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Extremely high photocatalytic activity of polymer nanospheres embedded with CdS nanoparticles prepared by a novel method

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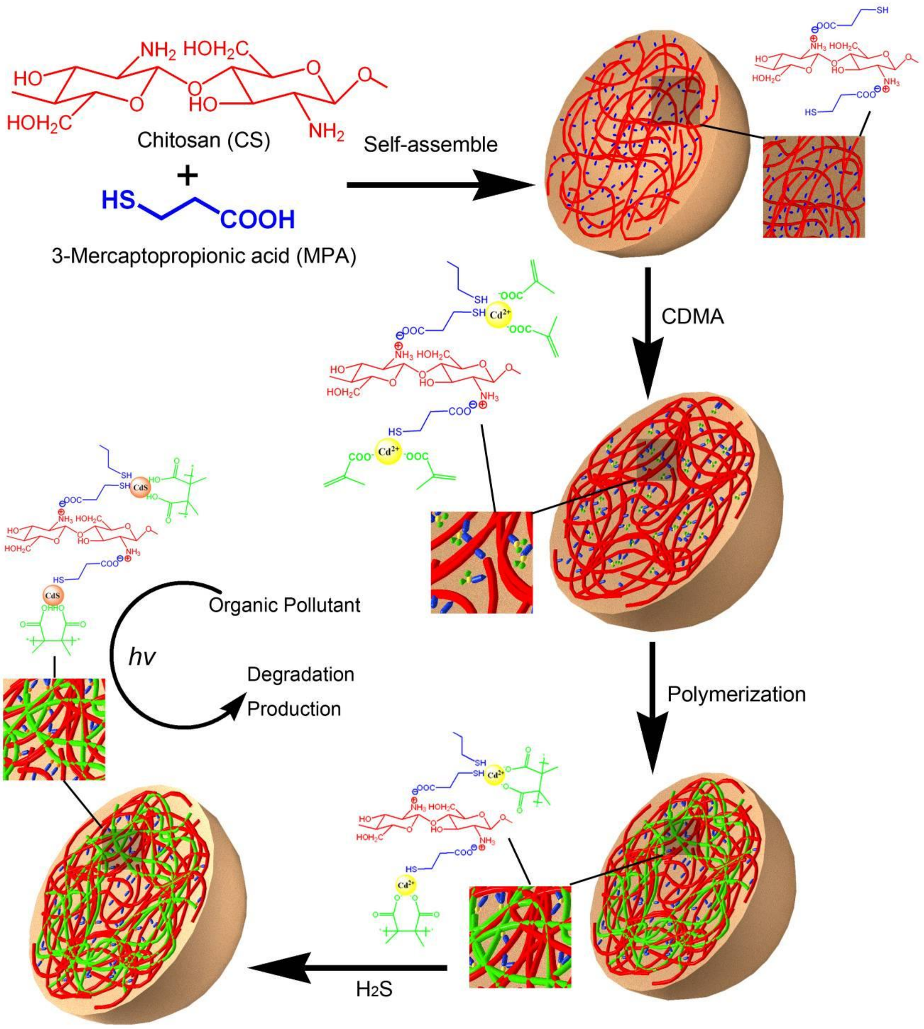
Abstract: A novel, practicable and convenient route has been developed to prepare polymer nanospheres embedded with CdS nanoparticles which show an extremely high photocatalytic activity compared with other photocatalysts. In this method, polymer nanospheres were fabricated through the polymerization of cadmium dimethacrylate which was introduced into self-assembly system of chitosan and 3-mercaptopropionic acid. Then CdS nanoparticles were prepared in-situ by inflating H_2S into the polymer nanospheres.

