Fluorescent Carbon dots obtained from chitosan gel

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Electronic Supplementary Information (ESI)

Materials

Low molecular weight chitosan was purchased from Sigma Aldrich, Glycerol (about 98% purified), hydrochloric acid and sodium hydroxide pellets (purified) were purchased from Merck. Acetic acid glacial was purchased from Qualigens Fine Chemicals. All other materials used were of analytical reagent grade from commercial sources.

Experimental Procedure

The Chitosan/Ag or Au nanocomposites were prepared using the same procedure as used for the preparation of chitosan hydrogels. The nanocomposites were prepared in two different ways: in-situ and ex-situ incorporation of Ag or Au NPs into the gel matrix.

In-Situ process: Incorporation of Ag or Au NPs into the hydrogel

The in-situ incorporation of silver nanoparticles (Ag NPs) was done prior to stirring by adding 3 ml of prepared Ag NPs solution to the chitosan-acetic acid-glycerol mixture. After 2 hours of continuous stirring a light brown coloured solution was obtained, this was then neutralized by 5N NaOH resulting in formation of the chitosan/Ag in-situ nanocomposites (CH-Ag-I). Similarly, for preparing light pink coloured chitosan/Au in-situ nanocomposites (CH-Au-

I) we followed the same procedure with the difference that instead of using Ag NPs we used gold nanoparticles (3ml of Au NPs) for obvious reasons.

Ex-Situ process: Embedding the Ag or Au NPs into the hydrogel

In this process, a small piece of as-prepared chitosan hydrogel was immersed in already prepared Ag NPs solution for 60 minutes (Ag NPs were prepared separately by reduction of $AgNO_3$ using citric acid under boiling condition). This step allows the loading of Ag NPs from the NPs solution to the hydrogel network. The process was also monitored with Uv-visible spectrophotometer and the prepared hydrogel was termed as chitosan/Ag ex-situ nanocomposites (CH-Ag-E). The chitosan/Au ex-situ nanocomposites (CH-Au-E) was prepared following the same above method, i.e., immersion of chitosan hydrogel in Au NPs solution for 60 minutes (Au NPs were prepared separately by reduction of $HAuCl_4$ using cysteine under boiling condition).

Characterization

Uv-visible study of as prepared CDs was done using Shimadzu UV Spectrophotometer-UV 1800. For PL intensity measurements was done in HITACHI F-2500 spectrofluorometer. Fluorescence microscopy was done using Leica DMI 3000-B Fluorescence microscope system. Samples for fluorescence microscopy was prepared by drop casted CDs on glass slides oven-dried (65 ^{0}C) for 24 hours. Size distribution and zeta potential of the CDs was done using Malvern Zetasizer NanoZS 90. Surface morphology of the CDs deposited on silicon wafer was investigated using scanning electron microscope (SEM) from Carl Zeiss (Σigma VP).

Figure S1 shows the FTIR spectrum of chitosan used to determine the degree of deacetylation. The deacetylation degree was determined using the equation (1)

$$DDA\ (\%) = 100 - [(31.918 * A_{1320}/A_{1420}) - 12.20] \qquad \text{--------} \quad 1$$

The degree of deacetylation (DDA) as calculated using equation (1) proposed by Monal, Desbrieres, and Rinaudo (2000) with a range of DDA = (0-100) % was found to be 77.7 %.

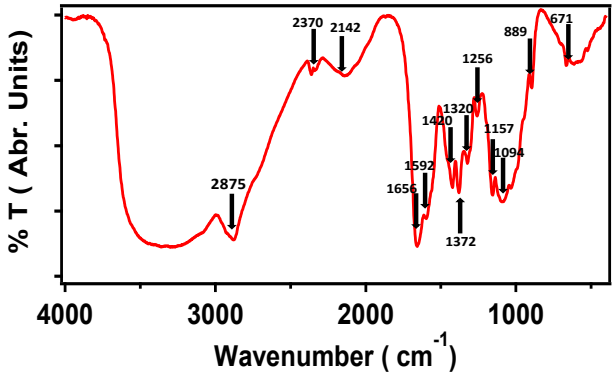

Figure S1. Fourier Transformed Infra-red (FTIR) spectrum of chitosan.

