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

Pritiranjan Mondal a*, Krishanu Ghosal a, Swarup Krishna Bhattacharyya a, Mithun Das a, Abhijit Bera a, Debabrata Ganguly a, Pawan Kumar d, Jaya Dwivedi d, R. K. Gupta b, Angel A. Martí c, Bipin Kumar Gupta* d and Subhabrata Maiti a

*aDepartment of Applied Chemistry and Industrial Chemistry, Ramakrishna Mission Vidyamandira, Belurmath, Howrah – 711 202, India,
E-mail: pritiranjanmondal21@gmail.com,
bDepartment of Chemistry, Pittsburg State University, Pittsburg, KS 66762, USA

cDept. of Chemistry and Bioengineering, Rice University, Houston, TX 77005

dNational Physical Laboratory (CSIR) Dr K S Krishnan Road, New Delhi 110012, India ; E-mail:bipinbhu@yahoo.com

Electronic Supplementary Information

Materials and instruments:

HAuCl₄ (30 wt. %) solution, 11-aminoundecanoic acid were purchased from Sigma, USA. Silver nitrate, citric acid, sodium borohydride, p-nitrophenol, o-nitrophenol, m-dinitrobenzene, cetyltrimethylammonium bromide and other reagents were purchased from Merck (India) and were of highest analytical grade. The UV-visible absorption spectra were recorded on a Perkin-Elmer Lambda 25 spectrophotometer. Fluorescence spectra were measured in Varian Cary Eclipse luminescence spectrometer. Zeta potential was recorded in zetasizer Nano-ZS of Malvern instrument limited.

Synthesis of gold nanorod:

Gold nanospecies was formed by following the protocol described elsewhere (reference 10 in the main manuscript). Briefly, 5 mL of aqueous solution of cetyltrimethylammonium bromide (CTAB) was mixed with solution of HAuCl₄. The final concentrations of CTAB and HAuCl₄ were maintained at 0.1 M and 1 mM, respectively. Then, ascorbic acid and AgNO₃
were added in this solution so that the concentration of ascorbic acid and AgNO$_3$ was 2 mM and 0.10 mM. Finally, 50 $\mu$L of 1mM freshly prepared aqueous NaBH$_4$ solution was added. The colorless solution (yellow to colorless transition occurred upon addition of ascorbic acid) started to appear pink-violet within few min indicating the formation of gold nanorods among other species.

**Synthesis of carboxylate functionalized carbon dot (CD):**

CD was synthesized by following the reported protocol (Reference 11 in the main manuscript). For the synthesis of CD, initially 2 g H$_2$N(CH$_2$)$_{10}$COOH were added in 25 mL H$_2$O and neutralized by 0.45 g NaOH. The solution was added to 25 mL of an aqueous solution containing 2 g citric acid. The addition of citric acid resulted a thick precipitate after stirring and the precipitate was collected by filtration. It was partially dried overnight at room temperature. This gummy paste was further dried at 85 ºC for 2 h. The solid was crashed into a fine powder and directly oxidized in air at 300 ºC for 2 h in a muffle oven. The crude product was extracted with 25 mL of hot water using sonication. The mixture was then centrifuged to remove any insoluble particles and the supernatant aqueous layer was collected. The deep brown supernatant solution was precipitated by centrifuging at 14000 rpm for 1 h after addition of acetone at 1:10 volume ratio. The supernatant was removed and the precipitated brownish black mass was further dried in hot oven at 80 ºC until it became powder in nature.

**Catalytic study.** In a typical experiment, 2 $\mu$L of $p$-nitrophenol/ $o$-nitrophenol/ $m$-dinitrobenzene stock solution was added into 2.0 mL aqueous buffer of gold-CD nanoconjugate (of different composition, mentioned in the main manuscript), so that final concentration of the reactant was 0.1 mM. Stock solution of $o$-nitrophenol, $m$-dinitrobenzene was made in ethanol. To the mixed solution of catalyst and reactant, 0.1 mL of NaBH$_4$ was added with stirring to start the reaction (final concentration of NaBH$_4$ = 0.1 M). The progress
of the reaction was carried out by UV-vis study at ambient temperature (27 ºC). After the completion of the reaction, the total solution was centrifuged for 60 second to separate the catalyst. It was washed with MilliQ water and then, air dried for further using as catalyst.

**Calculation of the rate constant.** The pseudo-first-order kinetics with respect to the reactants could be applied to our experimental system. The approximately linear shape of the plot of \(-\ln \frac{A_t}{A_0}\) (\(A_0\) represents the initial and \(A_t\) the absorbance after time \(t\) at corresponding wavelength) versus time, as shown in Figure S3. As absorbance is proportional to concentration it corresponds to the concentration of the reactants. From, the slope of the linear equation the apparent rate constant \((k_{app})\) is calculated.

**TEM study:** For TEM, a drop of the gold nanospecies, CD and gold-CD nanocomposite solution was cast on 300-mesh Cu-coated TEM grid separately and dried under vacuum for 4 h before taking the image. TEM images were taken on a JEOL JEM 2010 microscope.

**Table S1:** Variation in \(k_{app}\) of \(p\)-nitrophenol reduction by NaBH\(_4\) in presence of anisotropic gold nanospecies (aGNS) of varying concentration in aqueous phosphate buffer (pH 7, 25 mM) at 25 ºC

<table>
<thead>
<tr>
<th>aGNS concentration</th>
<th>(k_{app}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.054</td>
</tr>
<tr>
<td>20</td>
<td>0.062</td>
</tr>
<tr>
<td>30</td>
<td>0.068</td>
</tr>
<tr>
<td>50</td>
<td>0.072</td>
</tr>
<tr>
<td>100</td>
<td>0.074</td>
</tr>
</tbody>
</table>
Fig. S1 TEM images of a) synthesized gold nanospecies b) anionic carbon dot.

Fig. S2 Time-dependent UV-vis spectra of p-nitrophenol reduction in presence of gold-CD nanocomposite in aqueous phosphate buffer (pH 7.0, 25 mM) at 25 °C.
**Fig. S3 a)** The change in absorbance of p-nitrophenol with respect to time in presence and absence of catalyst and **b)** plot of $-\ln A_t/A_0$ against time to find the rate constant for p-nitrophenol reduction.

**Fig. S4** TEM image of gold-CD nanocomposite after fourth cycle of p-nitrophenol reduction.
Fig. S5 UV-vis spectra of \textit{p}-nitrophenol in absence and presence of gold-CD nanocomposite in aqueous phosphate buffer.
**Fig. S6 a)** The change in absorbance of o-nitrophenol in presence of the gold-CD catalyst and **b)** plot of $-\ln A_t/A_0$ against time to find the rate constant for o-nitrophenol reduction.
Fig. S7 Time-dependent UV-vis spectra of \( m \)-dinitrobenzene reduction in presence of gold-CD nanocomposite in aqueous phosphate buffer (pH 7.0, 25 mM) at 25 °C.

Fig. S8 UV-vis spectra of \( m \)-dinitrobenzene in absence and presence of catalyst in aqueous phosphate buffer.
**Fig. S9** Plot of $-\ln A_t/A_0$ against time to find the rate constant for m-dinitrobenzene reduction.