Synergistic Effects of Carbon Dots and Palladium Nanoparticles Enhances the Sonocatalytic Performance for Rhodamine B Degradation in the Absence of Light

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**Keywords:** Carbon dot; Palladium nanoparticles; Sonocatalysis, Rhodamine B; Dye-degradation.
Abstract
Carbon dot (CD) and palladium nanoparticles (Pd NPs) composites are semiconducting materials having tremendous applications in catalysis with suitable bandgap. However, their combination with suitable polymer matrix in sono-photo-catalysis has not been explored. Herein, we have synthesized and characterized a new nano-hybrid catalyst from polyamide cross-linked CD-polymer and subsequent deposition of Pd NPs. Sonocatalytic activity of 99% rhodamine B dye-degradation was achieved in mere 5 minutes (min) under dark. Model catalyst replacing CD with benzene and other control studies revealed that synergistic effects of CD and Pd NPs enhances the sonocatalytic activity of nano-hybrid catalyst. Interestingly, visible light did not influence the activity significantly. While mechanistic investigations suggest that generation of reactive oxygen species on the surface of CD-polymer initiated by ultrasound which further facilitated by Pd NPs is the key for remarkable catalytic activity (rate constant 0.99 min\(^{-1}\)). Recyclable heterogeneous catalyst under ambient conditions are promising for the utility of exploring sono-assisted dark-catalysis for several avenues.

1. Introduction
Water pollution by industrial dye effluents has seriously affected the aquatic ecosystem and the human population.\(^1\) Synthetic dyes are widely used in the textile industry and their disposal pose serious concern for carcinogenic and teratogenic problems due to their chemical stability.\(^2\) Tremendous efforts have been made during the last several decades to reduce their deleterious impacts, including physical adsorption using activated carbon,\(^3\) clays,\(^4\) biological degradations using microorganisms,\(^5\) as well as chemical degradation using catalyst-mediated advanced oxidation processes.\(^6\) However, the obvious drawbacks of these methods, such as low efficiency, high cost and/or short service life, continuously drive the exploration of advanced materials for the degradation of synthetic dyes in polluted water.\(^7\) A various catalytic systems such as amorphous alloys,\(^8\) semi-conductor metal heterostructure,\(^9\) polymer-based nanocomposites,\(^10\) graphene oxide,\(^11\) carbon quantum dots,\(^12\) amorphous thin ribbons,\(^13\) nano powders and nonporous structures\(^14\) have been shown to exhibit relatively satisfactory performance in wastewater remediation for removing synthetic dyes and other organic pollutants.

A semiconductor photocatalyst generates redox centres at the conduction band (CB) and valence band (VB) on irradiation of light to generate the reactive oxygen species (ROS)
such as hydroxyl radical and superoxide which eventually takes part in the degradation process of the organic pollutants.\textsuperscript{15} Krishnan et al. have reported the synergistic effect of MoS\textsubscript{2}-RGO doping enhancing the photocatalytic performance of ZnO NPs and similarly N-doping on to the ZnO-MoS\textsubscript{2} binary heterojunctions enhancing the catalytic activity under visible light.\textsuperscript{16} However, light is the limiting factor as every catalyst responds to the visible and/or UV lights according to its band-gap structure. Hence, fabricating a semiconductor material which can develop ROS even in the dark would be desirable because of energy saving, avoiding restriction of light requirement, and indoor applications or places scarcity of sunlight.\textsuperscript{17} Only few reports were shown to exhibit catalytic activity even in dark, for example Suib et al reported that methyl orange can be fragmented into intermediates using perovskite-type material (LaNiO\textsubscript{3-δ}) in dark under ambient condition in 4 h time.\textsuperscript{18} Hussain et al. showed metal nanocomposite (Ag–In–Ni–S) catalyzed methylene blue degradation within 12 minutes (min) under dark condition.\textsuperscript{19} Rajagopalan et al. have reported that ZnO\textsubscript{2}/polypyrrole nanocomposite and its synergistic effect in dye degradation of methylene blue in dark and light.\textsuperscript{20} He et al. showed polymer-coated TiO\textsubscript{2} nanocomposite to catalyze the degradation in dark due to the intrinsic difference of their disordered atomic packing arrangement compared with the well-defined atomic ordering in crystalline materials.\textsuperscript{21} However, there is a need to improve catalytic performance further to see the light of practical applications by lowering the cost of the catalysts and conserving the energy. This can be achieved by increasing the reaction rate and reducing the reaction time with good recyclablility (Table S2, Supporting Information (SI)).

It has been reported that the combination of sonocatalysis and photocatalysis outperformed either of them alone in catalytic degradation of dyes.\textsuperscript{22-26} The combination of semiconductor and ultrasound is considered to be viable option as sonocatalysis due to safe and economical use of nanomaterials.\textsuperscript{24, 27-29} It has been reported that the sonocatalytic activity of nanoparticles dependent of the types of nanoparticles as well as materials with the increasing order of montmorillonite clay < anatase-TiO\textsubscript{2} < ZnO < rutile-TiO\textsubscript{2} < Fe\textsubscript{3}O\textsubscript{4} for the sonocatalytic degradation of 2-hydroxyethyl cellulose.\textsuperscript{30} To the best of our knowledge, so far only one report was mentioned about sonocatalytic dye degradation under dark condition using CdSe-graphene as catalyst but this catalyst is toxic and less reactive.\textsuperscript{31}

Till date, various photocatalysts have been tried among them palladium nanoparticles (Pd NPs) and light responding carbon materials have shown promising catalytic activity.\textsuperscript{32-36} It has been shown that Pd NPs decorated on carbon support enhances catalytic activity
greatly for the clean hydrogen generation.\textsuperscript{34} Also, Pd NPs supported by graphene-oxide (GO) was found to degrade dye solutions in the presence of NaBH\textsubscript{4} in aqueous solution.\textsuperscript{35} However, we hypothesize that the catalytic activity can be further improved by exhuming the synergistic characteristics of these materials with the help of ultrasound energy. To achieve this, we have designed the nano-hybrid catalyst comprising of Pd NPs anchored on to the amido-amine -functionalized carbon dot (CD)-polymer matrix. Herein, we describe the sonocatalytic efficiency of the said catalyst on dye-degradation of rhodamine B (RhB) and demonstrate the existence of synergistic effect of Pd NPs and CD mediated by ultrasound.