Silver and gold nanoparticles used in the experiments were prepared separately. Silver nanoparticles solution was prepared from 5mM $AgNO_3$ and 5mM trisodium citrate solution as reducing and stabilising agent. Similarly, gold nanoparticles solution was prepared by reduction of 0.16 M $HAuCl_4$ using 5mM cysteine solution as reducing and stabilising agent. Both the nanoparticles solution were characterised by UV-visible spectrophotometer and Dynamic Light Scattering (DLS) analysis (Figure S2). UV-visible study showed characteristic Surface Plasmon resonance peak for Ag NPs at 411 nm and for Au NPs at 530 nm. The average sizes obtained from DLS study for Ag NPs and Au NPs was found to be 25 nm and 32 nm respectively.

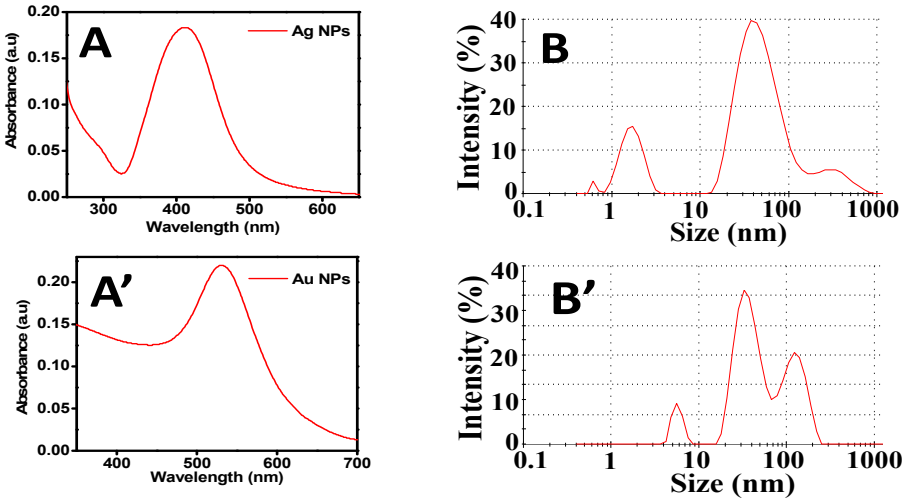

Figure S2. (A) UV- Visible spectrum **(B)** DLS of Ag NPs and **(A')** UV- Visible spectrum **(B')** DLS of Au NPs.

Photoluminescence studies were also carried out on CDs prepared from CH-Ag-I, CH-Ag-E, CH-Au-I and CH-Au-E labelled as Ag-I/CDs, Ag-E/CDs, Au-I/CDs, Au-E/CDs respectively. Figure S3 shows photoluminescence emission and absorption spectra obtained with progressively longer excitation wavelengths from 300 nm to 400 nm of Ag-I/CDs, Ag-E/CDs, Au-I/CDs, Au-E/CDs. Also shown photograph in each case. CDs prepared when viewed under UV lamp. It is evident from the spectra that CDs prepared from CH-Ag-I show a single emission peak and with typical red shift with longer excitation wavelength. It was observed that Ag-I/CDs gave emission at 388nm when excited at 300nm. A similar emission characteristic was observed for Au-I/CDs, red shifted with longer excitation wavelength. In this case excitation at 300nm gave emission at 383 nm. Photoluminescence is somewhat different for Ag-E/CDs and Au-E/CDs. There is a sharp peak followed by a broad peak. It was observed that Ag-E/CDs gave sharp emission at 333nm and a broad peak at 377nm when excited at 300nm. Similarly Au-E/CDs gave emission at 333nm and 385nm when excited at 300nm.

