



Cadmium sulfide decorated with carbon nanoparticles from peanut shells: An efficient photocatalyst

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Received 28 November 2019; revised and accepted 26 May 2020

Carbon decorated cadmium sulfide nanoparticles have been synthesized by chemical precipitation method in aqueous medium using dichloroacetic acid as a complexing agent to study their optical and photocatalytic properties. Carbon nanoparticles have been prepared from waste peanut shells by simple pyrolysis method. The as-prepared materials have been characterized by XRD analysis, UV-visible diffuse reflectance spectroscopy, spectrofluorometer, FTIR and BET analysis. SEM and TEM images indicate nano crystallites with spherical agglomeration of average 40 nm size. Band gap energy for pure CdS is observed in the order of 2.4 eV. As prepared carbon decorated CdS nanoparticles with increased surface area efficiently catalyzed the photodegradation of Rhodamine B dye solution under sunlight irradiation than pure CdS.

Keywords: Carbon nanoparticles, Cadmium Sulfide, Surface Area, Photocatalysis

In early years, use of solar energy as a visible energy source in photocatalytic reactions has great importance due green, free cost and renewable energy utilization. The semiconducting nanomaterials such as metal oxides and metal chalcogenides are widely used as a catalyst in photodegradation of water polluting dyes such as methyl orange, rhodamine etc. In photo degradation of dyes, composite nanomaterials are used in large scale due enhancing stability and change in desirable properties of composite nanomaterials. Some carbon quantum dot doped CdS material has enhanced photodegradation efficiency due to trapping of electrons by carbon dots at surface¹. The doping of semiconducting species with carbon dots or carbon nanomaterial enhances the electrical and optical properties of materials. It can be observed that the composite semiconducting nanomaterials efficiently absorbs visible light and has tendency to trap photoelectrons which hindered charge hole recombination and has improved photocatalytic activity. The carbon nanodots or carbon quantum dots from natural materials such as vegetable waste, fruit skin, coconut shell, rice husk or peanut shells by carbonization and pyrolysis is interesting method for preparation of carbon nanoparticles without chemicals²⁻⁵. The carbon nanoparticles are widely used in metal sensing, bio imaging due to its optical,

electrical and biological properties^{6,7}. Carbon nanoparticles prepared from peanut shells by simple pyrolysis method are highly photo luminescent and shows metal sensing abilities⁷. The semiconducting material as CdS has good optical and electrical properties due to considerable band gap energy. It can be used in optical devices, sensors, solar energy harvesting, electronic devices⁸. The composite CdS materials such as CdS/TiO₂ composite used for drug degradation under visible light illumination⁹. CdS/rGO shows efficient optoelectronic properties, photo electrochemical splitting of water to hydrogen¹⁰. CdS/g-C₆N₆ migration of electrons from CdS layer to g-C₆N₆ which results in the built-in electric field formation and promotes the effective visible light water-splitting photocatalysis¹¹. CdS/Se, CdS/CuSe shows formation of p-n junction and effective charge separations which improving optical, electrical and photo catalytic properties¹². Some researchers reported the change in band gap energies are observed in CdS material due to incorporation of dopant in material matrix which enhances existing properties of material^{13,14}.

In this work we have prepared, carbon nanoparticles from peanut shells by simple pyrolysis method and it was mixed with reaction mixture during formation of CdS in aqueous medium. The

homogeneous coating of carbon on CdS nanoparticles were occurred during process. The dichloroacetic acid (Cl_2CHCOOH) is used as a complexing agent first time during synthesis of CdS and carbon decorated CdS nanoparticles. The use of dichloroacetic acid during process fascinates the formation of CdS material due to inductive effect of two chlorine ions. As prepared CdS and carbon decorated CdS nanoparticles were studied for their optical and photocatalytic properties. The prepared material was tested for photodegradation of Rhodamine B dye solution under natural sunlight irradiation. The carbon particles at the vicinity of CdS nanomaterial harvest sunlight energy more efficiently for photo degradation of Rhodamine B dye solution.

Materials and methods

Materials and reagents

The dry Peanut shells were collected from Konkan region of M.S. India and they were washed with distilled water to remove soil particles. Soil free shells were preheated in oven for 8 h at 80 °C. The chemicals used were SD fine analytical grade cadmium carbonate (CdCO_3), dichloroacetic acid (Cl_2CHCOOH), thiourea, ammonia and double distilled water.