2. Experimental

2.1 Materials and methods

All reagents were analytical grade and used without further purification. Citric acid and thionyl chloride were supplied by Thermo Fisher Scientific. Palladium chloride, benzene-1,4-diamine (BDA) and benzene-1,3,5-tricarboxylic acid (BTC, 99\%) were supplied by TCI. Methanol (MeOH) and 1,4-benzoquinone were supplied by Sigma-Aldrich. Dimethylformamide (DMF) and diethyl ether were supplied by Spectrochem. Triethylamine, ethanol (EtOH), isopropanol and EDTA were procured from Spectrum, Merck, and SRL, respectively. Tetrahydrofuran (THF) was dried over sodium metal and benzophenone under inert atmosphere.

2.2 Synthesis of nano-hybrid catalyst Pd@CD-CONH

The target catalyst comprising of palladium nanoparticles (Pd NPs) supported by carbon dot (CD) polymer Pd@CD-CONH was synthesized in two steps starting from CD-COOH. Step 1 involves the synthesis of CD-CONH polymer by treating BDA with CD-COCl.\textsuperscript{37} Step 2 involves the decoration of Pd NPs onto the surface of CD-CONH polymer via interaction of palladium ions with the nitrogen (N) atoms of CD-CONH polymer.\textsuperscript{38} 

Step 1. Synthesis of amido-amine-functionalized carbon dots polymer (CD-CONH).
A solution of freshly synthesized CD-COCl (1 g) in dry tetrahydrofuran (THF, 50 mL) was treated with Et₃N (5 mL) at 25 °C for 10 min. After that BDA (0.23 g, 2.13 mmol) was added and continued stirring for 15 h. The solvent was evaporated in vacuo at 40 °C. The reaction mixture was transferred to the sintered funnel and washed with water (80 mL), hexane (20 mL) and diethyl ether (Et₂O, 20 mL). Then the residue was dissolved in MeOH. Evaporation in vacuo at 40 °C afforded CD-CONH (1.12 g) as deep-brown semi-solid.

Step 2. Synthesis of Pd@CD-CONH.

A solution of CD-CONH (0.25 g) in EtOH (30 mL) was treated with PdCl₂ (0.5 g) in the dark at 25 °C and stirred for 15 h. The solvent was evaporated in vacuo at 40 °C. The reaction mixture was then transferred to the sintered funnel and washed with water (80 mL). The residue was dried in the vacuum oven at 60 °C for 12 h to afford 0.6 g of Pd@CD-CONH as deep-brown solid.

2.3. Synthesis of model catalyst (Pd@BTC-CONH).

Synthesis of model catalyst (Pd@BTC-CONH) was achieved by a similar protocol followed in 2.2. except replacing CD-COOH with benzene-1,3,5-tricarboxylic acid (BTC-COOH).

The target model catalyst comprising of Pd NPs supported by BTC-polymer Pd@BTC-CONH was synthesized in two steps starting from BTC. Step 1 involves the synthesis of BTC-CONH polymer by treating BDA with BTC-COCl. The step 2 involves the generation of Pd NPs by treating PdCl₂ with BTC-CONH polymer.

Step 1. Synthesis of amido-amine-functionalized BTC-polymer (BTC-CONH).
A solution of benzene-1,3,5-tricarboxylic acid (BTC) (1.5 g) with neat thionyl chloride (SOCl₂) (20 mL) and few drops of dimethylformamide (DMF) under N₂ atmosphere was refluxed at 80 °C. After 2 h, excess SOCl₂ was removed by vacuum affording BTC-COCl. The freshly synthesized BTC-COCl (1 g) was dissolved in dry THF (15 mL) by stirring under N₂ in the dark for 10 min at 25 °C. Then BDA (0.3 g) was added and continued stirring for 15 h. The solvent was evaporated in vacuo and then transferred the residue in to the sintered funnel and washed with water (80 mL) and Et₂O (20 mL). The residue was dissolved in MeOH followed by evaporation in vacuo at 40 °C to afforded 1.4 g of BTC-CONH as black powder.

Step 2. Synthesis of Pd@BTC-CONH.

A solution of BTC-CONH (0.16 g) in EtOH (40 mL) was treated with PdCl₂ (0.5 g) and stirred for 15 h in the dark at 25 °C. The solvent was evaporated in vacuo at 40 °C. The reaction mixture was then transferred to the sintered funnel and washed with water (80 mL). The residue was dried in the vacuum oven at 60 °C for 12 h to afford the nano-hybrid catalyst Pd@BTC-CONH (0.2 g) as black solid.
Scheme 1. Synthesis of catalyst Pd@CD-CONH and the model catalyst Pd@BTC-CONH.