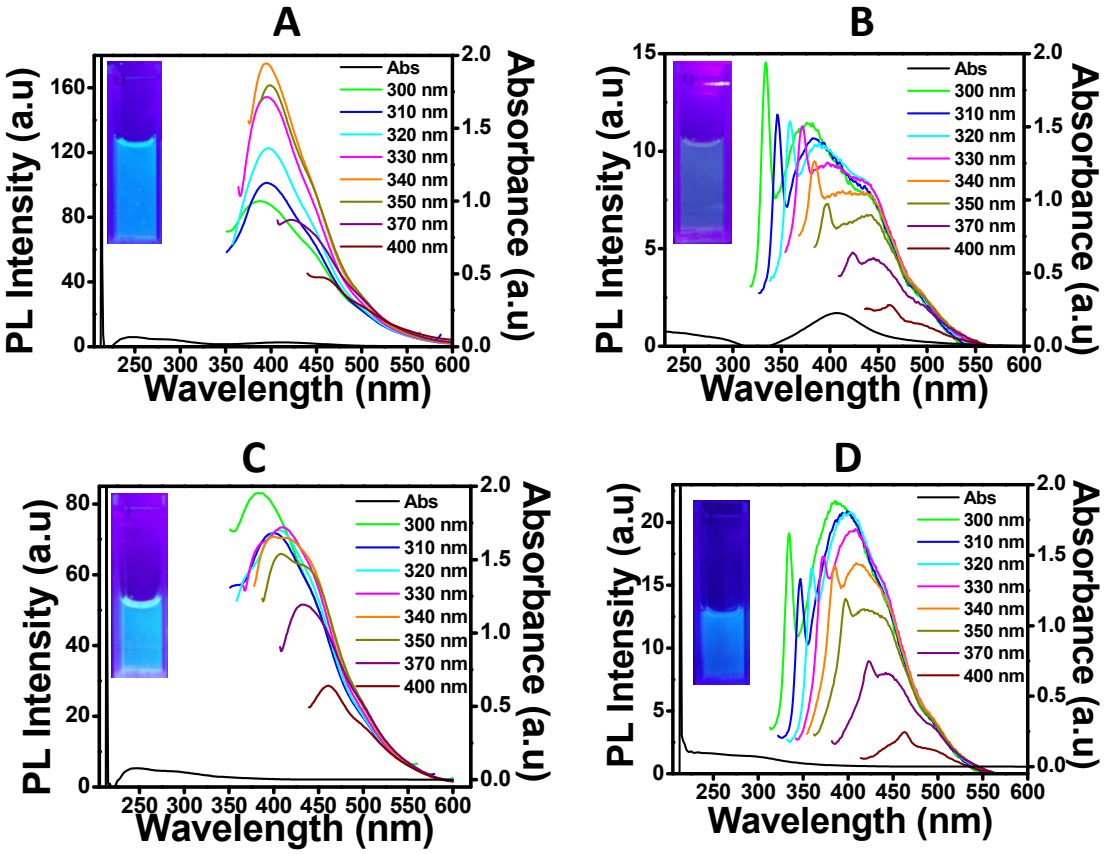

Figure S3. Photoluminescence emission and absorption spectra obtained with progressively longer excitation wavelengths from 300 nm to 400 nm of (A) Ag-I/CDs, (B) Ag-E/CDs, (C) Au-I/CDs, (D) Au-E/CDs. Also presented photograph of the corresponding CDs prepared when viewed under UV lamp.

Size distributions were determined of CDs prepared from Chitosan-Ag and Chitosan-Au in-situ and ex-situ nanocomposites labeled as Ag-I/CDs, Ag-E/CDs, Au-I/CDs, Au-E/CDs (detail in main text) using DLS. It was observed that CDs prepared from CH-Ag or CH-Au in-situ nanocomposites gave smaller size distribution than CDs prepared from CH-Ag or CH-Au ex-situ nanocomposites. Figure S4 show representative size distribution of Ag-I/CDs, Ag-E/CDs, Au-I/CDs, Au-E/CDs.

