular amphiphilic substances formed by amphiphilic polymer compounds, micro phases are more stable in thermodynamic and kinetic respects.

Beside those, characteristics of amphiphilic copolymers can be tuned by changing comonomers and molecular weights.

It is possible to control the chemical structure of these polymers by appropriate choice of repeating units, in the copolymerization. Surfactant vesicles can be polymerized inside bilayers or head groups as shown in Figure 2.6 [53].

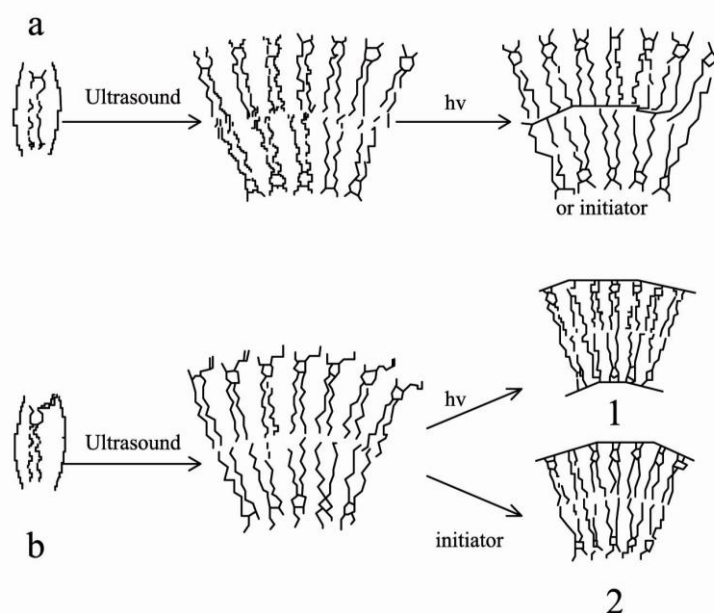


Fig 2.6: A scheme of polymerization of surfactant vesicle

Stabilization of nanoparticles can also be achieved with polyelectrolyte such as quaternized poly (vinyl pyridine) [54], poly (acrylic acid) [55], and poly (ethylene imine) [56-58].

Cationic polyelectrolytes, including poly (diallyldimethylammoniumchloride), Poly (methacrylamidopropyltrimethylammonium chloride), and poly (3-chlorine-2-hydroxypropyl-2-methacryloxyethyltrimethylammoniumchloride) [59] have been successfully used as stabilizer [60].

There is great interest in the use of polyelectrolyte carrying reducing agent. For instance oligothiophen based stabilizer has been used to generate gold nanoparticles from HAuCl_4 [61].

However stabilization by physically adsorbed surfactants or polymers on the nanoparticles does not provide permanent stability. And any external stimuli such as heat, electrical field or addition of third component may cause destabilization of nanoparticles and coalescences of the particles may take place. To provide permanent stabilities the nanoparticle surfaces must be modified chemically. The chemically bond organics provide protection and stabilization of the particles. An extension of this strategy involves surface initiated polymerization from the surface of the nanoparticles. Stöber et al. described a successful procedure for tailoring of silica nanoparticles by surface initiated polymerization strategy. [62].

In this approach a polymerization initiator is introduced to the surface of the nanoparticle and polymerization is initiated from the surface.

2.4. Applications of Nanoparticles

Nanostructured materials possess many unique features, and some examples of these have been included in Table 2.3. These properties are strongly dependent on their physical and chemical characteristics.

The list of applications for nanostructured materials is enormous and keeps growing. The catalysis in nanosizes are considered as extremely efficient catalysts [their large surface per unit mass. Another early application is the fabrication of arrays of particles for devices based on quantum confinement [64]. The use of nanoscale ceramic powders provides many advantages for processing, such as greatly reduced sintering temperature [65]. Very hard, wear-resistant coatings; super paramagnetic materials for magnetic refrigeration; net shape forming via super plastic deformation

and transparent ceramic windows are some potential applications for these materials [66-69].

Many inorganic nanostructured materials promising for practical application view points.

Table 2.3: Properties and applications for nanostructured materials

Property	Application	Examples of Materials
Surface area	Catalysts	ZnS, Ni, Co, Fe, MoS ₃
	IR Sensors	Au
Superior hardness and wear resistance	Materials with enhanced mechanical properties	WC, WC-Co
Single magnetic domain	Magnetic recording superparamagnetism	Fe/Co/Ni Fe, Co, Ni, Fe ₂ O ₃ ,
	Magnetic fluids	Fe ₃ N Fe ₂ O ₃ , Fe ₃ N
Quantum confinement	Nonlinear optical material	CdS, TiO ₂ , Au colloid
Nanosized filler	Nanocomposite with ultrahigh refractive index	PbS/polyoxyethylene
Nanosized pores	Inorganic membranes	TiO ₂ , ZrO ₂ , SiO ₂

Another large application area is the nanocomposites. Examples of inorganic-containing nanocomposites include biomimetic ceramic/polymer composites [64], super paramagnetic ceramic/ceramic nanocomposites [67] and nonlinear optical metal colloid polymer nanocomposites [71]. The synthesis of nanocomposites usually involves a multistep process, which may comprise several basic preparation techniques, such as sol-gel/polymerization, sol-gel/thermal pyrolysis, and intercalation/solidification. The critical issue for making nanocomposites with a homogeneous dispersion of the involved phases lies in a better understanding on the surface/interface chemistry [72]. Numerous studies have been devoted to this subject [73].

Nanocomposites of aluminum nitride and boron nitride (AlN/BN) have been prepared using boric acid, urea, and aluminum chloride via a sol-gel polymer

approach [74]. These have been first mixed in aqueous solution and subjected to ammonolysis to form a gel. Pyrolysis of the latter up to 1100 °C yielded the nanostructured AlN/BN composites. The average crystallite size of the resulting material has shown to increase by amount of the AlN(32. This process yields the molecularly uniform dispersion of AlN and BN phases. This methodology has been adapted to prepare other advanced ceramic materials such as Fe_xN/BN (x=3 or 4) nanocomposites for magnetic applications [67].

The advantage of polymer nanocomposite is that a small amount of silicate (< 6% by weight) is enough to reinforce the polymer and to improve its properties. For example, it has been shown that polyimide composites containing as low as 2 wt% of silicate exhibit a 60% decrease its water, permeability and the thermal expansion coefficient is reduced by 25% compared to the bulk polymer [75]. Nylon 6 /clay nanocomposites have been prepared by polymerization of ϵ -caprolactam in the montmorillonite interlayer [76]. The product was reported to show mechanical properties superior to those of a nylon/clay physical blend and nylon 6.