2.4. Characterization of nano-hybrid catalyst Pd@CD-CONH and model catalyst Pd@BTC-CONH

Fourier transform infrared (FT-IR) spectra were recorded on the Agilent Cary 660 spectrometer using the KBr pellet technique in a range of 4000–400 cm\(^{-1}\) to monitor the chemical synthesis at each step. Absorption spectra were recorded on a Shimadzu UV-vis spectrophotometer in 3 mL quartz cuvettes having a path length of 1 cm. Thermogravimetric analysis (TGA) was performed to determine the degradation/decomposition behavior of samples using thermogravimetric (TGA) analyser (Perkin Elmer STA 8000) at a N\(_2\) flow rate of 10 mL min\(^{-1}\) and a heating rate of 10 °C min\(^{-1}\). \(^1\)H nuclear magnetic resonance (NMR) spectra were measured on a Bruker Advance-II spectrometer at 400 MHz, respectively, in DMSO-\(d_6\) or MeOD. The chemical shift was reported in parts per million (ppm) relative to tetramethylsilane (TMS) as the internal standard. X-ray Diffraction (XRD) was performed using Bruker D-8 advanced diffractometer in the 2θ range of 10° to 90°. The average crystallite size of NPs with and without surface coating was estimated using the Scherrer equation. The elemental composition and composite homogeneity of the samples were investigated using an SEM-EDX scanning microscope JEOL-JSM IT 300 attached with Bruker signal processing unit. Transmission Electron microscopy (TEM) images were
acquired on a Jeol 2100 HR operating at 200 kV. Samples were prepared by depositing a drop of diluted nanoparticle suspension on 300 mesh TEM grid (Gold coated Carbon films on 300 mesh) and dried under vacuum for 15 h. TEM grids were purchased from Beeta tech India Pvt. Ltd. Atomic Force Microscopy (AFM) images were acquired using Bruker Multimode 8 and sample analysis was done in tapping mode. The samples were deposited on silicon wafers and analysis was performed at different sections at room temperature and ambient atmosphere. X-ray photoelectron spectroscopy (XPS) experiments were performed on an Auger Electron Spectroscopy (AES) Module, Model no PHI 5000 VersaProbe II FEI Inc using monochromatic Al Ka radiation (1486.6 eV) operating at an accelerating X-Ray power of 50W15KV. Before the measurement, the sample was outgassed at room temperature in a UHV chamber (<5 × 10^{-7} Pa). The sample charging effects were compensated by calibrating all binding energies (BE) with the adventitious C 1s peak at 284.6 eV. This reference gave BE values with accuracy at ±0.1 eV. X-ray photoelectron spectroscopy (XPS) survey of the as-prepared CD-CONH and Pd@CD-CONH indicating the presence of carbon, nitrogen and palladium photoelectron peaks (C 1s, N 1s, and Pd 3d) signals, respectively and its Pd LMM Auger), the oxygen peaks (O 1s and its OKLL Auger) and the photoelectron peak of the adventitious carbon (C 1s). Fluorescence spectra were recorded on an Edinburgh FS5 spectrofluorimeter. Fluorescence lifetimes were measured with Horiba Jobin-Yvon FL-1057 Fluorolog, using a 390 nm nano-LED.

2.5 Evaluation of the sonocatalytic activities of nano-hybrid Pd@CD-CONH and model Pd@BTC-CONH catalysts

For sonication: ultrasonic cleaner (model SK2210HP, Serial No. 14E0388) was used with operating frequency of 53 kHz, input 220 V, power consumption 100 W. The ultrasonication temperature was set to be 25 °C all through the experiment. The water bath assisted in keeping the temperature under control, around 25 – 30 °C. Unless otherwise mentioned for all degradation reactions were performed with sonication and in complete darkness. The dark condition was maintained by not exposing the solution to any light source by covering with aluminium foil and minimum room light. The concentration change of rhodamine B (Rhb) dye in the solution during the sonocatalytic experiments was monitored using UV-vis spectrometer at different time intervals in the presence and absence of the catalysts. For sonocatalytic degradation of RhB, the 0.05 g of Pd@CD-CONH nano-hybrid catalyst was added to the beaker containing 100 mL of deionized RhB (4.79 mg L^{-1}) dye solution. 3 mL of
the reaction mixture was taken out with different reaction time and centrifuged and filtered through 0.2 μL syringe filter in order to remove the catalyst particles prior to the analysis. The filtrate was analysed for the absorbance measurements in the 554 nm wavelength using a spectrophotometer.

3. Results and discussion

3.1. Synthesis and characterization of polymers (CD-CONH, BTC-CONH) and nano-hybrid catalysts (Pd@CD-CONH, Pd@BTC-CONH)

The final Pd-doped hybrid nanocatalysts (Pd@CD-CONH, Pd@BTC-CONH) were synthesized by two steps as shown in Scheme 1. The first step involves the polymerization of the acid chloride-functionalized monomers of CD and BTC leading to obtaining the amide-linked polymers CD-CONH, BTC-CONH, respectively upon reaction with benzene-1,4-diamine at room temperature. The acid chloride derivatives were in turn freshly prepared by the treatment of their corresponding acids (CD-COOH, BTC-COOH) with thionyl chloride (SOCl₂). CD-COCl and BTC-COCl are highly soluble in polar organic solvents such as THF, CH₃CN, and acetone, which can be easily isolated by evaporation of the excess thionyl chloride from the reaction mixture. The acid chloride derivatives are highly adaptable towards surface modification which does not require complex purification procedures, due to its high reactivity and absence of non-volatile by-products. The carboxylic acid capped CD (CD-COOH) was prepared by following the reported procedure by the thermal decomposition of citric acid. The second step was the formation of Pd nanoparticles (NPs) on to the amido-amine functionalized polymers of CD-CONH and BTC-CONH by treating with PdCl₂ under refluxing in EtOH as a solvent to provide the corresponding Pd NPs-doped hybrid nanocatalysts Pd@CD-CONH and Pd@BTC-CONH, respectively.

The surface modifications of the COOH functionalized CD and BTC into CONH functionalized CD and BTC followed by Pd NPs impregnated polymers of CD-CONH and BTC-CONH were characterized by Fourier transform infrared (FT-IR) spectroscopy, ¹H nuclear magnetic resonance (NMR), and transmittance electron microscopy (TEM) analysis.
As shown in Figures 1a and 1b, the FT-IR spectra of CD-COOH and BTC-COOH, conversion into the amide bond formation with BDA is clearly evident from the partial disappearance of peaks at 1720 cm\(^{-1}\) (CD-COH) and 1725 cm\(^{-1}\) (for BTC-COH) corresponding to C=O stretching frequencies of -COOH and new peak appearance at 1630 cm\(^{-1}\) (CD-COH) and 1634 cm\(^{-1}\) (BTC-COH) for the C=O stretching frequencies of the amide bond. Also, the presence of free amine-terminated polymer is indicated by the new N–H peak appearance at 3335 cm\(^{-1}\) (CD-COH) and for BTC-COH at 3412 cm\(^{-1}\) and 3336 cm\(^{-1}\). Similarly, the Pd NPs anchored on to the amide N–H (CD-COH) is indicated by the shift in the stretching frequency from 1630 to 1588 cm\(^{-1}\) (Figure 1a). Also, it is further evidenced by the peak shift of free NH\(_2\) peak from 3335 to 3400 cm\(^{-1}\). Similar to CD-COH, BTC-COH also exhibited peak shift from 1634 to 1612 cm\(^{-1}\) upon binding with Pd NPs. These observations are clearly point out that partial amide formation with BDA leading to formation of CD-COH and BTC-COH polymers. Further, Pd NPs being supported by CONH and NH\(_2\) functional groups in the catalysts Pd@CD-COH and Pd@BTC-COH. These results are also corroborated by \(^{1}\)H NMR investigation (Figures S1 and S6, SI). The presence of aromatic protons corresponding to the BDA moiety in CD-COH spectrum indicating the surface modification of CD-COCl with BDA (Figure S1, SI). The \(^{1}\)H-NMR spectra of BTC-COH and Pd@BTC-COH clearly indicate that the presence of both linker and BTC protons which matches well with similar polymer reported previously. The \(^{1}\)H NMR spectrum of BTC-COH polymer showed peaks for amide protons of terminal BDA moiety in the upfield region at 10.33 and 10.23 ppm due to the presence of amine in the para position (Figure S6a, SI). Whereas the inner chain amide appeared at around 10.67 and 10.75 ppm.
ppm. The $^1$H NMR spectrum (Figure S6b, SI) of Pd@BTC-CONH showed significant upfield shift values of 0.04 and 0.03 ppm for terminal amide protons upon treatment with Pd. Whereas inner chain amide protons showed a significant shift of 0.06 ppm for 10.69 ppm peak indicating partial binding of amide protons. This suggests that not all amide protons are to be available for metal binding probably due to stacking nature of the polymer. In contrast, the CD polymer catalyst showed binding of inner chain polymer as indicated by the inner phenyl proton shift (Figure S1). This is also facilitated by porous nature of CD polymer as indicated by the TEM images (Figures S3a and S7a, SI).