Preparation of carbon nanoparticles

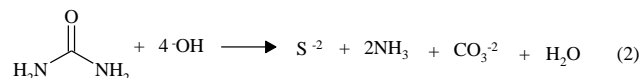
Carbon nanoparticles were synthesized from peanut shells by simple pyrolysis methods. For that 50 g preheated peanut shells were weighed and cuts into small pieces. It is then transferred to ceramic evaporation dish and introduced for heating in laboratory oven at 400 °C for 2 h. After heating the resultant black material were allowed to cool and crushed in mortar pestle to get fine powder. The obtained carbon powder was passed through 100 mesh sieves to get homogenous size. Then, 1.0 g of carbon powder was added to 50 ml double distilled water and then sonicated for 20 min gives highly dispersed solution of carbon nanomaterial¹⁴.

Preparation of Carbon decorated CdS and CdS nanoparticles

Carbon decorated CdS and pure CdS nanoparticles were synthesized by chemical precipitation method in aqueous medium. For that, to the 10 ml 0.2 M cadmium carbonate (CdCO_3) solution aqueous NH_3 solution was added dropwise from a burette in reaction mixture which gives first milky white precipitate of cadmium hydroxide. The excess aqueous ammonia was added to dissolve the

precipitate. To this, 10 ml 0.2 M thiourea solution prepared in de-ionized water was added as a source of S^{2-} ion. The equimolar solution of dichloroacetic acid Cl_2CHCOOH ($\text{pK}_a = 1.35$ at 25 °C) was added to the reaction mixture which is act as complexing agent. It gives cadmium dichloroacetate complex in which two electronegative Cl^- ions cause easy release of Cd^{2+} ions during growth of reaction. In our previous work we used monochloroacetic acid ($\text{pK}_a = 2.86$ at 25 °C) as a complexing agent which results in increase of rate of product formation¹⁵. The usage of dichloroacetic acid complexing agent fascinates reaction more efficiently than monochloroacetic acid due to the negative inductive effect of two electronegative Cl^- ions present in cadmium dichloroacetate $[\text{Cd}(\text{Cl}_2\text{CHCOO})_2]$ complex. During synthesis of CdS and carbon decorated CdS it was observed that the product formed within 30 min of reaction time. For the synthesis of carbon decorated CdS material, 10 ml (50 ppm) of dispersed solution of carbon was added in the reaction mixture which was kept in an oil bath at constant stirring. The temperature of the oil bath was optimized to 60 ± 5 °C. The obtained solid material was washed with deionized water for 5 times and dried at room temperature. These powdered materials were then heated in oven at 200 °C for 2 h and introduced for characterization.

Growth mechanism



Characterization and photocatalytic techniques

An annealed CdS and carbon decorated CdS nanomaterials were analyzed for crystallographic identification by X-ray diffractometer (JEOL-JSDX-60PA) with $\text{Cu K}_{\alpha 1}$ -radiation source has wavelength $\lambda = 1.54184$ Å and the energy $E = 8.052$ keV. For surface morphological analysis Cambridge Stereo Scan (USA) Scanning Electron Microscope (SEM) was used. The shape and phase of particles were investigated using transmission electron microscopy (TEM) (PHILIPS, CM 200) operating voltage 20-200 kV. The diffused reflectance spectra were recorded in the range of 200-600 nm on UV-visible-

NIR double beam spectrophotometer (JASCO, V-770). The photoluminescence (PL) spectra were recorded on spectrofluorometer (JASCO, FP-8200). FTIR spectral analyses were carried out on FTIR spectrometer (JASCO, 4600 JAPAN). For the investigation of surface area and pore diameter of material BET surface analyzer (Lab India) were used. The photocatalytic degradation of Rhodamine-B was investigated by time dependent counting of absorption data under visible region (400-800 nm) on UV-vis-NIR double beam spectrophotometer (Shimadzu UV310PC). For confirmation of degradation of Rhodamine-B samples were analyzed by FTIR (Bruker Alpha II). All investigations of optical measurements were carried out at the room temperature.

Results and Discussion

Structural characterization of pure CdS, pure carbon and carbon decorated CdS

Crystallographic studies of pure CdS, pure carbon prepared from peanut shells and carbon decorated CdS nanomaterials were carried out from the X-ray diffraction technique. The Fig. 1a shows single peak at 2θ value of 22.59° of pure carbon nano particles prepared from peanut shells which indicated the absence of any other X ray active impurities. The carbon nanoparticles prepared from pyrolysis of peanut shells have uniform nature and purest form. The Fig. 1b indicates peaks at 2θ values of 26.70° , 43.97° and 52.07° are due to (111), (220) and (311) planes, respectively corresponds to face centered cubic phase of CdS matches perfectly with 26.45° , 43.88° and 51.97° of JCPDS data (card no. 89-0440). In the case of carbon decorated CdS nano material XRD peaks shifts to smaller 2θ values because of change in lattice parameters of crystal due to carbon coated to CdS material. The lattice parameters of crystals have been calculated by using following equation.