Due to the properties coming from high band-gap interval, high surface to volume ratio and quantum size effect, CdS nanoparticles find large application areas such as bioorganic detector of proteins or DNA [77].

Nucleic acid-functionalized CdS nanoparticles turn blue upon hybridization with the target DNA due to the formation of an interparticle-coupled plasmon exciton.

Another application of CdS nanoparticles is catalysis [78]. The silica coated CdS nanoparticles in jingle-bell-shape have been prepared and were shown to be effective and stable photocatalyst for dehydrogenation of methanol. Irradiation of SiO₂/CdS suspended in an aqueous solution containing methanol resulted in the liberation of hydrogen (H₂).

CdS nanoparticles obtained by spin-coating in monolayer have been used as nanocrystal quantum dot light-emitting diodes (QD-LEDs) [79].

2.5. Preparation and Stabilization of CdS Nanoparticles

Of many semiconductor materials CdS is of special interest because of its high band gap between the valence and conduction bands (2.41 eV) as described above. There appear many significant reports in the literature dealing with preparation of CdS nanoparticles dispersible in organic medium *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 agent. Sastry et al 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 [80, 38]. Various sulfur compounds such as mercaptoacetic acid, 2-mercapto ethanol, thiourea and long chain alkyl xanthates, thioglycerol have been used as capping or stabilizing agents in preparing CdS nanoparticles [81- 85]. Bunker and Harruff were able to obtain stable nanoparticles in reverse-micelle system (water in hexane) by using only sodium dioctyl sulfosuccinate (AOT) as stabilizing agent [86].

Polymers such as poly (N-vinyl 2-pyrrolidone) and poly (oxyethylene)₁₀ nonyl phenol ether have been employed in stabilization of CdS nanoparticles [87].

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

Douglas et al were described preparation of CdS nanoparticles with controllable size by reaction with H₂S in micellar solution of styrene-2-vinyl pyridine block copolymers using tetrahydrofurane as solvent [88]. Also amphiphilic block copolymer, poly (styrene-*b*-ethylene oxide) has been used in stabilization of CdS nanoparticles by hydrogen bonding with the ethyleneoxide block [89].

Despite abundant reports dealing with oil soluble or dispersible CdS nanoparticles, there appear only few reports on the preparation of water-soluble CdS nanoparticles [90-92].

Goal of this work is to prepare water soluble CdS nanoparticles by stabilizing with DADMAC-NVP copolymers.

The use of quaternary ammonium compounds with long alkyl chains for stabilization of CdS nanoparticles was first reported by Agostiano and coworkers [93]. This group has described a useful procedure yielding relatively narrow size of CdS nanoparticles (35-40 nm) by cetyl trimethylammonium bromide (CTAB) forming reverse micelles in water-n-hexane mixture. Presumably the stabilization in this case occurs 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 [94]. Interestingly Moffitt and Eisenberg showed that CdS nanoclusters are obtained in the same reaction conditions in presence of random ionene-styrene copolymers [95].

Bearing these in mind, first copolymerizability of DADMAC with NVP was investigated. The copolymers with 25, 50, 75 % DADMAC (mol /mol) contents were employed as stabilizing agent for CdS nano species.

3. EXPERIMENTAL WORK

3.1 Chemicals

2,2'-Azobis-(2-methyl propionamidine) dihydrochloride (Aldrich), N,N-dimethyl N,N-diallylammonium chloride (DADMAC) (65 % aqueous solution), (Aldrich) NaS.H₂O (E. Merck), Cd(CH₃COO)₂.H₂O (E. Merck) were used as purchased.

3.2 Equipments and Experimental Set-up

Table 3.1: List of equipments used in this study.

Equipment	Brand
Hot Plate	HP 30 IKATHERM
Fourier transform infra-red (FT-IR)	Perkin-Elmer
Nuclear Magnetic Resonance Spectroscopy (NMR)	Bruker AC250
X-ray diffraction (XRD)	SHIMADZU
UV-Visible Spectrophotometer	Chebios Optimum-One
Gel-permeation Chromatography (GPC)	Hewlett Packard
Transmission Electron Micrographs (TEM)	JEOL-JEM
Sonication	Bandelin sonopuls
Particle Size Analyzer	Brookhaven 90
Fluorescence Emission Spectrum (FES)	Varian Cary Eclipse

3.2.1. Experimental Set-up for Determination of Hydrogen Evolution Rate

Hydrogen evolution rates were measured by an experimental set-up shown in Figure 3.1. The hydrogen was collected in an inverted burette of which one end was dipped into water in a cylindrical glass container. Prior to illumination of the yellow dispersion nitrogen was flushed through the system for 30 min to expel dissolved oxygen. This was found to be crucial for accuracy of the measurements.

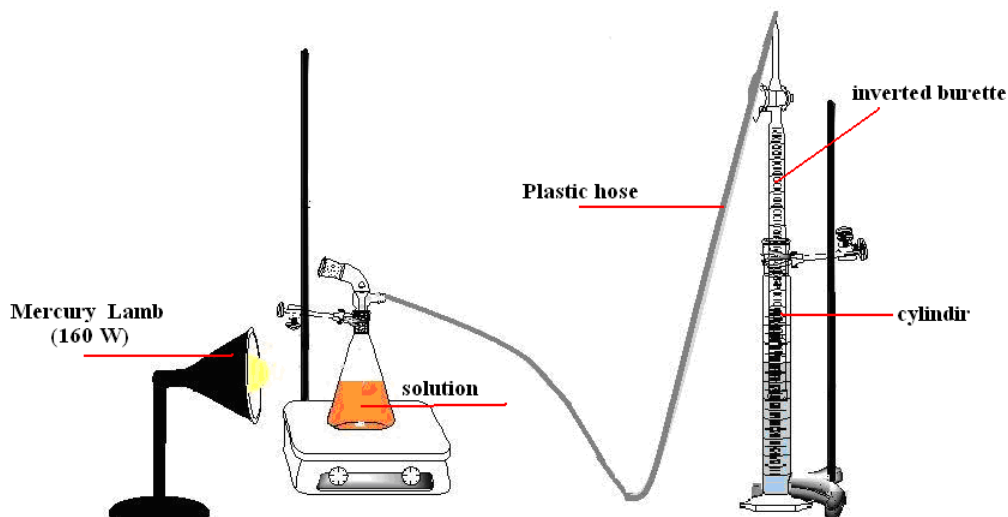


Figure 3.1: Experimental set-up.