After the structural characterization of CD-CONH, we studied the formation of Pd NPs on to the CD-CONH. The presence of Pd NPs are evidenced by XRD, FT-IR (vide supra), XPS, TEM, and Raman studies. We believe that upon addition of Pd$^{2+}$ ions in to the EtOH solution of CD-CONH, the Pd$^{2+}$ ions interact with the N-atoms of the amido-amine group and get reduced to Pd(0). The PXRD spectrum of Pd@CD-CONH showed the formation of the crystal face-centred cubic (fcc) lattice of Pd(0) indicated as (100), (111), (200), (220), (311), and (222), suggesting that the PdCl$_2$ has been reduced completely to form Pd NPs as shown in Figure 2. Similarly, the PXRD spectrum of Pd@BTC-CONH formation of the crystal face-centred cubic (fcc) lattice of Pd(0) indicated as (101), (102), (110), and (203), suggesting that the PdCl$_2$ has been reduced completely to form Pd NPs (Figure 2).

Figure 2. PXRD spectra of Pd@CD-CONH and Pd@BTC-CONH.
Further, the shape and size of the amido-amine functionalized CD polymer CD-CONH was determined by high-resolution transmission electron microscopy (HR-TEM) (Figure S3c, SI). The intralayer spacing of 2.4 Å showed lattice fringes corresponding to the 100 plane. The TEM image of CD-CONH showed the presence of spherical nanoparticles interlinked with each other having an average size of 5.5 ± 2.3 nm with a relatively broad size distribution (Figure S3b, SI). The powder X-ray diffraction (XRD) spectrum of CD-CONH showed diffraction peak centred at 29.8°, which corresponds to a lattice spacing of 3Å, similar to the (200) reflection (d002 = 3.4 Å) (Figure S2a, SI).

Figure 3. (a) TEM and (b) HR-TEM images of Pd@CD-CONH, (c) Histogram.

The TEM image of as-prepared Pd@CD-CONH showed the formation of spherical Pd NPs deposited on the amido-amine polymer (CD-CONH) with an average diameter of ~3.25 nm (Figure 3). Figure 3b shows the HR-TEM image with the intralayer spacing of 2.3 Å lattice fringes corresponding to the 111. The Pd peak is observed in the EDX mapping of Pd@CD-CONH along with C, N and O indicating that the Pd NPs has been clearly homogeneously distributed throughout the entire CD polymer (Figure 4). The Atomic force microscopy (AFM) images of Pd@CD-CONH have shown that the spherical shaped Pd NPs have been successfully deposited over the CD-CONH polymer (Figure S4, SI). The particle size distribution (PSD) of the as-prepared Pd@CD-CONH as well as the model catalyst Pd@BTC-CONH have showed similar size distribution ~3 nm (Figures 3 and S7).
Figure 4. (a) TEM images of Pd@CD-CONH, (b) EDX mapping of some area of catalyst (c) Carbon, (d) Oxygen (e), Nitrogen and (f) Pd.

We carried out the X-ray photoelectron spectroscopy (XPS) analysis to get insight on the surface electronic structure of as-synthesized Pd NPs. As shown in Figure 5a, the XPS survey spectrum of Pd@CD-CONH indicates the presence of palladium, nitrogen and carbon with corresponding characteristic binding energies peaks at 335.6, 340.9, 398.95 and 284.4 eV, respectively. There are two chemical states indicated in Pd NPs with a lower binding energy of Pd 3d profile. The presence of binding energies at 335.6 and 340.9 eV is due to Pd(0) whereas the other higher binding energy at 336.4 and 342.4 eV is due to the presence of Pd(II) (Figure 5b).\textsuperscript{38,43} Furthermore, high magnification of N 1s profile in CD-CONH showed 397.93 eV binding energy indicating the presence of N-functionality in the polymer. However, the N 1s profile in Pd@CD-CONH showed a significant shifting of binding energy 397.93 to 398.95 eV (Figure 5c).\textsuperscript{38,44} We infer that this shift is due to the Pd NPs and its interaction with N-functionality. Whereas, there is no significant change in the peak fitting of the C 1s (Figure 5d). These results indicate that Pd NPs has been successfully impregnated on to the CD-CONH.
3.2 UV-vis absorption study of nano-hybrid Pd@CD-CONH and model Pd@BTC-CONH catalysts

The UV-vis absorption spectra of Pd@CD-CONH and model catalysts in EtOH in comparison with the corresponding monomer and polymeric precursors are shown in Figure 6. The formation of Pd NPs clearly indicated by the appearance of surface plasmon resonance (SPR) band centred around 410 nm in the catalyst, which is absent in the polymer precursors. Furthermore, the direct optical band gap (Eg) based on the onset value was found to be 2.43 eV (510 nm) which is significantly lower (0.2 eV) than the CD polymer with Pd NPs. Though both the catalysts showed similar PSD (vide supra), the model catalyst with Pd NPs has showed high energy band gap of 3.35 eV indicating superior semi-conducting property for the nanohybrid Pd@CD-CONH catalyst owing to the better absorption of carbon quantum dot.