Introduction

The unique electronic and photonic properties of semiconductor nanoparticles have been used in a range of photoelectronic and photocatalytic applications [1-5]. Heterogeneous photocatalysis using the semiconductor is a general and efficient method for destroying organic pollutants in aqueous media, and its use has been increasing for the treatment of a number of industrial residues [4,5]. In order to improve the efficiency of catalysis, porous inorganic material has been synthesized as one of the prospective micro- or nanoreactors for photocatalysis due to their high porosity and specific surface area at large external size [6-12]. But, by this method, connectivity and availability ratio of pore-way is difficult to be controlled, therefore the enchancement of the catalytic activities of photocatalysts is limited through this approach. And in order to improve the water solubility, environmental benignancy and chemical stability of semiconductor nanoparticles, various capping ligands have been used to modify the surface of the nanoparticles. However, semiconductor nanoparticles, capped with small molecules such as mercaptoacetic acid, are easily degraded by hydrolysis or oxidation of the capping ligand [13]. To overcome this problem, different methods to prepare semiconductor nanoparticles embedded in polymer microspheres have been used, such as semiconductor nanoparticles stabilized in micelles, microemulsions or polyelectrolyte capsules, or introduced into suspension polymerization or atom transfer radical polymerization (ATRP) systems with polymerizable ligands [13-20].

Herein we report a novel, convenient, and more direct method (Scheme 1) to obtain a novel nanophotoreactor, namely water dispersible and stable polymer nanospheres embedded with CdS nanoparticles (PNECN), which shows an extremely high photocatalytic activity. In this method, a kind of polyelectrolyte-saccharide was introduced into nanophotoreactor to fill up space between well-dispersed CdS nanoparticles instead of pore-way as the media of transmitting reactants and products. Polyelectrolyte-saccharide in PNECN can extract organic or biological pollutants and concentrate them in the vicinity of semiconductor photocatalysts. So the polyelectrolyte-saccharide overcomes the obstacle of porous material and increases contact probability of semiconductor nanoparticles with reactants, which would enhance the catalytic activity of photocatalyst. Moreover, compared with other methods to prepare polymer spheres containing semiconductor nanoparticles, the method described in this paper is always performed in aqueous solution without any complex ligands, regular amphiphilic polymers, harsh reaction condition, as well as repeated absorption and washing process [13-20].



Scheme 1. A proposed scheme of the formation of the polymer nanospheres embedded with CdS nanoparticles.

Results and discussion

Chitosan (CS), which bears amino group, was chosen as the cationic polyelectrolyte-saccharide in this work. 3-Mercaptopropionic acid (MPA), which bears carboxylic and mercapto groups, was used as the anionic small molecule and metal-ion complexing agent. CS was dissolved in an aqueous solution of MPA with a stoichiometric molar ratio of 1:1 ([glucosamine unit]/[acid]). Transmission electron microscopy (TEM) pictures in Fig. 1a shows that the self-assembled structure of CS-MPA in aqueous solution is sphere-like. Then, aqueous solution of cadmium dimethacrylate (CDMA, a metal-containing monomer containing two C=C bonds) was added into the solution. Fig. 1b shows that the self-assembled structure of nanospheres is kept. The CDMA involved in the self-assembly process combined with mercapto group of MPA. Meanwhile the carboxyl group of MPA interacted with amino of CS by electrostatic force. And then polymer nanospheres (Fig. 1c) were fabricated through polymerization initiated by potassium persulfate at 80 ^{o}C which was allowed to proceed for 90 min. After that CdS nanoparticles (Fig. 1d,e) were synthesized in-situ by inflating hydrogen sulfide into solution of polymer nanospheres. Thus PNECN was formed.