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \quad \dots (5)$$

Where 'd' is the interplanar distance and (h k l) are Miller indices of the lattice planes. The lattice parameter 'a' for CdS and carbon decorated CdS was found to be in the order of 5.8383 \AA and 5.9956 \AA , respectively¹⁵. The grain size (D) of CdS and carbon decorated CdS have been calculated by using Scherrer's formula.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \dots (6)$$

Where K is constant (0.94), $\lambda = 1.54184 \text{ \AA}$ is the wavelength of the X-ray used, θ is Bragg's diffraction angle (in rad) and β is broadening of diffraction line measured at half of its maximum intensity. The grain size for prepared CdS is calculated as 24.28 nm while for carbon decorated CdS is 33.78 nm , which is also investigated by TEM images shown in Fig. 4. The increase in grain size was observed for carbon decorated CdS as compared to pure CdS nanoparticles as shown in BET data analysis.

The Fig. 2 shows FTIR spectrum for annealed samples of pure carbon and carbon decorated CdS nanomaterials. In this spectrum, peaks observed between 600 to 4000 cm^{-1} as 2969.84 cm^{-1} (-C-H Asymmetric stretching), 1742.37 cm^{-1} (-C-O stretching of carbonyl), 1368.25 cm^{-1} (-C-C stretching), 1213.01 cm^{-1} (-C-O stretching), 674.96 cm^{-1} (-C-H bending). Sharp peak at frequency 652.78 cm^{-1} was

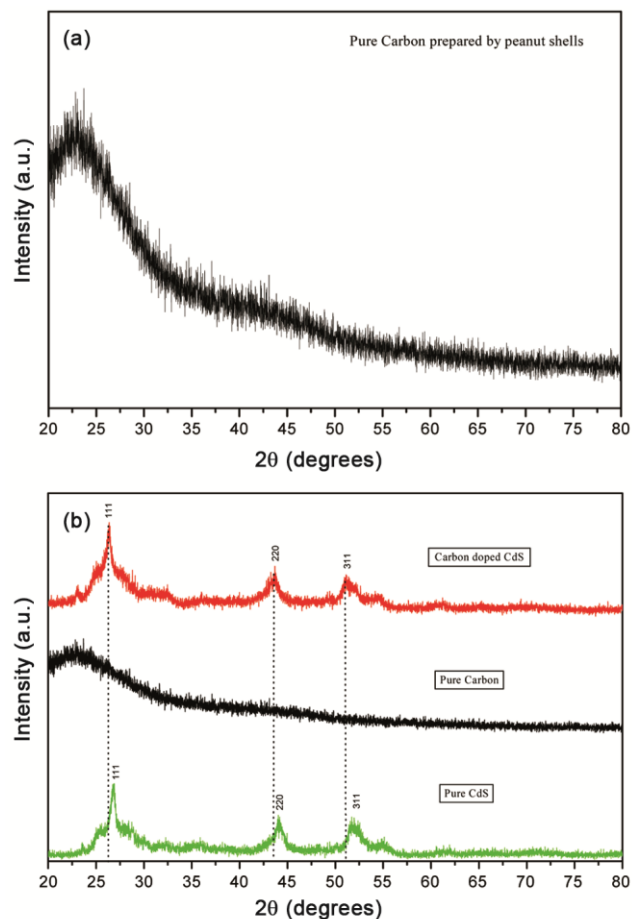


Fig. 1 — XRD of (a) carbon nanoparticles prepared from peanut shell and (b) of pure CdS, carbon and carbon decorated CdS nanoparticles.