Figure 6. UV-vis spectra of a) Pd@CD-CONH b) Pd@BTC-CONH in EtOH at 25 °C.
3.3. Sonocatalytic activities of nano-hybrid Pd@CD-COH and model Pd@BTC-COH catalysts

The sonocatalytic performances of synthesized 50 mg of hybrid nanocomposites Pd@CD-COH and Pd@BTC-COH were tested for the degradation of 100 mL of 10^{-5} M aqueous solution of RhB organic dye under sonication in dark. To our delight, the degradation reaction was completed within 5 min as indicated by the disappearance (99.9%) of absorption band $\lambda_{\text{max}}$ (554 nm) of RhB in dark using the catalyst Pd@CD-COH (Figure 7a). Various control studies were performed to unravel the role of each parameter which is responsible for this excellent activity (Figure 7b). Initially, the degradation experiments were carried out in the absence of the catalyst and only either with light or ultrasound (US) + visible light or US + dark. None of these conditions led to significant degradation of RhB dye molecules. In contrast, the nano-hybrid catalyst Pd@CD-COH and US in dark condition showed excellent activity. Surprisingly, the same reaction in the presence of room visible light did not exhibit superior performance, probably due to the poor absorption in the visible region as indicated by the UV-vis spectrum (Figure 6a). Further, similar to other control experiments, we tested the sonocatalytic activities of individual components such as Pd powder and CD-COH polymer as well as semiconductor ZnO (Figure 7b).

![Figure 7](image.png)

**Figure 7.** Time-dependent sonocatalytic degradation absorption spectra of RhB in the presence of (a) Pd@CD-COH and (b) various control catalysts.

Interestingly, the semiconductor ZnO as well as Pd powder catalysts along with the US showed negligible sonocatalytic activity in the absence of light, indicating the reaction was completely sealed from the light source (Figure 7b). Whereas, the non-metal containing CD polymer with the US has shown significant activity of 16% in dark. However, prolonging the
reaction time up to 24 h showed no further activity suggesting dye physisorption on the polymer coupled with the semiconducting nature of CD in presence of US might generate hydroxyl (•OH) and hydrogen (H•) radicals from water upon the formation of cavitation bubble implosion (CBI) as it has been reported that the US can generate even without catalyst.\textsuperscript{23, 46–48} These results indicate that the observed sonocatalytic activity is not due to any one of the precursors but due to the synergistic effects of Pd NPs, carbon dots and ultrasound.

This is also further corroborated by the comparison with the model catalyst Pd@BTC-CONH \textit{i.e.} CD replaced with benzene on the Pd@CD-CONH catalyst under similar conditions (Figure 8a). TEM analysis indicated that the particle size distribution (PSD) of Pd NPs in the control catalyst Pd@BTC-CONH (2 to 6 nm centred around 3 nm, Figure S7) was found to be quite similar to the Pd@CD-CONH (2 to 5 nm centred around 3.25 nm, Figure 3). Other than ensuring the model catalyst is structurally similar, this is important for fair comparison, as the PSD play critical role in the catalytic activity. Figure 8b shows the rate constant of 0.99 and 0.47 min\textsuperscript{-1} for Pd@CD-CONH and Pd@BTC-CONH, respectively indicating at least 50\% reduced sonocatalytic activity was observed than the catalyst with CD under similar condition. Furthermore, we have also synthesized another Pd NPs capped with coffee ingredients by following the reported protocol \textit{i.e} Pd@cof\textsuperscript{49} with PSD of 2 to 7 nm centered around 5 nm (Figure S8, SI). This catalyst is also showed 48\% reduced activity over Pd@CD-CONH (Figure 7b). The inferior sonocatalytic activity for the model Pd@BTC-CONH is more evident when reduced the catalyst amount from 50 mg to 10 mg, which led to the partial completion of the reaction for the model catalyst while Pd@CD-CONH retained the catalytic activity (Figure S9, SI). Upon decreasing the catalyst amount the reaction time gets increased to 80 min for the 93\% degradation of RhB for Pd@CD-CONH whereas the 46\% degradation for model catalyst Pd@BTC-CONH. Continuation of reaction up to 24 h also did not yield complete degradation for the model catalyst (48\% up to 24 h), whereas, nano-hybrid catalyst Pd@CD-CONH showed complete degradation for the same time. The outstanding catalytic activity for the Pd@CD-CONH over the model- as well as Pd@cof- catalysts despite having similar PSD clearly imply that the synergistic effects between the Pd NPs and CD play a major role in the catalytic activity mediated by US in dark. Notably, in comparison with other reported catalytic systems in dark reported in literature, the sonocatalytic degradation efficiency of Pd@CD-CONH nano-hybrid catalyst was found to be better (Table S2 in SI).\textsuperscript{22,27,31, 46–47}
3.4 Mechanistic studies

