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ARTICLE TYPE

Formation of gold-carbon dot nanocomposite with superior catalytic ability towards reduction of aromatic nitro group in water†

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We report the synthesis of gold-carbon dot nanocomposite and its utility as a recyclable catalyst for reduction of aromatic nitro group. Presence of carbon dot on gold nanosurface enhanced the reduction rate by two-fold.

Nanotechnology has emerged as new prospect across scientific disciplines owing to their specific physicochemical and optoelectronic properties. In this context, since the pioneering work of Haruta, researchers found the usefulness of nanomaterials towards catalyzing chemical reactions.¹ Till then, noble metallic nanoparticles like gold, silver are being used in catalyzing diversified class of reactions ranging from carbon monoxide oxidation, C-C coupling to hydrogenation.¹⁻³ The advantages of using gold nanostructures in modulating catalysis lie in their straightforward synthesis in different forms, stability, and surface functionalization, among others.^{4,5} Typically, smaller nanoparticles showed higher catalytic ability in various kinds of reactions.⁵ However, in the case of redox reactions, anisotropic nanostructures with high electron transporting ability such as nanocages or nanoboxes have been observed to enhance the catalytic rate.⁴

Amalgamation of carbon nanostructure and metal nanoparticle are providing some as exceptional features in terms of its catalytic, electronics or photovoltaic properties.⁶⁻⁷ To this end, among the family of nanodimensional allotropes of carbon, carbon dots (CDs) (the newest but exciting) are showing interesting visions ranging from sensing, biomedical to

photocatalytic applications, courtesy to their intrinsic photophysical properties.⁸ CDs can also exhibit high electron transporting ability as it has an electron rich graphitic core. At this point, a nanocomposite comprising CD and anisotropic gold nanospecies (like GNR) can be of high interest towards catalyzing redox type of reactions. GNR stabilized with cationic cetyltrimethylammonium bromide (CTAB) can be conjugated with carbon dot having anionic carboxylate functional groups. In principle, the designed composite might offer several advantages: i) presence of anisotropic gold nanospecies (aGNS) which is already known for its high catalytic efficiency due to presence of different facets; ii) The availability of the graphitic core of CDs, which can expedite the transfer rate of electrons; and most importantly, iii) the hydrophobic domain between aGNS and CD can help trapping hydrophobic molecules which would allow aqueous catalytic reactions of water-insoluble compounds. Thus, aGNS-CD nanocomposite is an interesting approach for the development of superior nanocatalyst. Thus, gold-CD nanocomposite is an interesting approach for development of superior nanocatalyst.

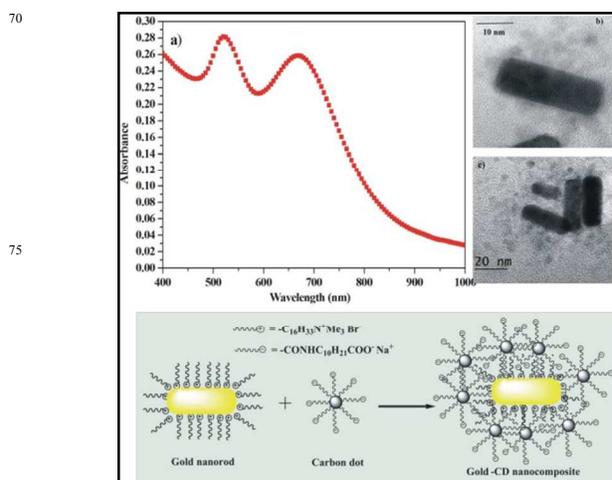


Fig. 1 a) UV-vis spectra, b-c) TEM images of synthesized aGNS-CD nanocomposite ($[Au] = 100 \mu M$, $[CD] = 100 \mu g mL^{-1}$) d) schematic representation of the formation of the aGNS-CD nanocomposite.