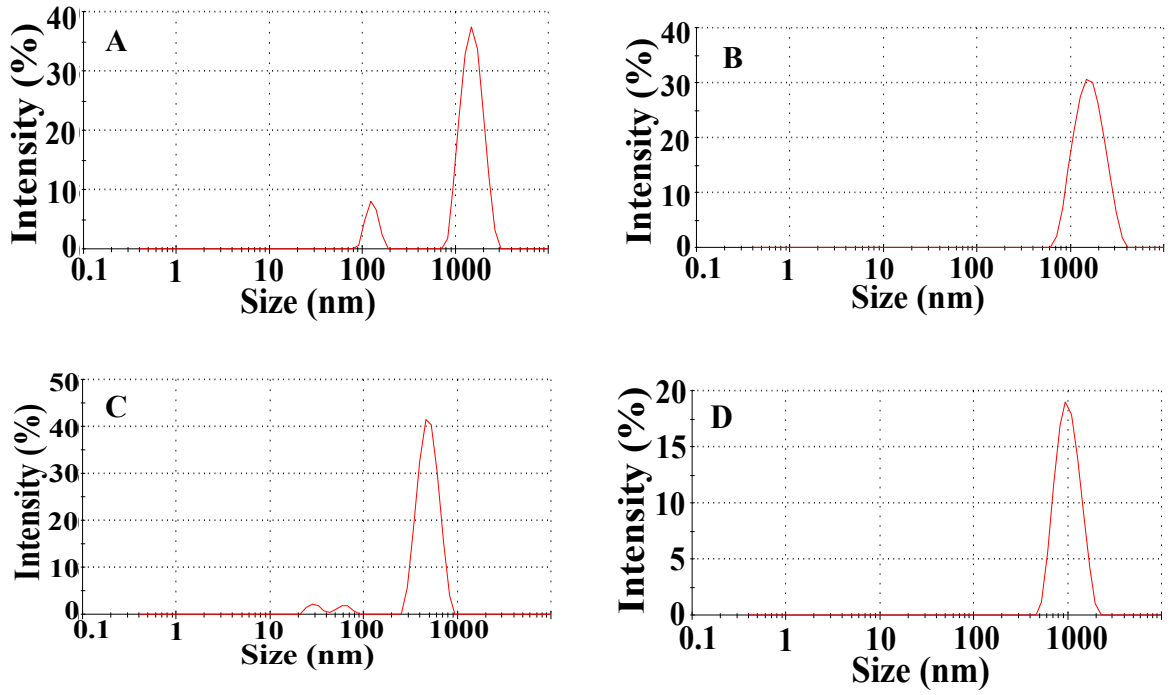

Figure S4. DLS graphs of (A) Ag-I/CDs, (B) Ag-E/CDs, (C) Au-I/CDs, (D) Au-E/CDs

It was observed from DLS measurement that Ag-I/CDs gave sizes 128 nm and 1.5 µm while Ag-E/CDs gave size of 1.6 µm. Particle size was found to be 31 nm, 62 nm and 0.5 µm for Au-I/CDs while Au-E/CDs gave 1 µm sized particles.

Figure S5 is showing photoluminescence spectra and size distribution plot of carbon dots (CDs) prepared from chitosan-glycerol-acetic acid solution dissolved in 0.1 M acetic acid. It is clear from the spectra itself that the peaks are not well defined and there is also a broad peak followed by a sharp peak unlike CDs prepared from chitosan gel dissolved in 0.1 M acetic acid (figure 2 of main text). This irregular behavior in the photoluminescence spectra is also supported by size distribution plot.