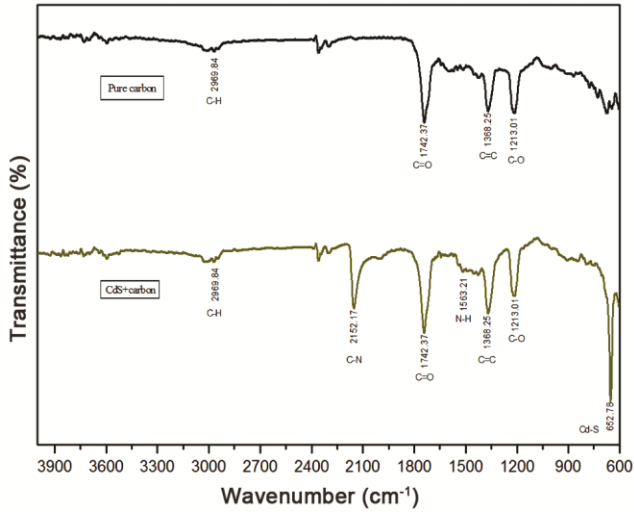


Fig. 2 — FTIR spectrum of carbon prepared from peanut shell and carbon decorated CdS nanoparticles.

due to Cd-S bond stretching of cadmium sulphide^{16,17}. The peaks at 1563.21 cm^{-1} (-N-H bending) and 2152.17 cm^{-1} (-C-N stretching) are due to ammonia used during synthesis of nanoparticles.

The Fig. 3a and 3b shows SEM micrographs of pure CdS and carbon decorated CdS materials. It can be observed that the particles are spherical shaped with agglomeration together. It is also indicating crystalline nature of material. Fig. 4a shows TEM image of pure carbon indicates uniform nature and nearly spherical morphology of carbon nanoparticles. Fig. 4b shows carbon decorated CdS nano material, it is observed that CdS nano crystallites are uniformly coated with carbon nanoparticles prepared from peanut shells. The carbon coated CdS nanoparticles have average particle size of 40 nm. The crystalline nature of prepared material with cubic phase^{18,19} which is confirmed by selected area electron diffraction (SAED) pattern as shown in Fig. 4c.

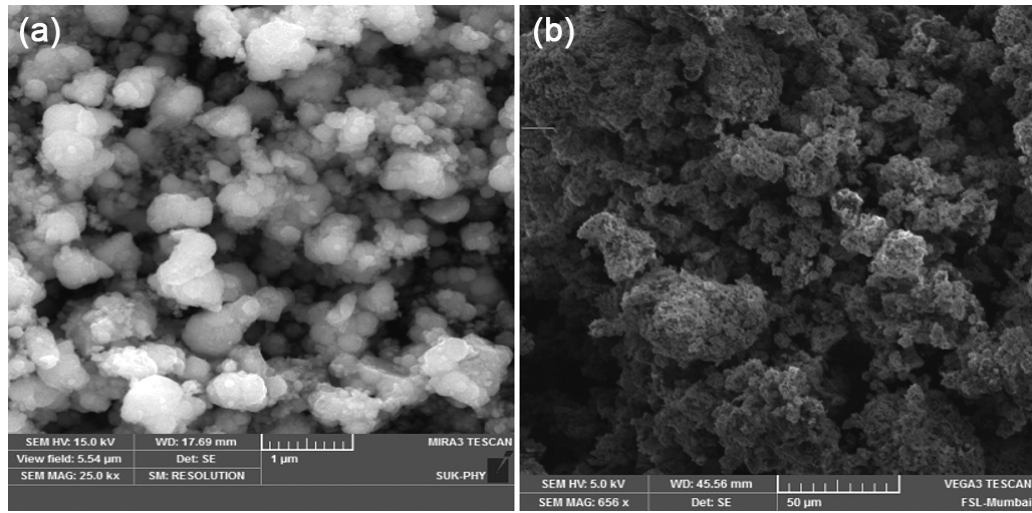


Fig. 3 — SEM images for (a) pure CdS and (b) carbon decorated CdS.

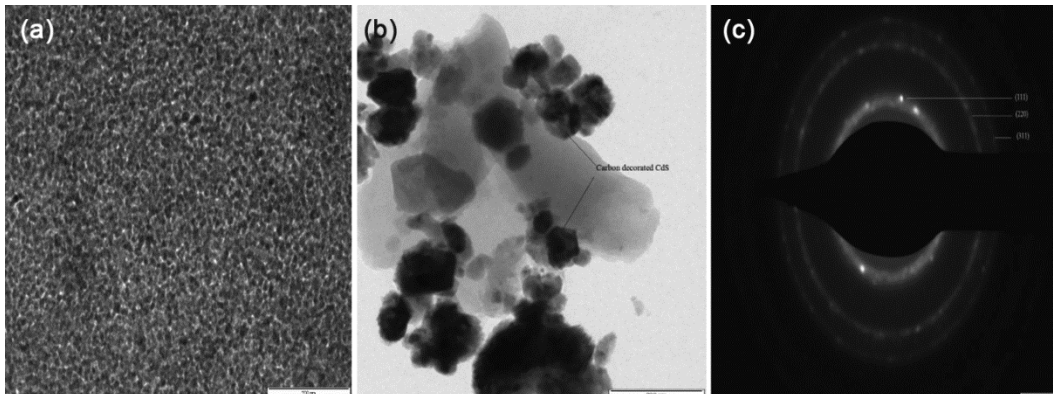


Fig. 4 — TEM images for (a) pure carbon prepared from peanut shell and (b) carbon decorated CdS, and (c) SAED pattern for carbon decorated CdS.