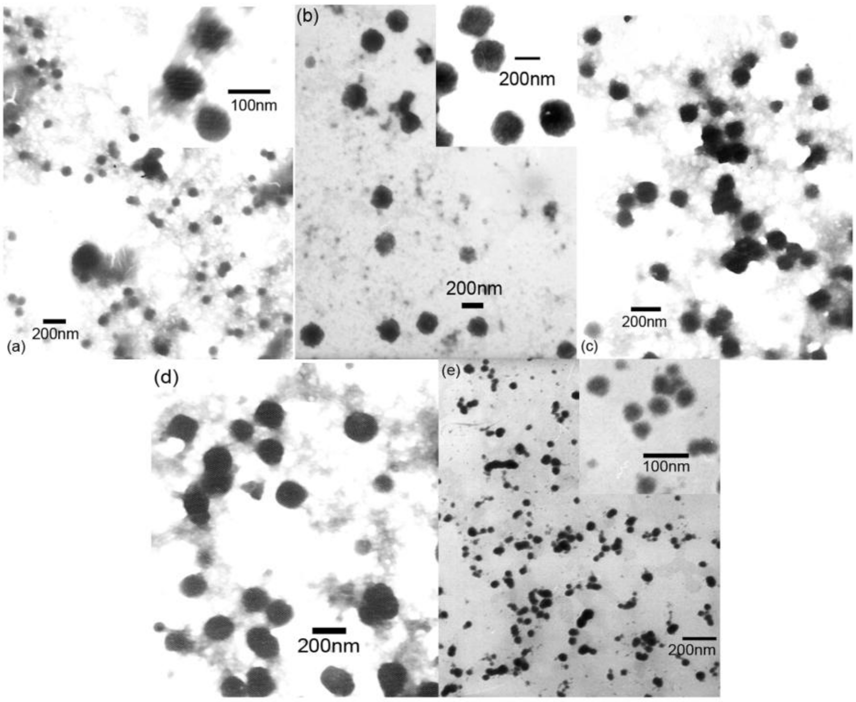


Fig. 1. TEM micrograph of CS-MPA self-assembled structure (a), CS-MPA-CDMA self-assembled structure (b), CS-MPA-PCDMA nanospheres (c), PNECN (d, e). The samples (a,b,c and d) were stained by phosphotungstic acid but (e) was observed without any staining agents. The inset is a higher magnification micrograph.

In order to verify the necessity of introducing C=C bond into self-assembly system for fabricating polymer nanospheres, cadmium nitrate was added into CS-MPA self-assembly system instead of CDMA. After inflating hydrogen sulfide into solution in the same way, there were not any sphere-like structure but only some CdS nanoparticles capped with CS (CNCC) in the solution (Fig. S1).

A typical X-ray powder diffraction of PNECN is shown in Figure 2. There are three sharper peaks corresponding to (111), (220) and (311) planes of cubic CdS phase [21]. The PNECN XRD peaks are relatively broad due to quantum size effect of CdS nanoparticles. A selected area electron diffraction pattern also justifies the presence of cubic CdS (Fig. 2). Moreover, the CdS nanoparticles embedded in the polymer nanosphere show an absorption edge at about 2.62 eV, which is similar to CNCC (Fig. S2). In addition, thermogravimetric analysis test data indicates there are 40% (mass percent) CdS in the polymer nanosphere (Fig. S3).

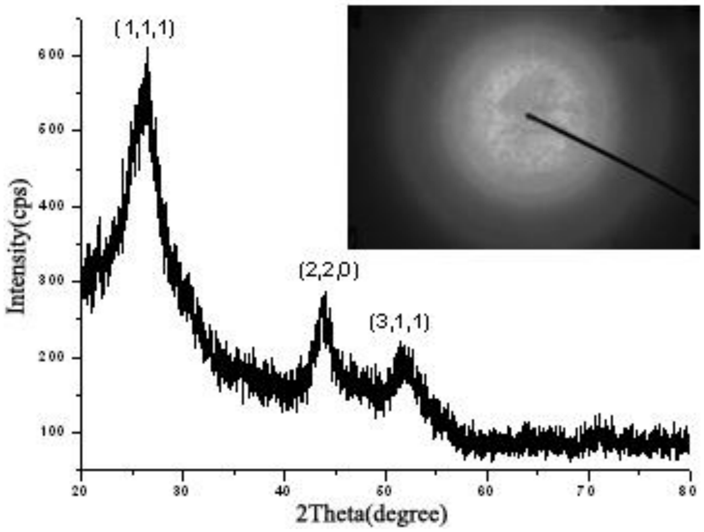


Fig. 2. XRD and SAED patterns of PNECN.