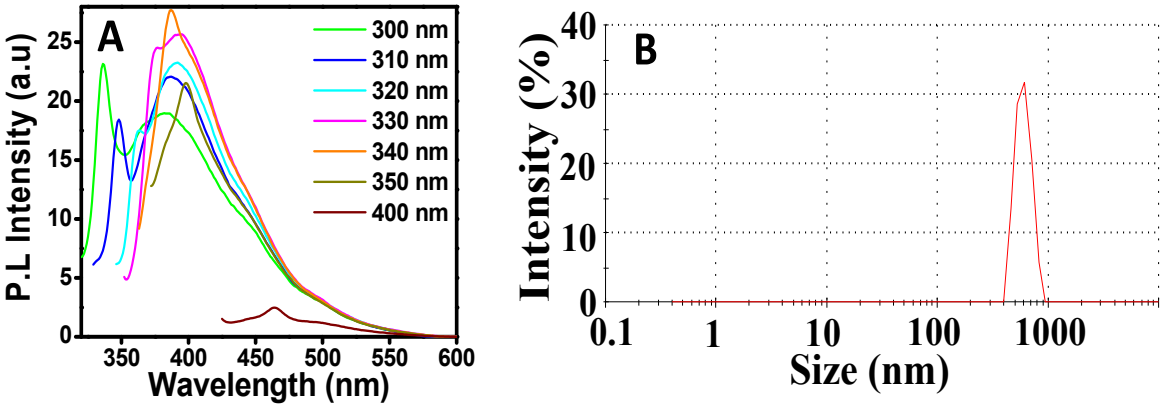

Figure S5. (A) Photoluminescence emission spectra obtained with progressively longer excitation wavelengths from 300 nm to 400 nm of CDs prepared from Chitosan- Glyerol- acetic acid solution (B) DLS graph of CDs prepared from Chitosan- Glyerol- acetic acid solution.

Zeta potential indicates the charge and stability of colloidal dispersions. Zeta potentials were determined for CDs prepared from chitosan gel, Ag-I/CDs, Ag-E/CDs, Au-I/CDs, Au-E/CDs. The values were found to be 27.2mV, 37.8mV, 44.6mV, 33.5mV and 34.4mV respectively. The zeta potential values indicate positive charge on the surface of CDs.

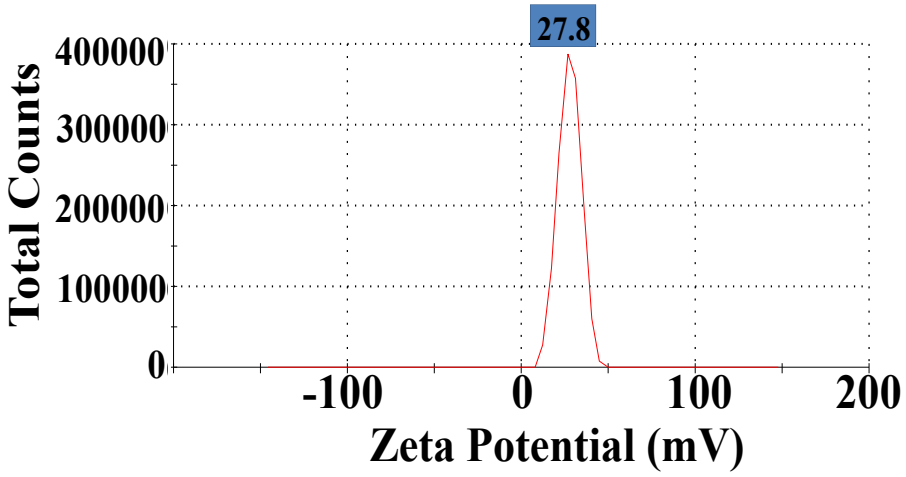

Figure S6. Zeta potential graph of the C-Dot (CDs) prepared from 0.1 M acetic acid. The zeta potential value was found to be 27.8 mV as shown in the graph.