Optical characterization of CdS and carbon decorated CdS

The Fig. 5 shows the UV-visible diffuse reflectance spectra of pure CdS and Carbon decorated CdS nanoparticles. The reflectance characteristics for both are similar with small change in absorption edge. The pure CdS and carbon decorated CdS exhibits strong absorption in the UV region with wavelength between 250-350 nm and visible light region with wavelength range between 400-600 nm. The absorption of carbon decorated CdS is higher than CdS in both UV and visible region, carbon nanoparticles prepared from peanut shells acts as an good electron acceptor indicating the carbon decorated CdS would exhibit excellent photocatalytic activity than pure CdS nanoparticles^{20,21}. The optical band gap of pure CdS nanomaterial is calculated by plotting $(\alpha h\nu)^2$ versus the photon energy ($h\nu$). In order to get the value of the direct allowed optical band gap (E_g), extra plotted straight line to intercept photon energy axis. The observed band gap energy for pure CdS is 2.4 eV which is fairly close to the values reported in literature²². The Fig. 6 shows photoluminescence (PL) spectra of CdS and carbon decorated CdS. It can be observed the quenched PL intensity with blue shift of peak for carbon decorated CdS as compared to pure CdS. It indicates hindrance of charge recombination due to reduced electron-hole combination with increased electron density which enhances the photocatalytic ability of carbon decorated Cd nanoparticles²³.

Surface area analysis for CdS and carbon decorated CdS

The Fig. 7a and 7b show the N₂ adsorption-desorption isotherm for pure CdS and carbon

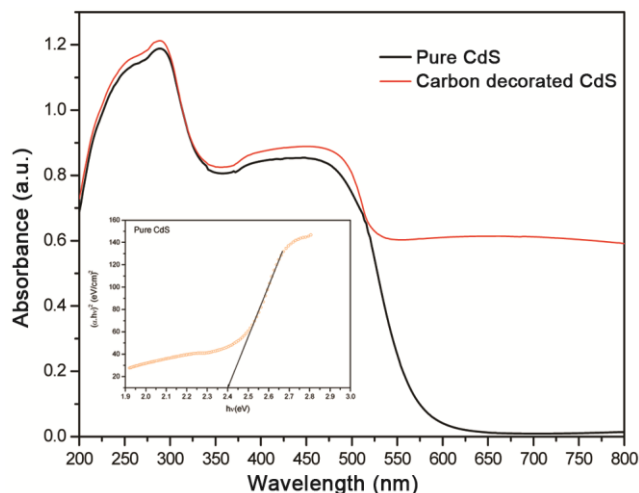


Fig. 5 — Diffuse reflectance spectra of CdS and carbon decorated CdS nanoparticles.

decorated CdS, respectively. It was analyzed to investigate Brunauer, Emmett and Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pre size distribution which shows Type IV isotherm with hysteresis loop. The synthesized nanoparticles indicate existence of mesoporous. The multipoint BET surface area for pure CdS and carbon decorated

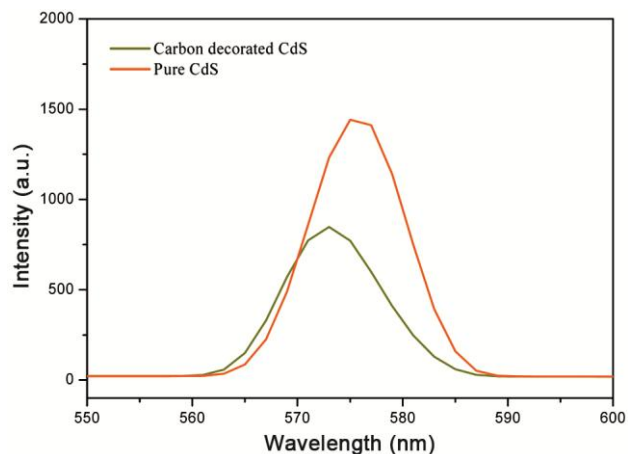


Fig. 6 — Photoluminescence (PL) spectra of CdS and carbon decorated CdS nanoparticles.