3.3. Preparation Methods

3.3.1 Investigation of Copolymerizability of DADMAC with NVP monomer in Aqueous Solution

To inspect copolymerization reactivity ratios of the monomers, a series of small scale batch polymerizations were performed using various DADMAC (monomer-1) to NVP (monomer-2) ratios in the same conditions. The polymerizations were terminated after 30 min by precipitation in acetone to attain low conversions (22.7- 60.5 %). DADMAC contents of the conversions attained were low (22.7-60.5 %). DADMAC contents of the copolymers were assigned by analysis of the chloride anion. The resulting data were evaluated by Finemann-Ross method based on so called “copolymerization equation”.

$$\left(\frac{f_1}{1-f_1} \right) \times \left(\frac{2F_1-1}{F_1} \right) = \left(\frac{f_1}{1-f_1} \right)^2 \times \left(\frac{1-F_1}{F_1} \right) \times r_1 - r_2 \quad (3.1)$$

Where, r_1 and r_2 are the reactivity ratios of the monomers respectively for DADMAC. F_1 and f_1 denote molar ratios of DADMAC in the copolymer and in feed composition respectively [96].

3.3.2. Preparation of DADMAC-NVP Copolymers

In a 250 mL volume of three-necked flask equipped with a reflux condenser and a nitrogen inlet there were added 24.9 g commercial N,N-diallyl N,N-dimethylammonium chloride solution (65 % , 0.1 mol), 11.2 g (0.1 mol) 1-vinyl 2-pyrrolidone (99.5 %) and 0.562 g 2, 2'-azo bis-(2-methyl propionamidine) dihydrochloride (2×10^{-3} mol) under nitrogen. Then 32.4 mL distilled water was added so that final total monomer concentration was to be 40 % by weight. The flask was placed in a thermostated oil bath. The reaction was conducted at 60 °C under continuous stirring for 1 h. 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 and dried at 70 °C under vacuum for 24 h. DADMAC contents of the copolymers were assigned by analysis of the chloride anion.

3.3.3. Preparation of CdS Nanoclusters

The monomer mixtures with 1 / 3, 1/ 1 and 3 /1 molar ratios of DADMAC / NVP were polymerized at constant total monomer concentrations (40% w/w) by the same procedure to obtain copolymers in different compositions.

The aqueous dispersions of CdS nanoclusters were prepared by gradual addition of cadmium acetate 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) $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was dissolved in 60 mL water. The solutions were combined and a solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (23.75 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 (at 30 % power out, using MS 72 probe). A faintly yellow and nearly transparent solution was obtained.

3.3.4. Determination of the Photo Catalytic Activities

The samples (50 mL) containing 0.1 g CdS nanocluster were prepared by appropriate dilution of above dispersions. Then, 1.9 g (15 mmol) Na_2SO_3 and 2.4 g (10 mmol) $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ were dissolved in it. The resulting yellow solutions were transferred into 100 mL volume of Erlenmeyer-flasks. The flasks were mounted to the hydrogen measurement apparatus in Fig-3.1. After de-oxygenation of the system by nitrogen flow, the mercury lamp (160 W) was turned on and volume of the hydrogen gas evolved was measured based on displacement of water level in the inverted burette.

To investigate effects noble metals the hydrogen evolution yields the experiments were repeated in the presence of elemental Pt and Pd. K_2PtCl_6 and $\text{Pd}(\text{CH}_3\text{COO})_2$ were used respectively as source of these metals. These metals were *insitu* generated from their solutions mixed in mother liquor by 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.

3.4. Characterization

3.4.1 Fourier Transforms Infra-Red (FT-IR)

FTIR spectra were recorded on a Perkin-Elmer FTIR Spectrum One spectrometer.

3.4.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

^1H NMR spectra were recorded in D_2O with $\text{Si}(\text{CH}_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument.

3.4.3 X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns of the samples were recorded using a SHIMADZU XD- D1 diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$)

3.4.4. UV-Visible Spectrophotometer

UV-visible spectra were obtained a Chebios Optimum-One UV-Visible Spectrophotometer.

3.4.5. Gel-Permeation Chromatography (GPC)

Molecular weights were determined by gel-permeation chromatography (GPC) instrument equipped with Waters styragel column (HR series 2, 3, 5E) with water as the eluent at a flow rate of 0,1 mL/min and a Waters 410 differential refractometer detector.

3.4.6. Transmission Electron Micrographs (TEM)

The transmission electron micrographs (TEM) 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.

3.4.7. Sonication

Sonifications were carried out with a Bandelin sonopuls HD 3200 homogenizer at 20 KHz (at 40 % power out), using MS 72 probe.

3.4.8. Particle Size Analyzer

The particle sizes obtained from DLS measurement were carried out Brookhaven 90 Plus particle size analyzer.

3.4.9. Fluorescence Emission Spectroscopy (FES)

The fluorescence emission measurements were done using Varian Cary Eclipse Fluorescence Spectrophotometer at 90° position.

3.4.10. Determination of DADMAC Percentage in the DADMAC-NVP Copolymer

The monomer mixtures with 1 / 3, 1/ 1 and 3 /1 molar ratios of DADMAC / NVP were polymerized at constant total monomer concentrations (40% w/w) by the same procedure to obtain copolymers in different compositions. The copolymer compositions were assigned by colorimetric analysis of chloride contents, using mercuric thiocyanate method.

3.4.11. Determination of Viscosity of the Aqueous Solution of DADMAC-NVP Copolymer

Typical polyelectrolyte behavior of the copolymers in aqueous solution obeys the Fuoss-Strauss equation, (3.1).

Fuoss-Strauss equation:
$$\frac{\eta_{sp}}{C} = \frac{A}{1 + B\sqrt{C}} \quad (3.1)$$

Indeed C/η_{sp} versus $\sqrt{C}$ plots (Fig-1) give straight lines which are characteristics of polyelectrolytes. Where A is intrinsic viscosity and B is a factor associated with electrostatic interaction of polymer with the solvent.