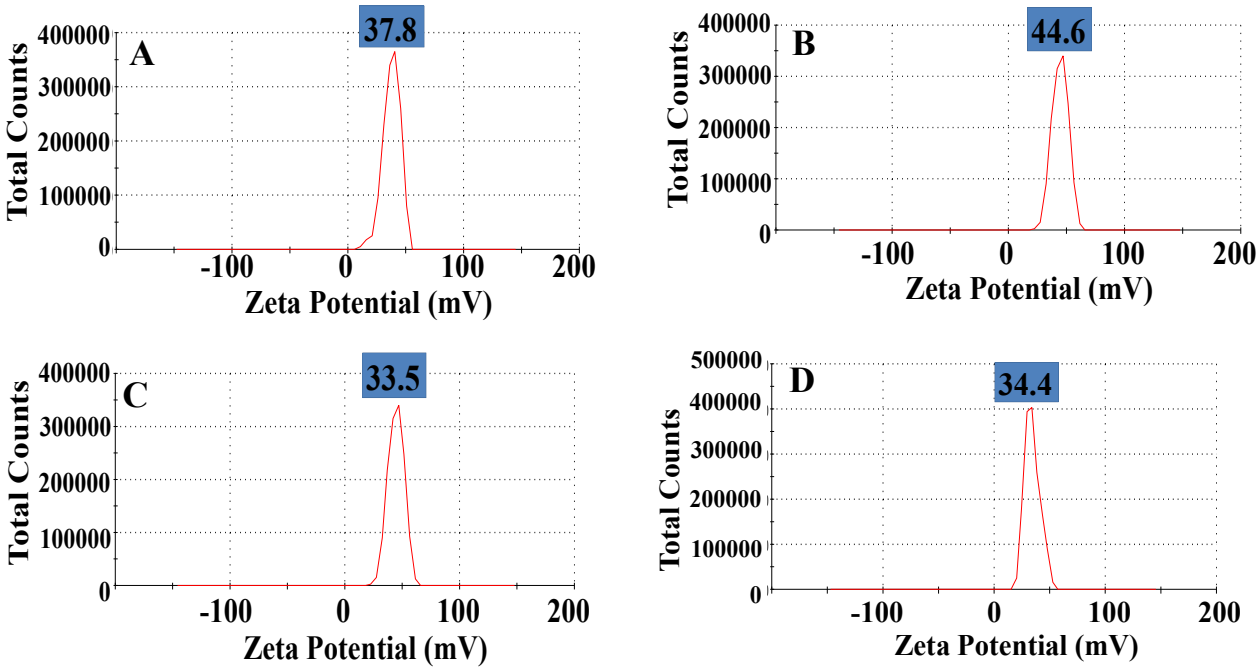

Figure S7. Zeta potential graphs of the as-prepared C-Dots. The zeta potential values of the C-Dots are shown in their respective graphs itself. (A) Ag-I/CDs, (B) Ag-E/CDs, (C) Au-I/CDs, (D) Au-E/CDs.

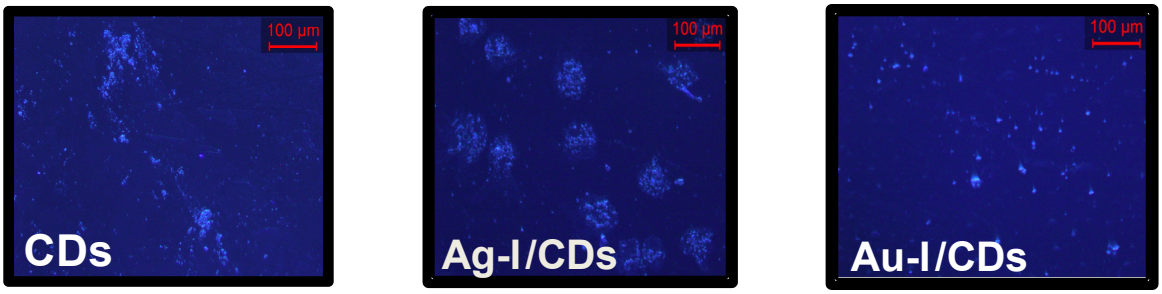

Figure S8. Fluorescence microscope images of the CDs, Ag-I-CDs and Au-I/CDs.