Initially, we have synthesized aGNS with a transverse surface plasmon peak (λ_{trans} , SPR) at 520 nm and longitudinal peak (λ_{long})

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†Electronic Supplementary Information (ESI) available: Details of synthesis of GNPs and CDs, other experimental details, TEM images, UV-vis spectra, kinetics graph, see DOI: 10.1039/b000000x/

at 695 nm using standard protocols (Fig. 1a).¹⁰ Details of the synthetic procedure can be found in the electronic supplementary information (ESI). Transmission electron microscope (TEM) images revealed that the width of the aGNS (among some other gold nanospecies like nanocube) is 10 ± 2 nm, having aspect ratio of 2.8 ± 0.3 (Fig. 1b-c and S1a, ESI). The synthesized aGNS are highly stable as these are stabilized by the quaternary ammonium group of cetyltrimethylammonium bromide (CTAB).¹⁰

In order to produce the aGNS-CD nanocomposite, we have designed carbon dot functionalized with long chain anionic carboxylate (Fig. 1d). CDs were synthesized by thermal coupling between sodium-salt of 11-aminoundecanoic acid and citric acid as discussed elsewhere (Fig. 1d).¹¹ Here citric acid acts as the carbon source and 11-amino undecanoic acid covalently linked with the carbon nanoparticle via amide bond. The size of the CDs are of 3 ± 1 nm as found from TEM images (Fig. S1b, ESI). Also a negative zeta potential (ζ) value of -23.8 ± 2 mV confirms the presence of carboxylate moiety on the surface of the CD.

The synthesized aGNS solution was centrifuged at 14,000 rpm for 90 min to remove excess CTAB and the residual material was redispersed in aqueous phosphate buffer (pH 7.0, 25 mM). This buffered aGNS solution was then used to make the conjugate with CD functionalized with carboxylate moiety. The nanoconjugate was prepared by mixing aGNS and CD solutions in phosphate buffer at different ratio. The formation of the aGNS-CD

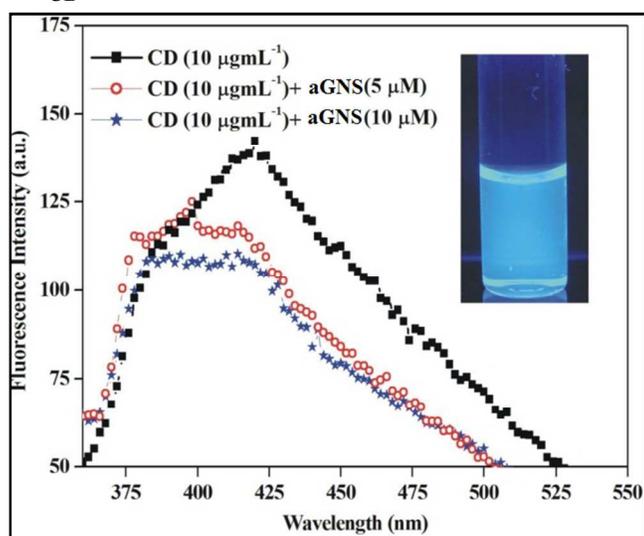


Fig. 2 Fluorescence spectra of CD in absence and presence of aGNS of varying concentration (Inset: Visual fluorescent image of CD).

nanoconjugates was confirmed both by spectroscopic and microscopic method. The strong photoluminescence properties of the CD (emission and excitation wavelength maxima = 420 and 340 nm) was quenched in presence of aGNS as gold nanomaterials are known for quenching the emission of fluorophores in close proximity (Fig. 2).⁵ The blue-shift in emission maxima (almost by 20 nm, from 420 nm to 400 nm) in presence of aGNS is likely due to the interaction between nanogold and CD. In addition, the TEM images (Fig. 1b-c) show the occurrence of CDs over the gold surface, which is consistent with the formation of the gold-CD composite. We propose that the electrostatic attractive force between cationic aGNS and

anionic CDs as well as the hydrophobic attraction of the long carbon chain plays a crucial role in nanocomposite formation (Fig. 1d).