4. RESULTS and DISCUSSION

The main purpose of this study was preparation of stable and concentrated CdS nanoclusters in aqueous solutions. *In situ* generation of CdS in aqueous solution of diallyl dimethyl ammonium chloride (DADMAC)-*N*-vinyl 2-pyrrolidinone (NVP) copolymers resulted in nearly transparent solutions which are stable over 45 days at room temperature. These dispersions were then used as catalysts for the photo induced decomposition of water. The photo catalytic activities were tested by measuring volume of the evolved hydrogen in the absence and presence of noble metals, Pd and Pt. The highest hydrogen evolution rate ($0.264 \text{ mmol g}^{-1} \text{ min}^{-1}$ or 5.9 mL per gram of CdS in min) was detected in the presence of Pt metal, while illuminating with mercury lamp.

Three steps of work were carried out:

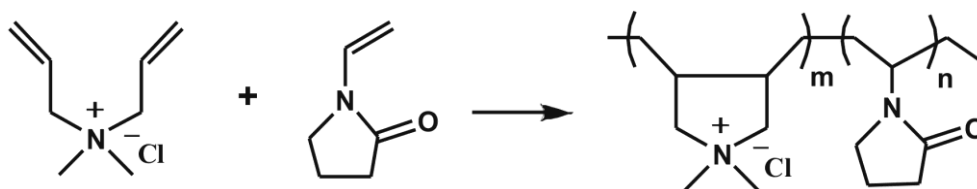
In the first step, N,N-diallyl N,N-dimethyl ammonium chloride (DADMAC)-*N*-vinyl 2-pyrrolidinone (NVP) random copolymers were prepared for stabilizing CdS nanoclusters.

In the second step, DADMAC-NVP copolymer stabilized CdS nanoclusters were prepared.

In the third step, the photocatalytic activity of this cluster was investigated with and without activators in order to hydrogen generation.

4.1 Synthesis of DADMAC- NVP Random Copolymer

Radical polymerization of DADMAC-NVP mixture in aqueous solution gave copolymers in high yields (Scheme 4.1).



Scheme 4.1: Copolymerization of DADMAC with NVP

To inspect copolymerization reactivity ratios of the monomers, a series of batch polymerizations employing various ratios of DADMAC (monomer-1) to NVP(monomer-2) were terminated after 30 min by precipitation in acetone. The conversions attained were low (22.7-60.5 %). DADMAC contents of the copolymers were assigned by analysis of the chloride anion and data were collected in Table-2.

The resulting data were evaluated by Finemann-Ross method based on so called “copolymerization equation”.

$$\left(\frac{f_1}{1-f_1} \right) \times \left(\frac{2F_1-1}{F_1} \right) = \left(\frac{f_1}{1-f_1} \right)^2 \times \left(\frac{1-F_1}{F_1} \right) \times r_1 - r_2 \quad (4.1)$$

Where, r_1 and r_2 are the reactivity ratios of the monomers respectively for DADMAC. F_1 and f_1 denote molar ratios of DADMAC in the copolymer and in feed composition respectively.

Table 4.1: Compositions and copolymerization parameters of DADMAC-NVP copolymers, estimated based on chlorine analysis.

Total monomer conc. % (w / w)	f_1	Chlorine Content (mmol g^{-1})	F_1	$\left(\frac{f_1}{1-f_1}\right)^2 \times \left(\frac{1-F_1}{F_1}\right)$	$\left(\frac{f_1}{1-f_1}\right) \times \left(\frac{2F_1-1}{F_1}\right)$
30	0.25	1.92	0.2363	0.3591	- 0.744
	0.40	2.72	0.3475	0.8345	- 0.585
	0.50	3.13	0.4132	1.420	- 0.420
	0.60	3.65	0.4974	2.2735	- 0.016
	0.75	4.26	0.6040	5.9006	1.033
40	0.40	2.86	0.3710	0.2914	-0.4636
	0.50	3.64	0.4954	1.0186	-0.0186
	0.60	4.07	0.5700	1.6974	0.3684
	0.80	5.18	0.7790	4.5392	2.8652

A plot of the left term of the equation versus coefficient of r_1 on the right hand side gives straight line (Figure 4.1). From the slope and intercepts of the plot the reactivity ratios are found; $r_1 = 0.79$ and $r_2 = 0.82$, for the copolymerization with 40 % total monomer concentration.

This result can be ascribed to high tendency of the monomers to the copolymerization. However, in the case of 30 % of the total monomer concentration, chloride analyses of the copolymers revealed significantly different reactivity ratios, $r_1 = 0.32$ and $r_2 = 0.84$.

Such an unusual result implies concentration dependency of the reactivity ratio of DADMAC component. This is not surprising because copolymerization of this monomer with acrylamide was also reported to be concentration dependent [97].

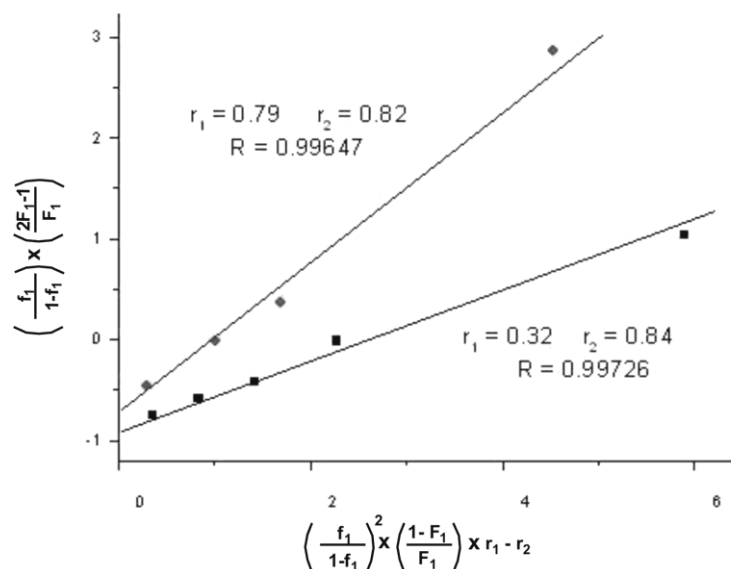


Figure 4.1: Finemann-Ross plot for the copolymerization of monomers in 40% concentration (upper curve) and in 30 % concentration (lower curve).

This result implies less preference of the growing radical with DADMAC end units to the same monomer in dilute conditions, due to Coulombic repulsion between the quaternary ammonium groups.

These investigations showed that copolymerization of N,N-diallyl N,N-dimethyl ammonium chloride (DADMAC) with N-vinyl 2-pyrrolidinone (NVP) gives nearly alternating copolymers in concentrated aqueous solutions.