CdS, as a widely studied semiconductor, has been used as a photocatalyst for the hydrogen production from water, the cis-trans photoisomerization, reduction or oxidation of certain organic molecules [22-26]. To demonstrate the potential application of the present polymer nanospheres in these applications, we investigated their photocatalytic activities compared to those of CNCC (prepared as described before), bulk CdS and a commercial photocatalyst (Degussa P25 titania), with the photocatalytic degradation of methyl orange (MO) as a model reaction. The characteristic absorption of MO at 464 nm was chosen as the monitored parameter for the photocatalytic degradation processes. The color of the MO solutions gradually faded and the absorbance value corresponding to the molecule of MO gradually diminished with reaction proceeding and all completely disappeared after about 150 minutes in the presence of the PNECN (Fig. 3).

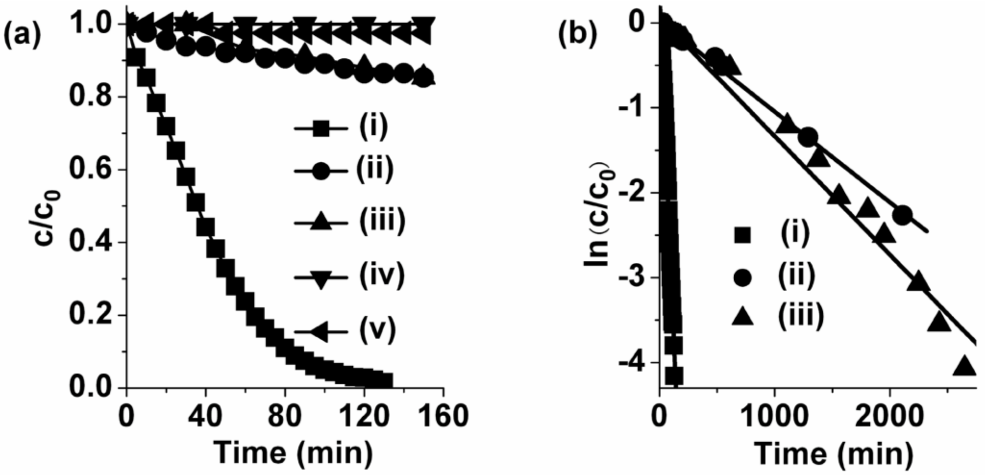


Fig. 3. (a) Photodegradation of methyl orange (40 mg/L, 120 ml) under different conditions: (i) with PNECN (containing CdS 40 mg) and UV light, (ii) with Degussa P25 titania (40 mg) and UV light, (iii) with CNCC (containing CdS 40 mg) and UV light, (iv) with bulk CdS powder (40 mg) and UV light, (v) with PNECN in the dark. (b) Plot of ln(c/c0) versus time for the photodegradation of methyl orange.

The comparative experiment was carried out to investigate the catalytic activity. The solution of MO was subjected to a series of experimental conditions: (i) with PNECN (containing CdS 40 mg) and UV light, (ii) with Degussa P25 titania (40 mg) and UV light, (iii) with those CNCC (containing CdS 40 mg) and UV light, (iv) with bulk CdS powder (40 mg) and UV light, (v) with PNECN (containing CdS 40 mg) in the dark. MO cannot be degraded with bulk CdS or in the dark, but can be degraded with Degussa P25 titania and CNCC with UV light. However, in the presence of PNECN, it was much faster degraded. Fig. 3b shows a linear correlation with time, that is, $\ln(c/c_0)$ versus time plot. Under the same condition, the degradation reaction constants of PNECN, Degussa P25 titania and CNCC for MO are $3.26\text{x}10^{-2}$ min^{-1}, $1.07\text{x}10^{-3}$ min^{-1}, $1.39\text{x}10^{-3}$ min^{-1}, respectively. It is noteworthy that the photocatalytic activity of the PNECN was over ten times to both Degussa P25 titania and CNCC, while photocataylic activities of those porous semiconductor nanomaterials were only few times of Degussa P25 titania [8-12].

To further confirm the photocatalytic activity of the PNECN, photodegradation of crystal violet (CV) was carried out, and the result shows the PNECN still have extremely high activity for photodegradation of CV (Figure 4). The degradation reaction constants of PNECN, Degussa P25 titania and CNCC for CV are $2.63\text{x}10^{-2}$ min^{-1}, $4.58\text{x}10^{-3}$ min^{-1}, $2.65\text{x}10^{-3}$ min^{-1}, respectively.