The presented nano-hybrid catalyst Pd@CD-CONH is belongs to heterogenous catalysis driven by adsorption of the dye on the polymeric support mediated by surface reaction. As the reaction occurs under dark ambient conditions, thermal effect provided by ultrasound might conduct the reaction. To test the effect of temperature, we have varied the temperature of sonicator bath to 273, 298 and 323 K and found that the reaction rate increased considerably higher, thus reducing the reaction time from 20, 5, 3 min, respectively (Figure S10, SI). It is well accepted that thermal catalysis process using heterogenous catalysts undergoes major step of adsorption\textsuperscript{50,51} (eq. 1), followed by the ultrasound-mediated generation of holes in valency band (VB) of the semiconducting catalyst which converts the water molecules in to hydroxyl radical and H\textsuperscript{+} driven by the cavity bubbles implosion (CBI) due to ultrasound waves (eq. 2). In our control studies (Figure 7b), we found that only with room light no reaction was observed, whereas only with US and in dark yielded slight (4\%) degradation indicating ROS generation occurs due to water splitting by the US as it has been reported that in presence ultrasound water can undergo splitting due to CBI.\textsuperscript{51} The generated electrons in the conduction band (CB) would react with dissolved oxygen to generate superoxide radical anion (O\textsubscript{2}\textsuperscript{−•}) (eq. 4). Subsequently, the superoxide radical anion can react with H\textsuperscript{+} to generate hypoperoxyl radical (HO\textsubscript{2}•), which can further form hydrogenperoxide (H\textsubscript{2}O\textsubscript{2}) upon dimerization. The hydroxy can be generated by from the decomposition of H\textsubscript{2}O\textsubscript{2} in the presence of US with electrons surface of the catalyst. Thus, three species such as O\textsubscript{2}•\textsuperscript{−}, •OH, and HO\textsubscript{2}• are responsible for the degradation of dye molecules under sonocatalytic
conditions (eq.8). To verify that these species are formed in the reactions we have conducted study on the RhB oxidation over Pd@CD-CONH nano-hybrid catalyst using different scavengers such as p-benzoquinone as superoxide scavenger, isopropanol as hydroxyl radicals (•OH) scavenger, and EDTA as hole scavenger. Since Pd@CD-CONH nano-hybrid catalyst could mediate the degradation even in dark upon using these scavengers the rate of the reaction should be altered. Figure 9 shows the rate of RhB dye degradation greatly reduced up to 84% in case of superoxide scavenger (p-benzoquinone), whereas 52% and 18% was observed for hydroxyl and hole scavengers, respectively indicating superoxide ion plays major role in the degradation pathway while hydroxyl ion significantly contributing for the degradation. The origin of enhanced nano-hybrid sonocatalytic activities come from efficient separation of electron–holes pairs, which either directly react water with h⁺ or contributes to forming active species, hydroxyl radicals (•OH) and superoxide radicals (O₂•⁻) through the reduction of the electron.²²,⁵¹

**Figure 9.** Effect of scavengers on the degradation of RhB (100 mL of 10⁻⁵ M in water) using Pd@CD-CONH (50 mg).

Based on these results, the following equations are proposed for the mechanism steps involved for the thermal catalysis process under dark ambient conditions.

\[
\begin{align*}
\text{dye + catalyst} + \text{US} & \rightarrow \text{catalyst (dye.ads)} \quad (1) \\
\text{catalyst (dye.ads) + US} & \rightarrow \text{h}_\text{VB}^+ + e^-_{\text{CB}} \quad (2) \\
\text{H}_2\text{O} + \text{h}_\text{VB}^+ & \rightarrow •\text{OH} + \text{H}^+ \quad (3) \\
e^-_{\text{CB}} + \text{O}_2 \text{(dissolved)} & \rightarrow \text{O}_2^{•⁻} \quad (4) \\
\text{O}_2^{•⁻} + \text{H}^+ & \rightarrow \text{HO}_2^{•} \quad (5) \\
2\text{HO}_2^{•} & \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \quad (6) \\
\text{H}_2\text{O}_2 + e^- + \text{US} & \rightarrow •\text{OH} + \text{OH}^- \quad (7) \\
\text{O}_2^{•⁻} / •\text{OH} / \text{HO}_2^{•} + \text{dye/dye}^+ & \rightarrow \text{sono-degraded small organic product} \quad (8)
\end{align*}
\]
Figure 10 shows the schematic representation of the whole mechanism involved in the sonocatalytic dye degradation process catalyzed by the nano-hybrid catalyst. 

![Figure 10. Proposed mechanism for ultrasound-mediated degradation of RhB dye using Pd@CD-CONH nano-hybrid catalyst. Black star indicates cavitation bubbles implosion (CBI).](image)

In order to ensure that the catalytic degradation nature of RhB is not due to phosphorescent nature of the catalyst and/or due to UV-vis light assistance, we have studied the lifetime measurement using time-correlated single photon counting (TCSPC) method and another dye methylene blue (MB) degradation were investigated. The TCSPC data revealed that the catalyst showed the nanosecond lifetimes of 2.6 (76%), 2.3 (18%), and 1.9 (10%) clearly indicating that it is not a phosphorescent material (Figure S11, SI). Further, we have tested the catalytic performance of Pd@CD-CONH (50 mg) of nano-hybrid catalyst for the degradation of 100 mL of $10^{-5}$ M aqueous solution of MB in the dark (Figure 11). It was found that the decrease in the absorbance at 664 nm and the band got disappeared almost completely (99%) within 20 min in dark.

![Figure 11. Time-dependent sonocatalytic degradation absorption spectra of MB in the presence of Pd@CD-CONH nano-hybrid catalyst.](image)
In order to ensure that the sonocatalytic degradation is indeed happening and not due to simple adsorption on the catalyst, we have conducted FT-IR study of fresh and the recovered catalyst which clearly show that dye molecules are not adsorbed on to the catalyst (Figure S14, SI). To corroborate this aspect, the degradation products were studied using liquid chromatography-mass spectrometry (LC–MS) in order to determine the end small molecules (Figure S12, SI). Without any catalyst, RhB has shown the molecular ion peak at 443.5 Daltons. Whereas in the presence of nano-hybrid catalyst, when the reaction followed at time intervals 0 to 5 min. The LS–MS spectra obtained during the course of the reaction showed fragmentation peaks and led to small molecules of 74 and 81 Daltons at the end of the reaction. The possible degradation products are provided in the Figure S12, SI and the observed fragmentation molecules are matches well with the previous reports.52–55

3.5. Recyclability and Stability
The recycling experiments for the sonocatalytic degradation of RhB in the dark were performed in mid and high catalytic regimes in order to study the efficient recyclability and stability of the as-prepared Pd@CD-CONH nano-hybrid catalyst (Figure S13, SI). The catalyst was collected upon centrifugation and washed with water followed by filtration using Whatman filter paper and subsequent drying of the catalyst. Interestingly, the sonocatalytic activity of Pd@CD-CONH was tested for up to three cycles in mid and high catalytic regimes and observed no significant loss in the sonocatalytic activity. The TEM image of the reused nano-hybrid catalyst after three runs did not show any significant change in the morphology and size of the Pd NPs (Figure S13c, SI). Further, the FT-IR spectra analysis of the fresh- and recovered-catalyst showed clearly that the recovered catalyst is free of RhB dye as well as the characteristic peaks corresponding to the catalyst are retained (Figure S14, SI). These results demonstrate that the Pd@CD-CONH nano-hybrid catalyst is stable during the degradation process.