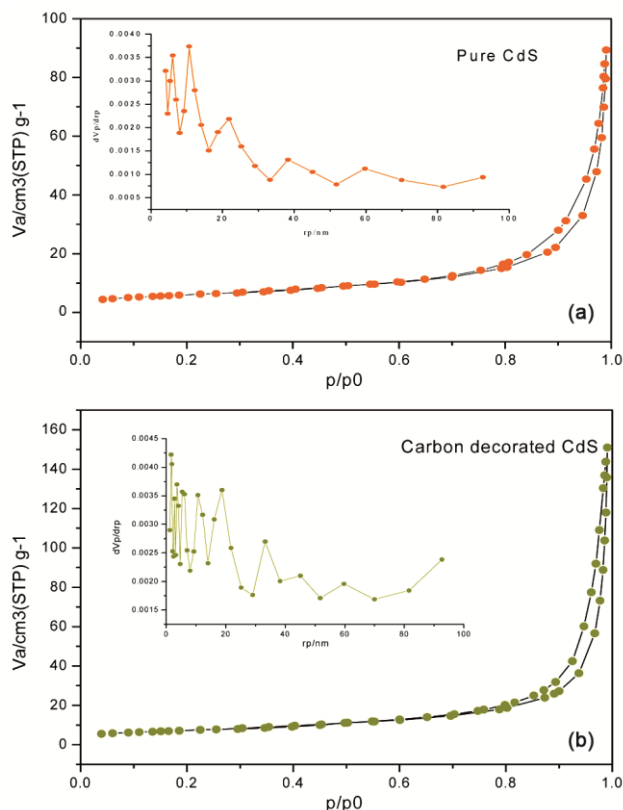


Fig. 7 — BET surface analysis graph of (a) pure CdS and (b) carbon decorated CdS.

CdS was found to be 11.182 m²/g and 35.295 m²/g, respectively, these indicates carbon decorated CdS shows higher surface area and have a greater nitrogen adsorption capacity than pure CdS material^{24,25}. The physical parameters of nitrogen isotherms, such as surface area (m²/g), BJH average pore diameter (nm) and the pore volume V_p (cm³/g) shown in Table 1.

Photocatalytic degradation of Rhodamine B solution

Photocatalytic activity of CdS and carbon decorated CdS photocatalyst was studied against Rhodamine-B under natural sunlight irradiation. The photo catalytic test performed at neutral pH. For that 0.1 g of photocatalyst material was added to 100 ml of 5 ppm Rhodamine-B dye solution in 250 ml clean and dry glass beaker. Before irradiation to sunlight, the solution mixed with material was sonicated for 15 min then it was kept in the dark for at least 1h allowing the adsorption/desorption equilibrium to be reached. Then, the solution was irradiated under sunlight of average intensity of 6.66 kwh/m²/day (Latitude: 16.75 longitude: 74.25). First sample was taken before the irradiation in order to determine the Rhodamine-B concentration in dark, the absorption value considered as the initial concentration (A_{initial}). The samples were then withdrawn regularly from the beaker by an order of 30 min, 60 min, 90 min and 120 min irradiation and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by using a UV-visible spectrophotometer at wavelength range from 400 to 800 nm and the value of 120 min was taken (A_{final}). The efficiency of CdS and carbon decorated photocatalyst in presence of sunlight was estimated at 120 min. The efficiency of material was calculated by using following equation.

$$\text{Efficiency } (\eta) = \frac{[A_{\text{initial}} - A_{\text{final}}]}{A_{\text{initial}}} \times 100 \% \quad \dots (7)$$

It was observed that prepared pure CdS material has 25% efficiency for degradation of Rhodamine-B shown in Fig. 8a, for pure carbon it was 60% shown in Fig. 8b. and carbon decorated CdS material has

Table 1 — Physical parameters of nitrogen adsorption isotherms for CdS and carbon decorated CdS

Photo catalyst	Surface area (m ² /g)	Average pore diameter (nm)	Pore volume (cm ³ /g)
Pure CdS	11.182	24.277	0.1286
Carbon decorated CdS	35.295	33.798	0.2137

85% efficiency shown in Fig. 8c, which is enhanced photocatalytic property than CdS material. Fig. 9 indicates graph of concentration (C/C₀) against time for change in concentration with time reveals reaction growth kinetics. The decrease in concentration were observed more in the case of carbon coated CdS as compared to pure carbon and pure CdS material.