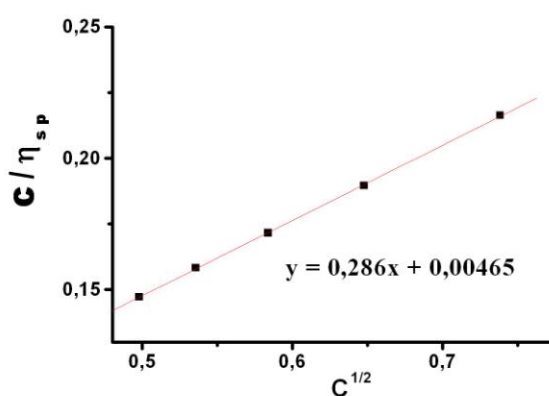


Figure 4.2: Fuoss- Straus plot of the copolymer with 24.7 %DADMAC content.

Aqueous solutions of the DADMAC-NVP copolymers do not show linear viscosity-concentration relationship. As it is expected, aqueous solution of this copolymers show typical polyelectrolyte behavior and the viscosity measurement data obey the Fuoss-Strauss equation (3.2).

Figure 4.1 shows Fuoss-Strauss plot of the copolymer with low DADMAC content (24.7 %).

^1H -NMR spectrum of the copolymer (Figure 4.2) represents pyrrolidinium and pyrrolidone units in the structure. The down field signal at 3.8 ppm is associated with methyne protons of PNVP component. Protons of the methylene and methyl groups attached to the quaternary nitrogen in poly (DADMAC) segment represent broad signal in 3.1-3.4 ppm range.

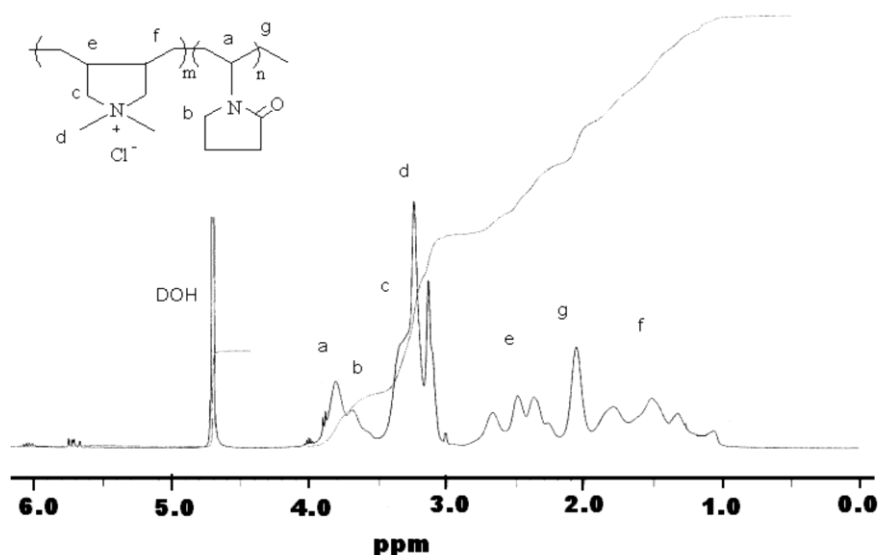


Figure 4.3: ^1H -NMR spectrum of copolymer obtained by polymerization equimolar DADMAC-NVP mixture in concentrated aqueous solution (40 % w/w).

Other aliphatic proton signals lie below 2.7 ppm. The signal at 4.7 ppm indicates DOH originating from extremely high hygroscopic nature of the copolymer. The peaks in 1-1.4 ppm range are absent in the spectra of the homopolymers. These signals can be ascribed to main chain methylene protons at the connecting points of alternating monomers.

Integral ratio of the a and b signals to those below 3.5 ppm indicates a molar ratio of 0.489 DADMAC in the copolymer, which is slightly lower than that of the feed composition.

Similarly DADMAC ratios of the copolymers are somewhat less than those of the feed compositions. However the molar compositions fairly match with those predicted by the chlorine analyses as shown in Table 4.2.

Table 4.2: Characteristics of the copolymers obtained by initiation with ABP in aqueous solutions with various monomer ratios (Conditions; total monomer conc. 40.0 % w / w, ABP / [Monomers] = 1 / 100, at 60 °C).

<i>DADMAC /NVP molar ratio</i>	<i>Reac. time</i>	<i>Yield^a (%)</i>	<i>[η]^b (dLg⁻¹)</i>	<i>Chlorine Content (mmolg⁻¹)</i>	<i>Molar ratio of DADMAC (by Chlorine analysis) (by NMR)</i>		<i>GPC (in water) M_n M_w</i>	
1 / 3	1 h	90.6	13.5	2.00	24.7 %	24.2 %	13900	16000
1 / 1	1 h	78.8	9.2	3.70	50.6 %	48.9 %	11000	14700
3 / 1	1 h	87.0	5.1	5.04	75.1 %	74.2 %	9600	11500

a) Isolated yields.

b) Intrinsic viscosity in aqueous solution at 25 ± 2 °C (from Fuoss-Strauss plots).

The copolymerization proceeds rapidly in concentrated solutions and reasonably high conversions (up to 70 %) are attained within 80 min for the case of 30 % (w/w) total monomer concentration, as shown in the conversion-time plot in Fig-3a. These data give linear semi logarithmic plot in Figure 4.3(2) indicating first order kinetics with a rate constant of $2.48 \pm 0.003 \times 10^{-4} \text{ s}^{-1}$, for the copolymerization of 1/1 mixture of the monomers at 60 °C.

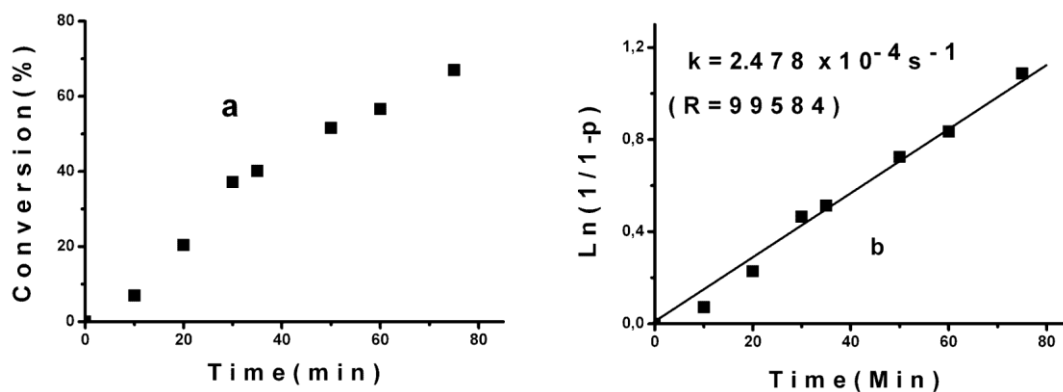


Figure 4.4: Conversion-time plots for the copolymerization of DADMAC-NVP mixture (1/1) (a), and its relevant first order kinetics plot (b).