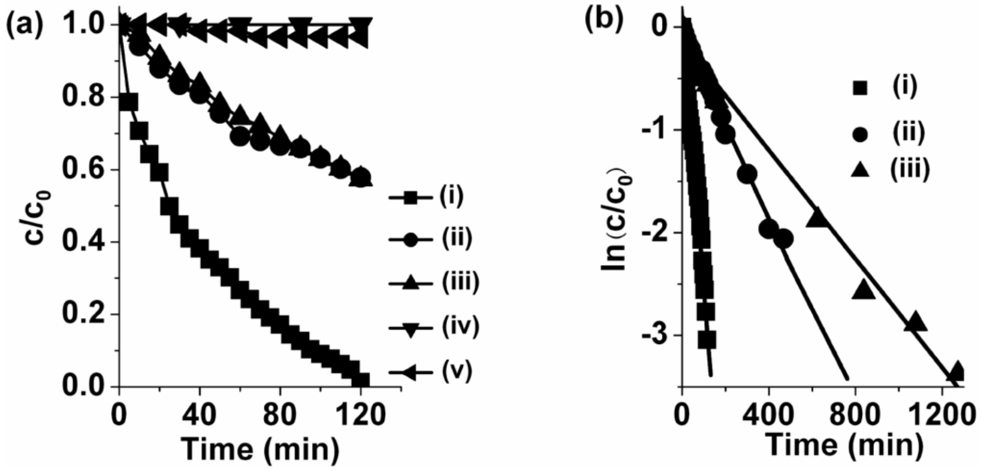


Fig. 4. (a) Photodegradation of crystal violet (10 mg/L, 120 ml) under different conditions: (i) with PNECN (containing CdS 40 mg) and UV light, (ii) with Degussa P25 titania (40 mg) and UV light, (iii) with CNCC (containing CdS 40 mg) and UV light, (iv) with bulk CdS powder (40 mg) and UV light, (v) with PNECN in the dark. (b) Plot of $\ln(c/c_0)$ versus time for the photodegradation of crystal violet.

We explain that the extremely high photocatalytic activity could be attributed to four factors. First, the CdS nanoparticles were prepared in-situ and immobilized in the polymer network, whose availability avoided the aggregation of CdS nanoparticles. At the mean time, CdS nanoparticles were enriched in some small regions, not like CNCC which were evenly distributed in the whole solution. Second, there are obviously more individual CdS nanoparticles finely dispersing in the polymer nanospheres compared with those porous nanomaterials. In the porous inorganic nanomaterials, a lot of nanocrystals congregated and concentrated to be more stable but sacrificed exposure probability with reactants. Third, CS is a good material to adsorb certain organic and biological pollutants [27], which makes the polymer nanosphere to be an ideal nanoreator. There are polymer networks consisting of a great deal of CS and polymethacrylate in PNECN, not like CNCC which only has few layers of polyelectrolyte capped with CdS nanoparticles (Fig. S3). Organic pollutants continuously entered into the nanosphere and were concentrated around those CdS nanoparticles; meanwhile degradation products were released from the nanoreator. Lastly, the nanosphere has good light transmittance in contrast to other porous or hollow inorganic semiconductor spheres, which avoids a great deal of dispersion of light and increases the availability of light.

In summary, we have designed a new nanophotoreactor, namely polymer nanosphere embedded with CdS nanoparticles, which was prepared through a novel, practicable and convenient route in aqueous solution. As nanoreactors, they show an extremely high photocatalytic activity compared to that of Degussa P25 titania or CdS nanoparticles capped with polyelectrolytes, which have been demonstrated in the photodegradation of methyl orange and crystal violet at ambient temperature. The prepared method of the as-synthesized nanophotoreactor skillfully makes use of the properties of polyelectrolyte-saccharide and semiconductor nanoparticles and conquers some defects of porous inorganic materials. This method provides a new thought for enhancing the photocatalytic activity of nanoreactor.