To test the catalytic ability of the synthesized nanocomposite, we have chosen the reduction of *p*-nitrophenol as the model reaction.¹² The conversion of *p*-aminophenol from its nitro analogue is a reaction of versatile applications that includes antipyretic or analgesic drug development, dye industry, and corrosion removal.^{13,14} Moreover, the reaction does not proceed in absence of any catalyst. The progress of the reaction can be easily monitored by observing the rate at which the characteristic 400 nm peak of *p*-nitrophenol decreases as it converts to *p*-aminophenol, with a generation of a new peak at 300 nm (Fig. S2 and S3a, ESI). The reaction followed pseudo first order kinetics as the concentration of NaBH_4 is in excess (almost 1000 times higher) than that of *p*-nitrophenol.

Initially, we have monitored the apparent rate constant (k_{app}) of the reaction in presence of varying concentration of aGNS ($[\text{Au}] = 10\text{-}100 \mu\text{M}$). We have observed an increase in k_{app} (from 0.05 to 0.072 s^{-1}) with increasing Au concentration up to $50 \mu\text{M}$ and then remain almost constant (Table S1, ESI). At this point, the gold-CD composite was fabricated by varying CD concentration from 12.5 to $100 \mu\text{g mL}^{-1}$ while concentration of aGNS was kept constant ($50 \mu\text{M}$). Increasing aGNS concentration resulted in colloidal instability of the composite. Interestingly, an increase in the CD concentration in the gold-CD composite (up to $50 \mu\text{g mL}^{-1}$) led to a 2-fold increase in the k_{app} from 0.072 to 0.143 s^{-1} , while further increase in the CD concentration ($100 \mu\text{g mL}^{-1}$) caused almost no effect in the k_{app} at 0.135 s^{-1} (Fig. 3 and S3, ESI). However, presence of only CD led to an almost negligible effect towards catalyzing the reaction (Fig. S3, ESI).

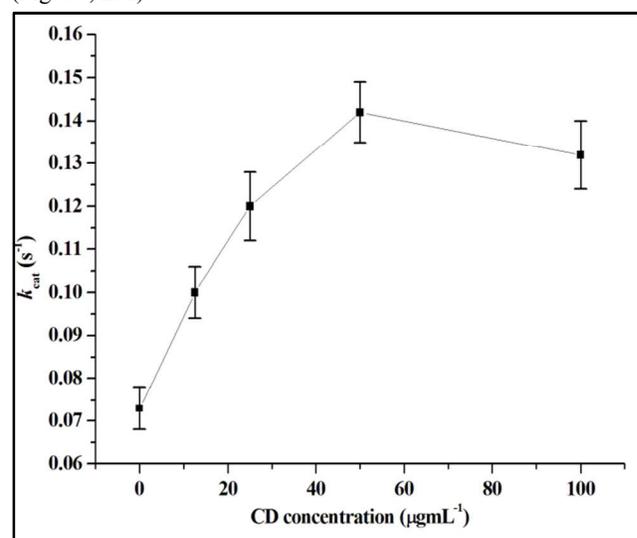


Fig. 3 Variation in k_{app} of *p*-nitrophenol reduction by NaBH_4 in presence of aGNS-CD nanocomposite in aqueous phosphate buffer (pH 7, 25 mM) at 25°C ($[\text{Au}] = 50 \mu\text{M}$ in all aGNS-CD composite).

Furthermore, we have also monitored the recyclability of the gold-CD nanocomposite in catalyzing the reduction. Our experiments showed that the catalytic ability remained about 80% even after completing the fourth reduction cycle (Fig. 4). In fact,

the TEM image of the gold-CD nanocomposite revealed the encirclement of the CD on the gold nanosurface even after the fourth cycle (Fig. S4, ESI). However, the gradual loss in the catalytic ability might be due to detachment of parts of CD (probably during purification of the composite by centrifugation after each run) from the gold nanosurface and corresponding decrease in electron transfer efficiency by the CD as the number of cycle is increased. This cyclic stability and retainment of the catalytic activity of this nanocomposite is of high significance in terms of its use as a potential catalyst.