4. Conclusions
In this work, we have successfully polymerised the carbon dots using organic linker (BDA) which efficiently anchor the Pd NPs in order to utilise their promising properties of carbon dots and Pd NPs in catalysis. Further, we demonstrate the sonocatalytic activity of Pd@CD-CONH against rhodamine B dye-degradation without shining of any light. Comparison studies with model compounds suggest that the synergistic effects of Pd NPs and carbon dots
greatly enhances the generation of ROS for the fast degradation of RhB (5 min) in dark. LC-MS and recovered catalyst IR studies clearly indicate that the disappearance of the absorption peak is due to sonocatalytic degradation and not because of adsorption. Detailed mechanistic investigation suggests that the origin of enhanced sonocatalytic activities of nano-hybrid catalyst come from efficient separation of electron–hole pair and subsequent reaction with water mediated by US, which contributes to form ROS such as •OH, O₂^− and HO₂• that degrade the dye molecules. A simple protocol for the synthesis of Pd@CD-CONH nano-hybrid catalyst combined with the fast degradation, filtration-based good recyclability along with non-requirement of other parameters (radiation, temperature, pressure and electric filed) are promising for the perspective of industrial waste-water management. This study opens up new avenue for developing sono-assisted dark-catalytic systems for other reactions as well, for example biomass conversion and our lab is currently working in this direction.

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Supporting Information

Synergistic Effects of Carbon Dots and Palladium Nanoparticles Enhances the Sonocatalytic Performance for Rhodamine B Degradation in the Absence of Light

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1. Section A. Characterization

Part 1. Characterization of Pd NPs decorated on the amide-functionalized carbon dot (CD) polymer (Pd@CD-CONH) and its precursors CD-CONH, CD-COOH

Part 2. Characterization of Pd NPs decorated on the amide-functionalized benzene (BTC) core polymer (Pd@BTC-CONH) and its precursors BTC-CONH, BTC-COOH

1.1. Characterization of CD-CONH and Pd@CD-CONH polymers

Pd@CD-CONH and its precursors CD-CONH, CD-COOH were characterized by FT-IR, UV-Vis, TEM, AFM, TGA, CHN and NMR analysis. The details are discussed below:

^1^H NMR data

CD-CONH: ^1^H NMR (400 MHz, CD$_3$OD, 298 K): $\delta = 6.89$ [Phenyl proton for inner polymer chain, (e)], 7.62–7.59 [Phenyl proton for terminal polymer chain, (b)], 7.73–7.70 [Phenyl proton for terminal polymer chain, (c)]. In Figure S1a, the amide (d) and amine (a) protons are not visible due to exchange with water present in MeOH-$d_4$.

Pd@CD-CONH: ^1^H NMR (400 MHz, CD$_3$OD, 298 K): $\delta = 6.93$ [Phenyl proton for inner polymer chain, (e)], 7.60 [Phenyl proton for terminal polymer chain, (b)], 7.71 [Phenyl proton for terminal polymer chain, (c)]. As shown in Figure S1b, the ^1^H NMR comparison study of CD-CONH and Pd@CD-CONH revealed that the aromatics protons of H$_b$ and H$_c$ did not show any difference in the chemical shift values. However, the inner aryl C-H protons H$_c$ showed a significant shift in the $\delta$ value of 0.04 ppm, indicating the amide group does exhibit some interaction with palladium NPs.
Figure S1. 400 MHz $^1$H NMR spectra of (a) CD-CONH and (b) Pd@CD-CONH in CD$_3$OD at 298 K. Peaks highlighted with * are due to triethylammoniumchloride and hexane solvent.

**Powder XRD and Raman of CD-CONH**

The powder X-ray diffraction (PXRD) spectrum CD-CONH (Figure S2a) showed a broad feature centred at 29.8° 2θ. The low signal-to-noise ratio is consistent with a significant portion of the sample being amorphous.$^1$ The Raman spectrum of the CD-CONH (Figure S2b) clearly showed the characteristics of both sp$^2$ carbon (G-band at about 1576 cm$^{-1}$) and disordered carbon (D-band at about 1366 cm$^{-1}$).$^2$
Figure S2. (a) PXRD and (b) Raman spectra of CD-CNH polymer.

Size determination by TEM-EDX and AFM data

Energy dispersive X-ray (EDX) spectra were measured using Transmittance Electron Microscope (TEM) equipped with EDX facility (Figure S3). Figure S4 shows the AFM images of CD-CNH polymer. The elemental composition and relative abundances are given in Table S1.

Figure S3. TEM images of CD-CNH.
Table S1. TEM-EDX spectrum measurement of CD-CNH.

| Element       | Kvalue   | Weight (%) |
|---------------|----------|------------|
| Oxygen (O)    | 0.525(Kα) | 12.90      |
| Carbon (C)    | 0.277(Kα) | 76.37      |
| Nitrogen (N)  | 0.392(Kα) | 10.07      |
| Chlorine (Cl) | 2.621(Kα) | 0.03       |

Figure S4. AFM images of CD-CNH.
TGA analysis of Pd@CD-CONH:

TGA analysis indicates that the decomposition of 66% organic components occur between 150 to 480 °C beyond which no further decomposition occurs indicating inorganic component present in the system (Figure S5).

Figure S5. TGA pattern of Pd@CD-CONH.

Elemental Analysis:

(CD-CONH): observed C 58.4%, H 8.2%, N 11.8%, O 13.6%. The degree of substitution is 92%.
1.2. Characterization of BTC-CONH and Pd@BTC-CONH polymers

Pd@BTC-CONH and its precursors BTC-CONH were characterized by FT-IR, UV-Vis, TEM, TGA and NMR analysis. The details are discussed below:

**1H NMR data of BTC@-CONH and Pd@BTC-CONH (FigureS6):**

**BTC-CONH:** ¹H NMR (400 MHz, DMSO-d₆, 298 K): δ = 3.95 [Amine proton, (a)], 6.58 [Phenyl proton for terminal polymer chain, (b)], 6.40 [Phenyl proton for terminal polymer chain, (c)], 7.88–7.82 [Phenyl proton for inner polymer chain, (b’,c’)], 8.76–8.64 [Phenyl proton for BTC moieties (e,e’)], 10.75 [amide protons (d,d’)].