Experimental part

Materials

Chitosan (CS) was purchaed from Sigma Co., Ltd and purified with the reprecipatation method according to reference [28]. 3-Mercaptopropionic acid (MPA) were purchased from Aldrich and used as received.
All other reagents were used as received from commercial sources.

Preparation

Preparation of polymer nanospheres embedded with CdS particles (PNECN): Purified CS (0.25 g; M_w 200 kDa) was dissolved in an aqueous MPA solution (50 ml; 0.17 ml MPA). Then cadmium dimethacrylate (CDMA) solution (5 ml; 0.08 g) was added under stirring. After that, polymerization was initiated by $K_2S_2O_8$ at 80 ^oC and allowed to proceed for 90 min. H_2S prepared by adding phosphoric acid to sodium sulfide was then inflated into the above solution.

CDMA was prepared according to the published procedure [20]. Briefly, methacrylic acid was dissovled in water and CdO was added under stirring. After complete reaction, the white powder, namely CDMA, was separated by filtering and dried in vacuum drier.

Preparation of CdS nanoparticles capped with CS (CNCC): Purified CS (0.25 g; M_w 200 kDa) was dissolved in an aqueous MPA solution (50 ml; 0.17 ml MPA). Then cadmium nitrate solution (5 ml; 0.08 g) was added into solution of CS-MPA. After completely stirring, H_2S was inflated into the solution.

Characterization

TEM images were collected by using JEM-100CX microscope working at 80 kV and equipped with an energy-dispersive X-ray analyzer.

XRD data were collected on a Shimadzu XD-D1 X-ray diffractometer employing Cu-κα radiation at 30 kV and 30 mA.

The absorption was measured at 464 nm and 510 nm with a UV-vis spectrophotometer (VARIAN cary 100 Con, USA).

X-ray photoelectron spectroscopy (XPS) was carried out on an XSAM-800 electron and take-off angle of 20^o was used with X-ray source.

Thermogravimetric analysis (TGA) was performed on a TA instrument Q50, at a scan rate of 10 ^oC min^{-1}, up to 800 ^oC under air atmosphere.

Photocatalytic activity measurement

A quartz flask (capacity ca. 250 ml) was used as the photoreactor vessel. The reaction system containing methyl orange ($C_{14}H_{14}N_3NaO_3S$, 40 mg/L, 120 ml) or crystal violet ($C_{25}H_{30}ClN_3$, 10 mg/L, 120 ml) and catalyst (40 mg) was magnetically stirred in the dark for 10 min to reach the adsorption equilibrium, and then exposed to light from ultraviolet lamp (360 nm, 40 w). UV-Vis absorption spectra were recorded at different intervals to monitor the reaction.

Acknowledgements

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Supporting Information

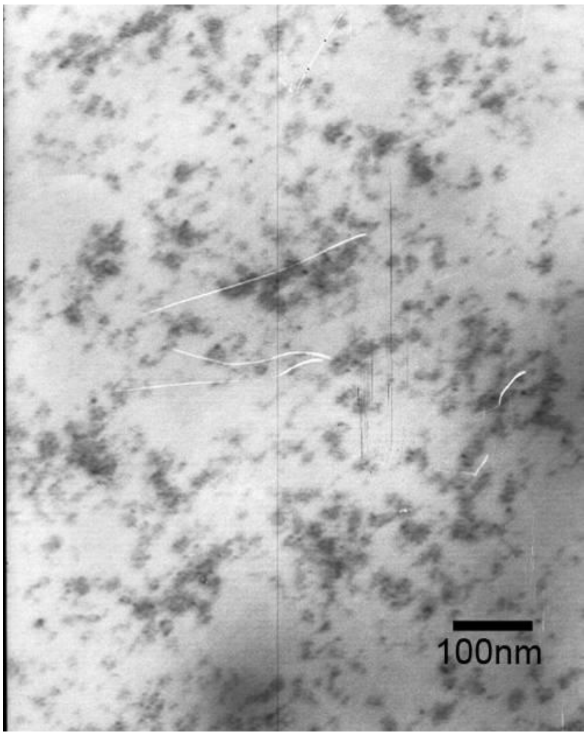


Fig. S1. TEM micrograph of CNCC without any staining agents.