It is obvious that the presence of CD resulted a 2-fold increase in the catalytic rate of the reduction of *p*-nitrophenol when combined with aGNS, which itself is known as a good catalyst for this reaction.⁹ This might be due to the acceleration of the electron transport through the graphitic carbonaceous core of the CD.¹⁵ In addition, *p*-nitrophenol is firmly placed within close proximity of the gold surface aided by the hydrophobic carbon chain of the nanocomposite. In fact, the presence of *p*-nitrophenol

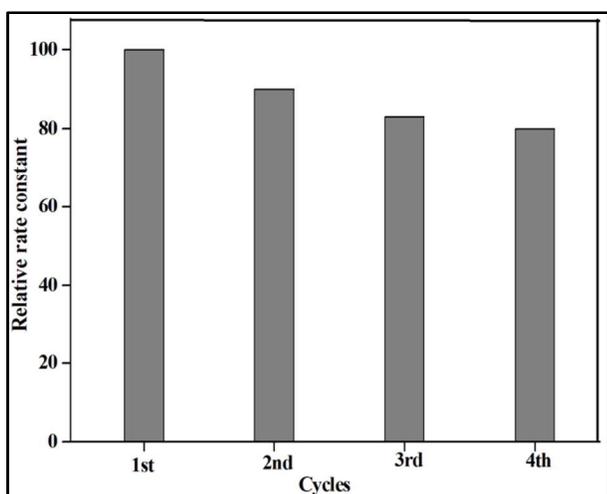


Fig. 4 Recyclability of the gold-CD nanocomposite as catalyst for the reduction of *p*-nitrophenol.

in the hydrophobic domain was consistent with a slight blue-shift in UV spectra of the compound in presence of aGNS-CD composite in the aqueous buffer (Fig. S5, ESI). Thus, it is likely that an enhanced capacity for transferring electron lead to an increase in catalytic rate of the reduction. However, beyond a certain concentration of the CD in the aGNS-CD nanocomposite, the rate of catalysis remained same probably due to the lack of penetration space by the reactant molecules to get close to the gold nanosurface.

To this end, we have also observed the ability of this gold-CD nanocomposite to catalyze reduction of *o*-nitrophenol to *o*-aminophenol. The concentration of Au and CD in the nanocomposite were maintained at 50 μM and 50 $\mu\text{g mL}^{-1}$. In this case, progress of this pseudo first order reaction was monitored spectrophotometrically by observing the rate of decrease in the absorbance at 420 nm (characteristic UV peak of *o*-nitrophenol) (Fig. S6, ESI). Here also, the rate of the reduction was increased by 1.6 fold in presence of CD. The observed k_{app} was 0.064 s^{-1} in only aGNS solution, which increased to 0.104 s^{-1} in the gold-CD nanocomposite in aqueous buffer (Fig. S6, ESI). However, in absence of the catalyst almost no reduction occurred.

We have also used one water-insoluble substrate (*m*-dinitrobenzene) to check the efficacy of our designed gold-CD nanocomposite towards its reduction. The *m*-dinitrobenzene reduced to *m*-phenylenediamine in presence of NaBH_4 and our nanocomposite in aqueous phosphate buffer.¹⁴ The corresponding change in UV-vis spectra also delineated this fact (Fig. S7, ESI). In addition, the gradual blue shift in UV-vis spectral maxima of *m*-dinitrobenzene (244 to 241 nm) in aGNS and gold-CD composite validates the presence of the compound in the hydrophobic domain of the nanocomposite (Fig. S8, ESI). In this case also, the pseudo first order rate constant of the reaction was found to be increased by 2 fold in presence of CD (from 0.14 s^{-1} to 0.28 s^{-1}) (Fig. S9, ESI).