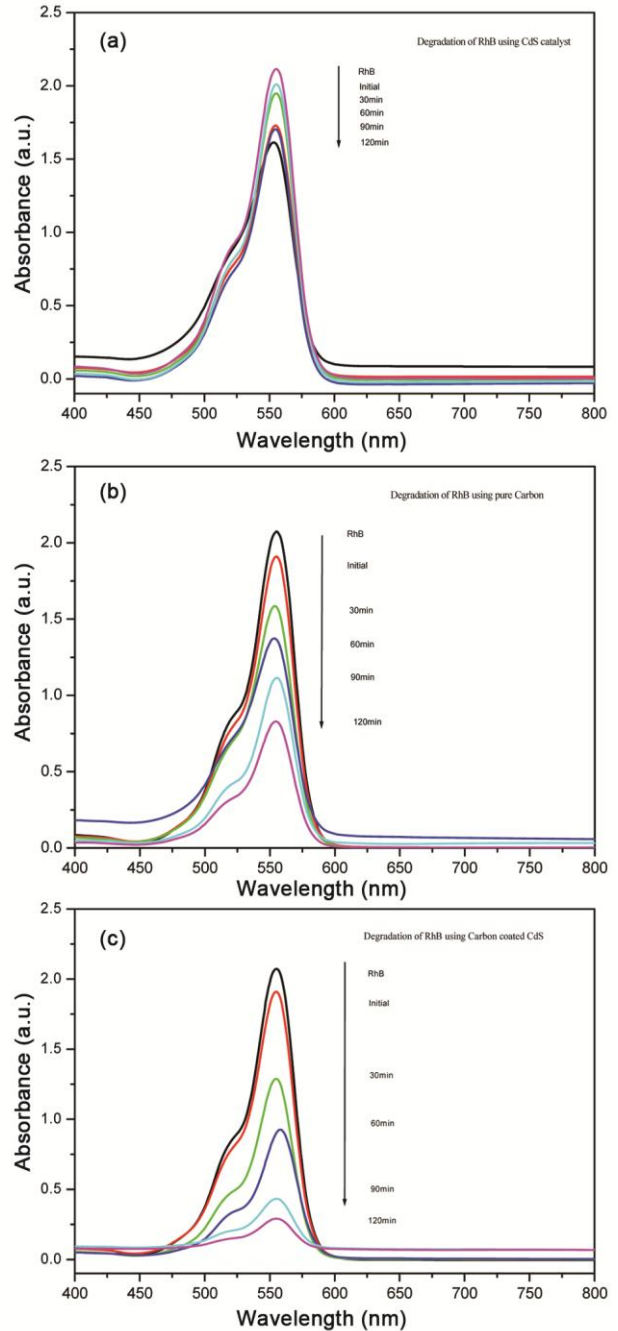


Fig. 8 — UV-visible spectra for degradation of RhB using (a) CdS photocatalyst, (b) pure carbon and (c) carbon decorated CdS photocatalyst.

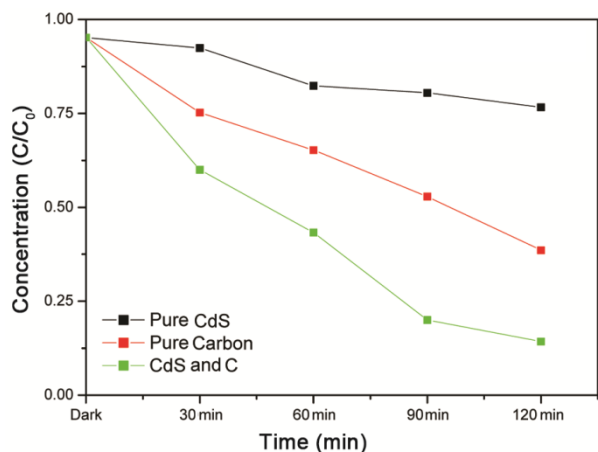


Fig. 9 — Plots showing change in concentration with time in the degradation of Rhodamine B using different catalysts.

The carbon present on the surface of CdS particles increases electron density in conduction band. The carbon traps photoelectrons at surface of composite material and hindered recombination of charge and hole^{1,2,3}. The free electrons probably react with dissolved oxygen molecules and produce oxygen peroxide radical $O_2^{\bullet-}$ the positive charged hole (h^+) may react with the OH^- derived from H_2O to form hydroxyl radical OH^{\bullet} . The Rhodamine B molecule then can be photo catalytically degraded by oxygen peroxide radical $O_2^{\bullet-}$ and hydroxyl radical OH^{\bullet} to forms CO_2 , H_2O and other mineralization products²⁶⁻²⁸ as shown in Fig. 10.