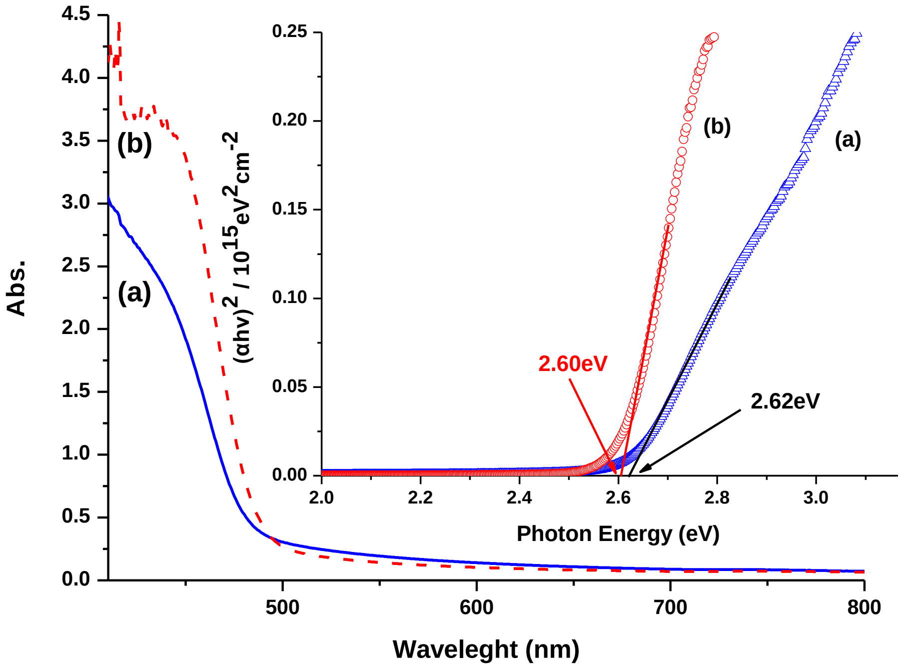


Fig. S2. The UV-vis absorption spectra of the CNCC (a) and PNECN (b). The insert one shows plot of $(Ahv)^{1/2}$ versus photon energy (hv) [1].