GPC traces of the copolymer samples showed unimodal curves indicating copolymer formation. Figure 4.4 shows chromatogram of the 1/1 copolymer as a representative example. The GPC traces indicate weight average molecular weights in 11.500-16.000 range depending on the reaction time and monomer ratios (Table 4.2).

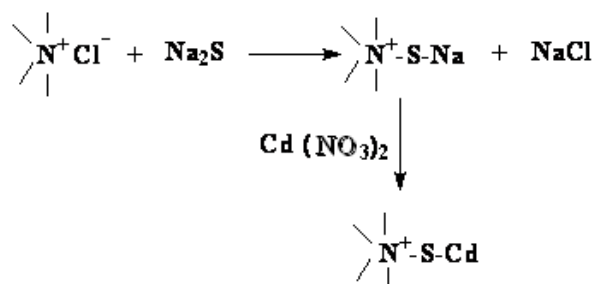


Figure 4.5: GPC trace of DADMAC-NVP (1:1) copolymer in water.

4.2 Preparation of CdS Nanocluster

The CdS nanoclusters were generated by gradual addition of cadmium acetate solution (1M) to the solution of sodium sulfide-copolymer mixture in water under sonication. This procedure gave nearly transparent and light yellow solutions. The solutions showed no evidence of flocculation upon standing for over 45 days at room temperature.

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 cadmium nitrate /polymer molar ratio was used as a measure of the stability limit for the copolymers. This ratio was found to be 160 for 1/1 DADMAC-NVP copolymer (Table 4.3).



Scheme 4.2: *In situ* formation mechanism of the CdS nanoclusters.

Regarding with the greater ratio for the copolymer with 75 % mole of DADMAC content, it is obvious that, the charged segments provide much higher stabilization, comparing with non-charged NVP units.

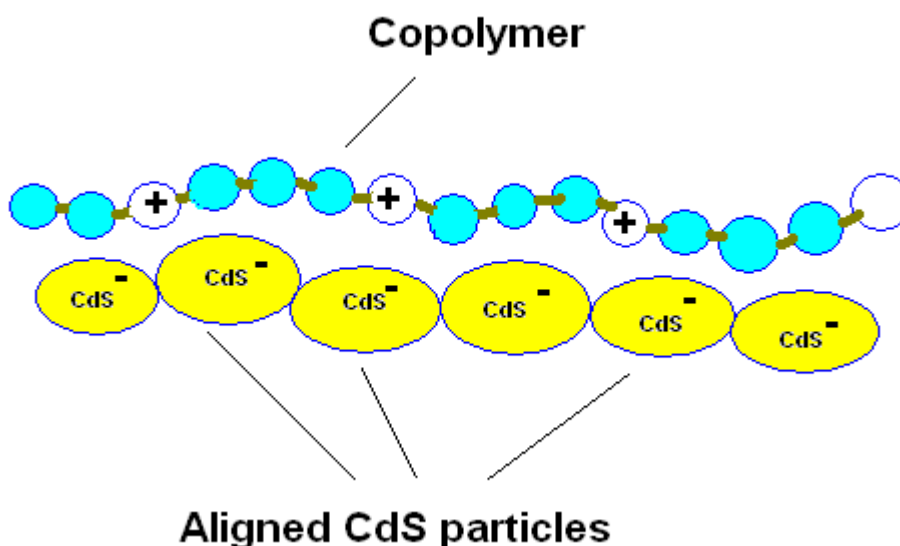


Figure 4.6: Schematic illustration of the stabilization of CdS nanoclusters by the cationic copolymer.

Most probably stabilization is being maintained by double salt formation between CdS^- and the quaternary ammonium group as depicted in the scheme 4.2 and in figure 4.5.

UV absorption spectrum of the CdS dispersion (Figure 4.6) stabilized with 1/1 DADMAC-NVP copolymer shows one maximum at 340 nm and a shoulder around 460 nm. The shoulder can be ascribed to the surface plasmon absorption of 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.

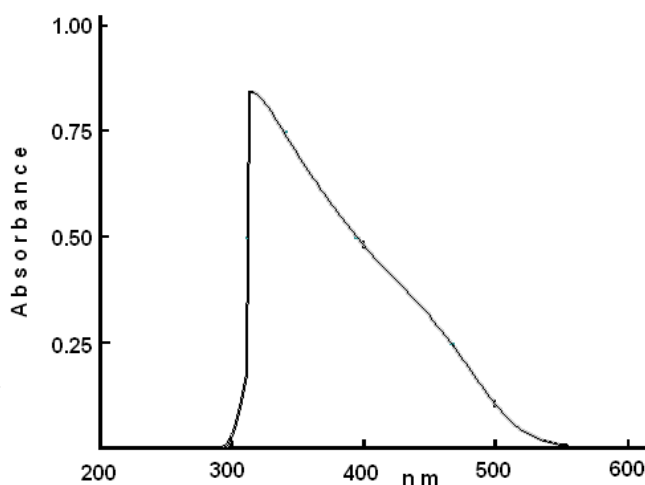


Figure 4.7: UV-Visible spectrum of aqueous CdS nanoparticle dispersion stabilized with $(\text{DADMAC})_{54.5}\text{-co-(NVP)}_{53}$

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 shows a broad emission band in 550-800 nm range as shown in Figure 4.7. Position of emission maxima and bandwidths are known to be related to the shape and size of the particles [97-98]. So the fluorescence at longer wavelength must be associated with the lengths of CdS clusters.