FTIR study of Rhodamine-B dye for photodegradation

Photo catalytic activity of CdS and carbon decorated CdS materials were confirmed by FTIR Spectroscopy analysis technique by using Rhodamine B dye. The Fig. 11 show FTIR spectra of Rhodamine B dye before and after photodegradation study. The spectrum of Rhodamine B dye shows peaks at 1574.04 cm^{-1} and 1407.31 cm^{-1} are due to aromatic C-C vibrations. The peak observed at 1339.43 cm^{-1} is due to bond vibrations of carbon-aryl group and peak at 1175 cm^{-1} is due to the alkyl chloride group. The peaks observed at 1065.38 and 1005 cm^{-1} are due to the asymmetric stretching of (C-O-C) bond. The peak observed at 681.72 cm^{-1} due to the bending vibrations of aromatic ring. The broad peak at near 3400 cm^{-1} is due to water contain²⁹. The solution of Rhodamine B with photocatalyst after 120 min analyzed under FTIR shows vanishing or decreased intensity of majority of peaks in the region of 600 to 1600 cm^{-1} confirms degradation of dye. It can be observed that carbon decorated CdS

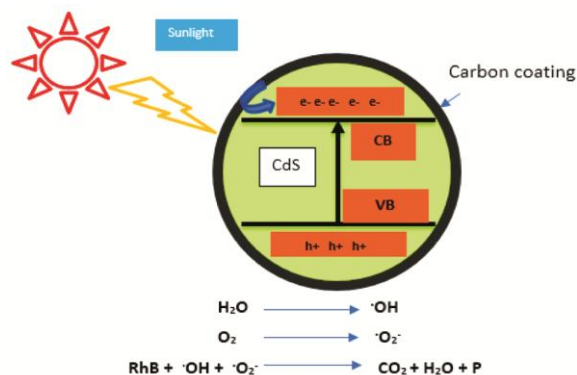


Fig. 10 — Schematic representation for the degradation mechanism of Rhodamine B.

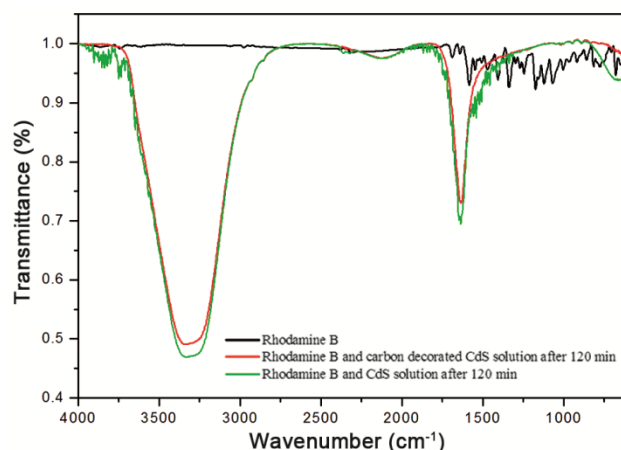


Fig.11 — FTIR spectra of pure RhB and solution of RhB after 120 min degradation using CdS and carbon decorated CdS.

efficiently degrades Rhodamine B dye solution than pure CdS under sunlight irradiation.

Conclusions

The carbon nanoparticles were successfully synthesized from natural waste peanut shells and it coated uniformly on CdS material. X-ray study revealed that CdS and carbon decorated CdS have crystalline nature with prominent cubic phase. The use of dichloroacetic acid as a complexing agent during synthesis of material fascinates more efficiently the reaction due to negative inductive effect of two Cl^- ions. SEM and TEM images show the material with spherical agglomeration of particles with average particle size of 40 nm . The diffuse reflectance spectra suggest the CdS and carbon decorated CdS shows strong photo absorption in UV-visible region with 2.4 eV band gap energy for pure CdS material. The carbon decorated CdS shows high ability of absorption of photoelectrons which

shows quenched PL intensity with blue shift. BET surface analysis confirms increase in surface area and pore diameter due to carbon coating. As carbon decorated CdS shows highly efficient photocatalytic activity than CdS. It degrades Rhodamine B dye solution up to 85% with natural sunlight irradiation. It can be used for photodegradation of organic pollutants such as Rhodamine-B and similar dyes in natural water.

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