In conclusion, we have developed a new class of gold-CD nanocomposite which shows high efficiency in catalyzing reduction of different aromatic nitrogroups. This novel catalyst is stable in water and has shown good recyclable efficiency towards catalysis. Importantly, to the best of our knowledge, this is the first report of the catalytic properties of carbon dot in conjugation with gold nanospecies, for the reduction of both hydrophilic and hydrophobic nitroarenes. We believe the presence of CD increased the rate of electron transfer as well as secures the localization of the reactant molecules within the catalyst, and thus a 2-fold enhancement in catalytic activity in comparison to only aGNS was found almost in every case. This novel catalyst is stable in water and has shown good recyclable efficiency towards catalysis. Most interestingly, the catalysis can also be efficiently performed in water-insoluble compound, like *m*-dinitrobenzene. Importantly, to the best of our knowledge, this is the first report of the catalytic properties of carbon dot in conjugation with aGNS, for the reduction of nitroarenes and thus present potential applications in the design of various industrially important catalysts.

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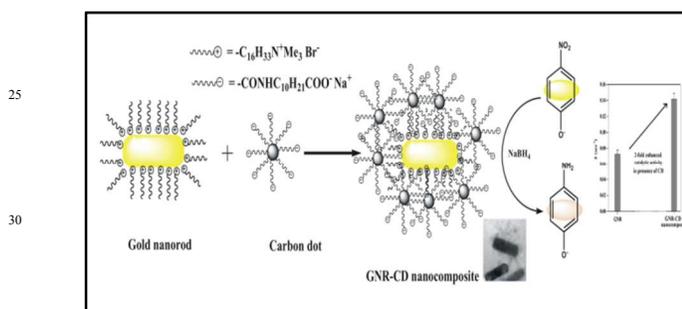
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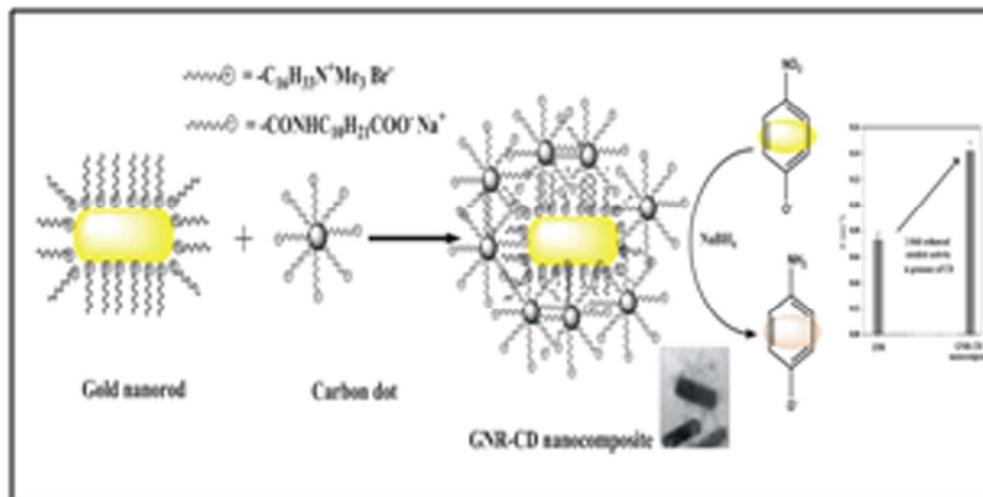
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Graphical Table of Content



- 35 Probing on the synthesis of highly-efficient aGNS-carbon-dot nanocomposite and its utility as a recyclable catalyst for reduction of aromatic- nitrogroup.



Probing on the synthesis of highly-efficient aGNS-carbon-dot nanocomposite and its utility as a recyclable catalyst for reduction of aromatic- nitrogroup.
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