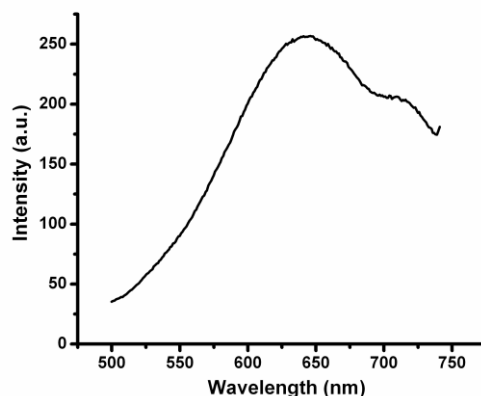


Figure 4.8: Fluorescence emission spectrum of aqueous CdS nanoparticle dispersions stabilized with (DADMAC)₉₇-*co*-(NVP)₃₄ (excitation wavelength, 390 nm).

Interestingly TEM images of the dispersions (Figure 4.8 right) show aligned and snake-like CdS clusters instead of nanospheres. Such an assembling must be due to template effect induced by cationic groups on the stretched copolymer chains. However, on left in the figure an individual CdS nanoparticle is observed. This might be due to the mechanical disintegration of the clusters while sonicating. Average lengths of the clusters are of order of 200-300 nm.

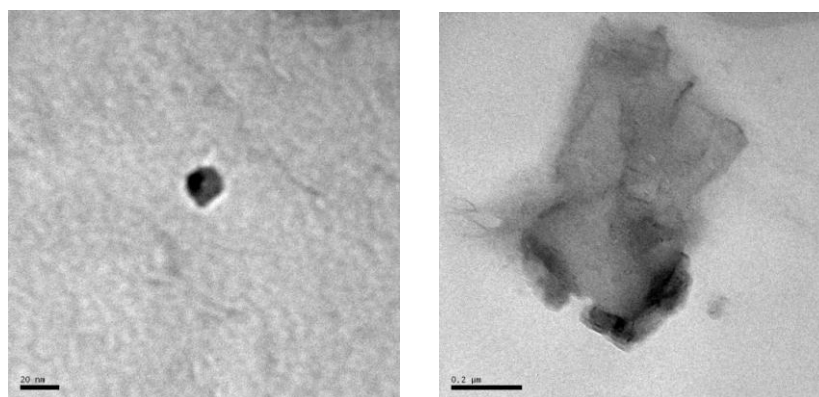


Figure 4.9: TEM images of CdS nanoparticle (left), and nanocluster (right).

These results are in consistent with the particle sizes obtained from DLS measurements in Figure 4.9. Histograms in this figure reveal significantly narrow size distribution of CdS clusters. Apparent average particle sizes in the figures increase from 194 to 290 nm as increasing DADMAC contents of the stabilizing copolymers. This is in accordance with the assumption of the template effect of the quaternary ammonium groups, discussed above.

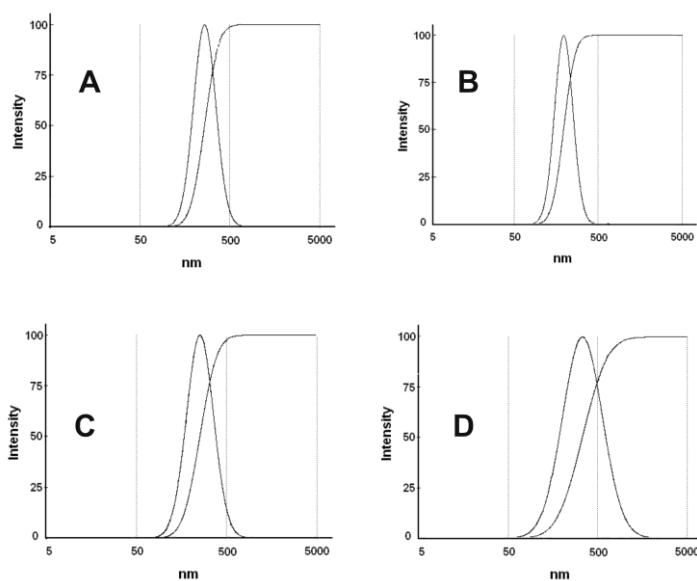


Figure 4.10: Particle size distributions of CdS nanoclusters in aqueous solution stabilized by copolymers with various DADMAC contents. 25% (A), 50% (B), 75% (C) and 100% (D).

XRD patterns of CdS powders (Figure 4.10) obtained by precipitation from the disperse samples show four 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 of β -CdS (JCPDS01-0647). The crystalline dimensions were found to be

$$a = b = c = 5.82 \text{ \AA}.$$

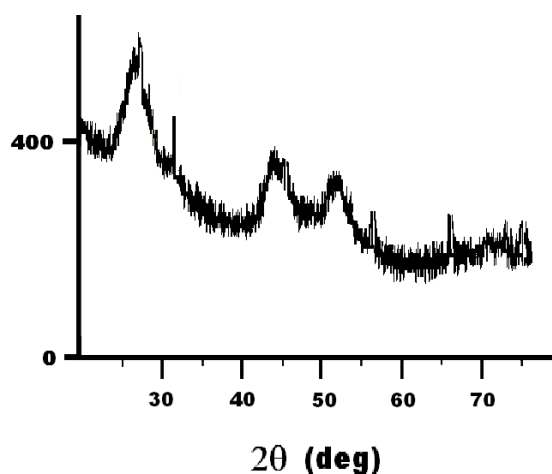


Figure 4.11: XRD pattern of CdS nanoclusters stabilized with DADMAC-NVP (1/1) copolymer.

4.3 Photocatalytic Hydrogen Generations

The aqueous dispersions (50 mL) containing 0.1 CdS were used for hydrogen generation in presence of Na_2S 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 photo corrosion of CdS. To avoid this problem a mixture of sodium sulfide and sodium sulfite was used as suggested in the literature [98]. However the use of more than 1 g of sodium sulfite resulted in sudden precipitation of CdS for the case of samples with $(\text{DADMAC})_{32}\text{-co-(NVP)}_{97.5}$ and $(\text{DADMAC})_{54.5}\text{-co-(NVP)}_{53}$. 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.