**Pd@BTC-CONH:** ¹H NMR (400 MHz, CD₃OD, 298 K): δ = 3.95 [Amine proton, (a)], 6.60 [Phenyl proton for terminal polymer chain, (b)], 6.45 [Phenyl proton for terminal polymer chain, (c)], 7.85 [Phenyl proton for inner polymer chain, (b’,c’)], 8.76–8.64 [Phenyl proton for BTC moieties (e,e’)], 10.69 [amide protons (d,d’)].
**Figure S6.** 400 MHz $^1$H NMR spectra of (a) BTC@-CONH and (b) Pd@BTC-CONH in DMSO-$d_6$ at 25 °C. Peaks marked with * are corresponding to $N,N'$-dimethylformamide.

**TEM:** Morphology of the structure BTC-CONH polymer and Pd@BTC-CONH catalyst

**Figure S7.** TEM images of (a) BTC-CONH polymer and (b) Pd@BTC-CONH catalyst and its (c) histogram.
Synthesis of Pd NPs with coffee extract Pd@Coff.\(^3\)

A solution of Nescafé classic instant coffee (0.1 g) in water (20 mL) was treated with 2 mL of PdCl\(_2\) (0.1N) and stirred for 25 h at 25 °C. Then the reaction mixture was centrifuged at the speed of 1000 rpm for 10 min and washed with water (2 × 15 mL). The residue was dried in the vacuum oven at 75 °C for 15 h to afford 0.08 g of the catalyst Pd@Coff as black solid.

**Figure S8.** TEM image of Pd@Coff catalyst.

2. Section B. Comparison of sonocatalytic activity of Pd@CD-CONH vs model vs reported catalysts

2.1. Comparison of sonocatalytic activity of Pd@CD-CONH vs model catalysts

**Figure S9.** Time-dependent sonocatalytic degradation absorption spectra of RhB in the presence of lower quantity (10 mg) of (a) Pd@CD-CONH and (b) Pd@BTC-CONH catalysts.
2.2 Comparison of reported catalysts catalytic activity in dark vs Pd@CD-CONH catalyst

Table S2: Comparison of catalytic activity observed for Pd@CD-CONH nano-hybrid catalyst with reported literature catalysts conducted in dark condition.

| S.No | Catalyst Used | Degradation time (min) | Source of light | Rate constant (min⁻¹) | Dye Used | Reference |
|------|---------------|------------------------|-----------------|-----------------------|----------|-----------|
| 1.   | ZnO/Au-Pd     | 60                     | UV–vis          | 0.0286                | RhB      | a         |
| 2.   | Zn/ZnO        | 1440                   | Dark            | n.d                   | RhB      | b         |
| 3.   | LaNiO₃₋δ      | 360                    | Dark            | n.d                   | MO       | c         |
| 4.   | Cu₂O/(Ag⁰@Ag-NPs)ₓ | 120       | Dark            | n.d                   | AO7      | d         |
| 5.   | RuO₂-TiO₂/DPA/PANI | 95            | Dark            | 0.105                 | MO       | e         |
| 6.   | Gr/Pd/TiO₂-NWs | 50                     | Dark            | n.d                   | RhB      | f         |
| 7.   | Ce(IO₃)₄      | 50                     | Dark            | n.d                   | RhB      | g         |
| 8.   | Fe₃O₄@SiO₂@TiO₂@MIP MNPs | 25            | Dark            | 0.09615               | CR       | h         |
| 9.   | ZnO₂/ppy      | 20                     | Dark            | 0.35                  | RhB      | I         |
| 10.  | (C₄N₂H₇)₂Bi₂Cl₁₀ (I) | 17             | Dark            | n.d                   | RhB      | J         |
| 11.  | Ag–In–Ni–S nanocomposites | 12         | Dark            | 0.26396               | MB       | k         |
| 12.  | CdSe–graphene composites | 150       | Dark+US”        | 0.0154                | MO       | l         |
| 13.  | CdSe–graphene composites | 150       | Dark+US”        | 0.026                 | RhB      | l         |
| 14.  | Pd@CD-CONH    | 5                      | Dark+US”        | 0.99                  | RhB      | m (This work) |

a Abbreviations MB, RhB, MO, CR, AO7 and US are stands for Methylene Blue, Rhodamine B, Methyl orange, Congo red, Acid Orange7 and Ultrasonic respectively.
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3 Section C. Mechanistic studies

3.1 Thermal effect

![Figure S10](image)

**Figure S10.** Effect of temperature under dark for the Pd@CD-CNH time-dependent sonocatalytic degradation of RhB dye.

3.2 Lifetime study

The time-correlated single photon counting (TCSPC) study was conducted for the Pd@CD-CNH to understand whether the mechanism is mediated by phosphorescent nature of the catalyst (Figure S11). The following lifetimes of 2.6 (76%), 2.3 (18%), and 1.9 (10%) nanoseconds were observed for Pd@CD-CNH indicating that the catalyst is not phosphorescent in nature.
Figure S11. Time decay profiles from the TCSPC data for the CD-CONH polymer and Pd@CD-CONH catalyst.

3.3 Characterization of degradation products of RhB by LC-MS

Figure S12. (a) Mass spectra of a) pure RhB dye (b) 1 min fraction, (c) 3 min fraction and (d) 5 min fraction during degradation reaction catalyzed by Pd@CD-CONH.
4. Section D. Recovery Studies

4.1. Recovery and reusability studies of nano-hybrid Pd@CD-CONH catalyst

Figure S13. Catalytic cycles in (a) low- and (b) high-catalytic regimes by reused catalyst Pd@CD-CONH (c) TEM image of third cycles recovered catalyst of Pd@CD-CONH.
4.2 Characterization of recovered catalyst by FT-IR

![FT-IR spectra](image)

**Figure S14.** FT-IR spectra of fresh catalyst Pd@CD-CONH, RhB and the recovered catalyst Pd@CD-CONH after degradation.

5. Section E. References

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