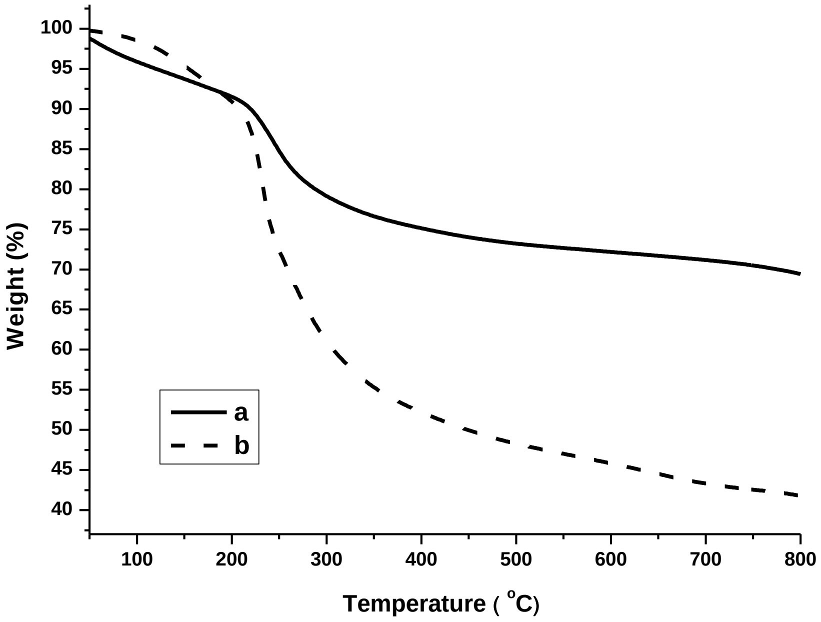
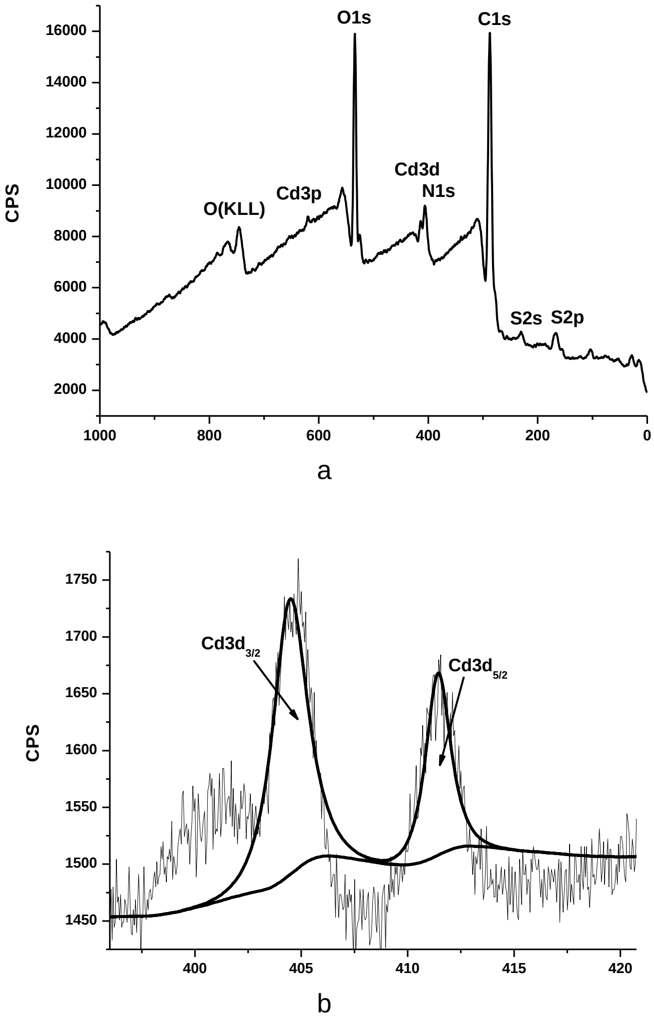


Fig. S3. TG curves of thermal decomposition of CNCC (a) and PNECN (b) at a heating rate of 10 °C/min under air atmosphere.



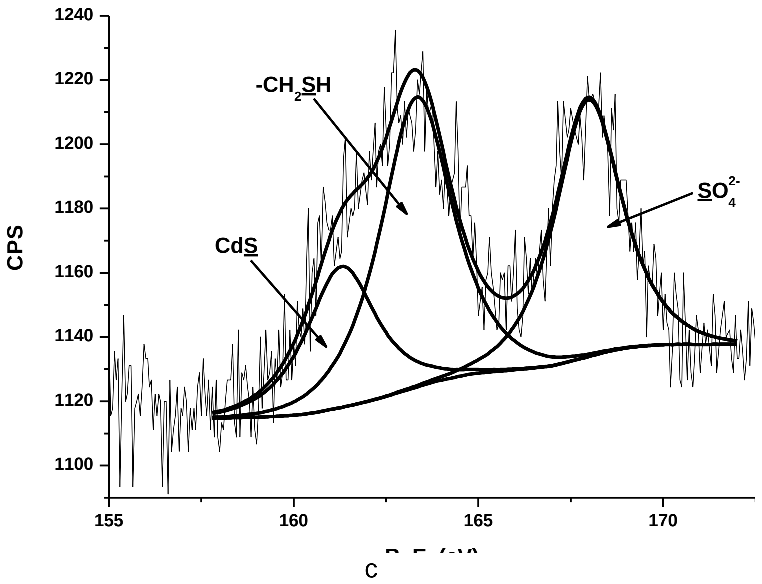


Fig. S4. XPS spectra of the PNECN: (a) survey spectrum, (b) Cd3d5, (c) S2.

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