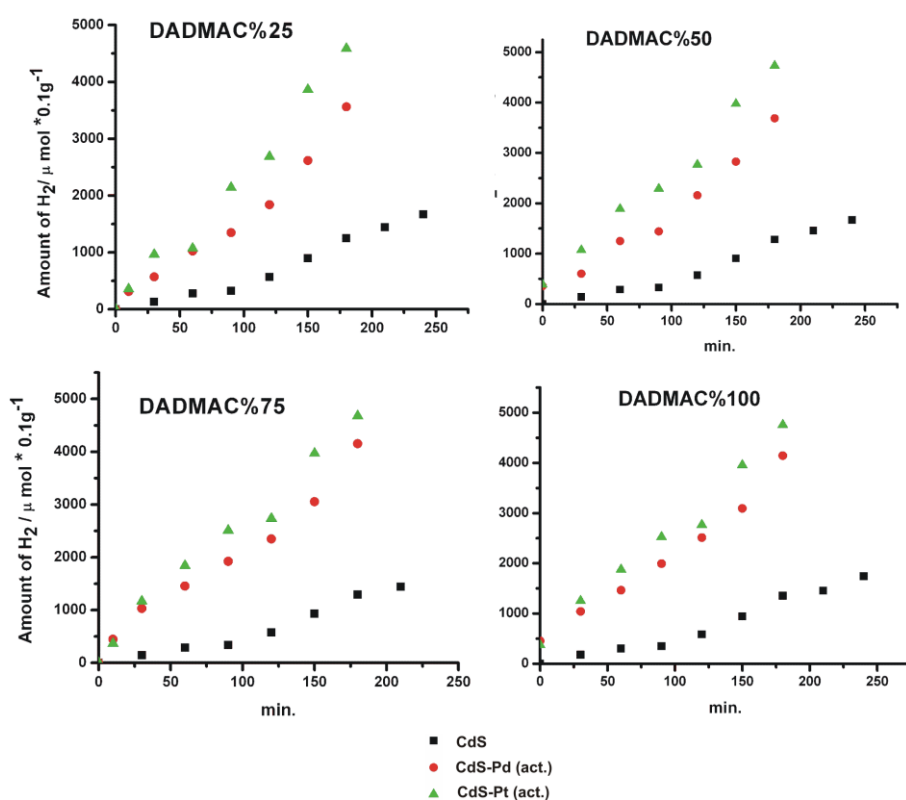


Figure 4.12: Hydrogen evolutions by photolysis of aqueous CdS nanoclusters stabilized with DADMAC-NVP copolymers, by illumination with mercury lamp (160W).

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 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 are linear as shown in Figure 4.11.

All the samples with different DADMAC contents represent similar behavior.

From the slopes of the curves hydrogen evolution rates of the samples were found to be in $0.264 \text{ mmol g}^{-1} \text{ min}^{-1}$ range. This reveals almost equal activity of CdS nanoclusters.

This might be due to nearly equal surface area of CdS cluster in the samples.

As to our knowledge, these hydrogen evolution rates measured are even higher than those for the CdS systems activated with noble metals [99].

Table 4.3: Comparison of the stabilizing limits of the copolymers.

Copolymer	Concentration Limit of CdS^a	$[\text{CdS}] /$ $[\text{DADMAC}]$	Stability under irradiation	Hydrogen ^a Evolution Rate ($\mu\text{mol}/0.1\text{g.min}$)
$(\text{DADMAC})_{32}\text{-co-(NVP)}_{97.5}$	0.05 M	1.0	fair	7.29
$(\text{DADMAC})_{54.5}\text{-co-(NVP)}_{53}$	0.071 M	0.82	good	7.32
$(\text{DADMAC})_{58}\text{-co-(NVP)}_{19}$	0.088 M	0.80	excellent	7.38
Poly (DADMAC)	0.104 M	0.81	excellent	7.49

(a): After appropriate dilution to give solution with 0.1 g CdS per 50 mL.

Moreover, we have also studied stabilities of the solutions against sun light irradiation. The stability limits of the solutions were simply estimated by exposure of the samples to sunlight. It was observed that the nanodispersions stabilized with 25-50 % of DADMAC.

4.3.1 Effects of Noble Metals on Photocatalytic Hydrogen Generation

Presence of noble metals has been reported to enhance catalytic activity of CdS in hydrogen generation [100] from water. Ranjit et al [101] 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 aqueous solution) metals. Fig-8 shows photo generated hydrogen as a function of irradiation time in the presence and absence of the noble metals. From the figure it is clearly seen that in the presence of Pt metal rate of the hydrogen evolution increases by a factor of 3.3.

Table 4.4: Effects of noble metals on the hydrogen evolution rates of the dispersions stabilized by DADMAC-NVP copolymers.

Copolymer	Hydrogen ^a evolution rate ($\mu\text{mol}/0.1\text{g.min}$) (without activator)	Hydrogen ^b evolution rate ($\mu\text{mol}/0.1\text{g.min}$) (activated with Pd)	Hydrogen ^c evolution rate ($\mu\text{mol}/0.1\text{g.min}$) (activated with Pt)
(DADMAC) ₃₂ - co -(NVP) _{97.5}	7.29	17.44	23.94
(DADMAC) _{54.5} - co -(NVP) ₅₃	7.32	18.26	23.48
(DADMAC) ₅₈ - co -(NVP) ₁₉	7.38	19.11	23.12
Poly (DADMAC)	7.49	19.30	23.16

(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.

For the case of Pd metal, the hydrogen evolution rate becomes 17.44 ($\mu\text{mol}/0.1\text{g.min}$), which is 3.5 times greater than that of the non-activated sample. This result is consistent with the results reported by Sathish et al [99].

5. CONCLUSION AND RECOMMENDATIONS

Generation of CdS in aqueous solutions of DADMAC-NVP random copolymers yields stable nanoclusters instead of nanospheres, most probably due to template effect of the quaternary ammonium groups of the copolymer in the stranded form. The resulting dispersions stabilized with poly (DADMAC) and the copolymer with 75 % DADMAC are highly transparent and stable for over 45 days at room temperature. Those dispersions show excellent photo activities in hydrogen generation upon irradiation. The hydrogen evolution rates are as high as 12-13 mmol per gram of CdS in hour, while illuminating with 160 W of mercury lamp. Although the dispersions with low DADMAC contents tend to precipitate within 6-8 h of illumination, in the case of the copolymers with higher DADMAC contents the dispersions are quite stable for longer irradiation times.

It is important to note that, the hydrogen evolution rates measured in this work are even higher than those reported by Sathish et al [99]. This must be largely due to stabilization of the particles without encapsulation, because the capsules surrounding particles are expected to induce some kind of shielding effect and passivates the catalyst particles.

Regarding to the commercial availability of the starting materials, the procedure presented in this work provides a means of easy access to stable CdS nanoclusters having high catalytic activities for photolysis of water. The results also show that even higher catalytic activities can be attained with more stable and more transparent nano size CdS in water. This study also implies that the concept of cost effective hydrogen generation by photo catalytic means is not unrealistic.

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