Supporting Information

Diffusion controlled simultaneous sensing and scavenging of heavy metal ions in water using atomically precise cluster – cellulose nanocrystal composites

Nishil Mohammed,[†] Avijit Baidya,[‡] Vasanthanarayan Murugesan,[‡] Avula Anil Kumar,[‡] Mohd Azhardin Ganayee,[‡] Jyoti Sarita Mohanty,[‡] Kam Chiu Tam[,†] and T. Pradeep[*,‡]*

[†] Department of Chemical Engineering, Waterloo Institute for Nanotechnology, University of Waterloo, 200 University Avenue West, Waterloo, ON, N2L 3G1, Canada

[‡] DST Unit of Nanoscience and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600 036, India

* mkctam@uwaterloo.ca, pradeep@iitm.ac.in

Table of contents

Supporting information 1: Hg^{2+} adsorption by CNCs

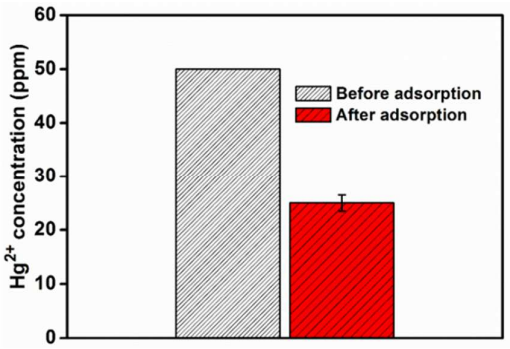


Figure S1. Concentration of Hg^{2+} before and after adsorption with CNCs (Adsorbent dosage = 10 mg/mL, Adsorbate concentration = 50 ppm, pH = 7, Temperature = 25 °C).

Supporting information 2: Cu^{2+} adsorption by nanocomposite

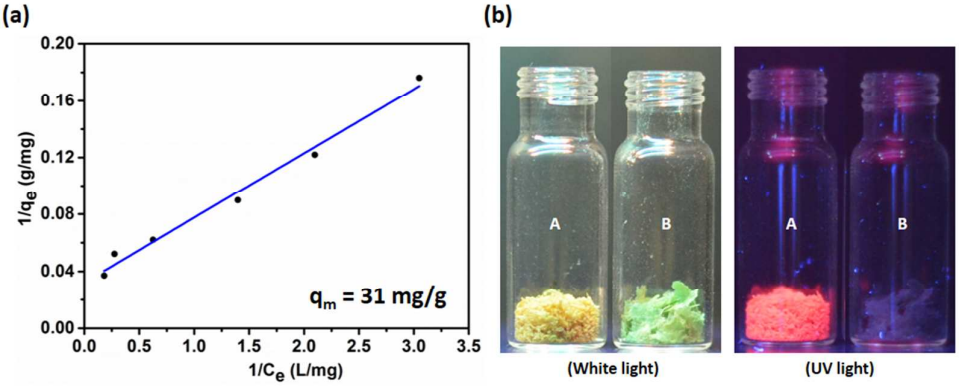
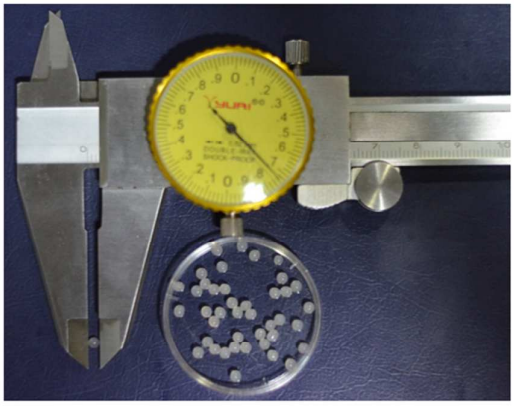


Figure S2. (a) Equilibrium Cu^{2+} batch adsorption data fitted using linearized form of Langmuir adsorption isotherm. (b) Digital photographs of the vials containing nanocomposite (A) before and (B) after adsorption of Cu^{2+} ions under white light and UV light, respectively.

Supporting information 3: Size determination of hydrogel beads using vernier caliper

(a)



(b)

Bead number	Diameter (mm)
1	2.75
2	2.80
3	2.60
4	2.70
5	2.60
6	2.70
7	2.80
8	2.70
9	2.70
10	2.70
Average	**2.705**

Figure S3. (a) Photograph of the vernier caliper used for the measurement of hydrogel bead diameter. (b) Average size distribution of the hydrogel beads used to measure the bead diameter.

Supporting information 4: SEM–EDS characterization of the control nanocomposite

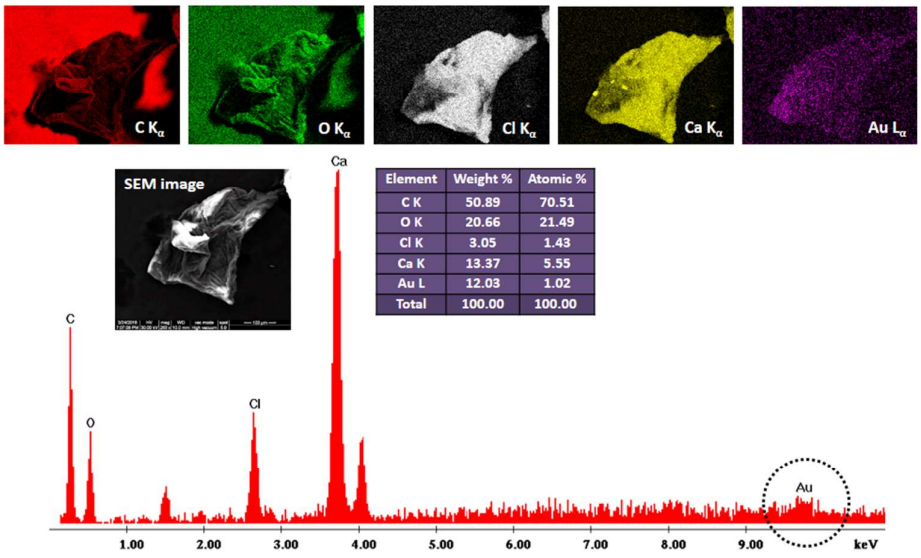


Figure S4. SEM-EDS elemental analysis and elemental mapping of control nanocomposite.

Supporting information 5: SEM–EDS characterization of the Hg^{2+} saturated nanocomposite

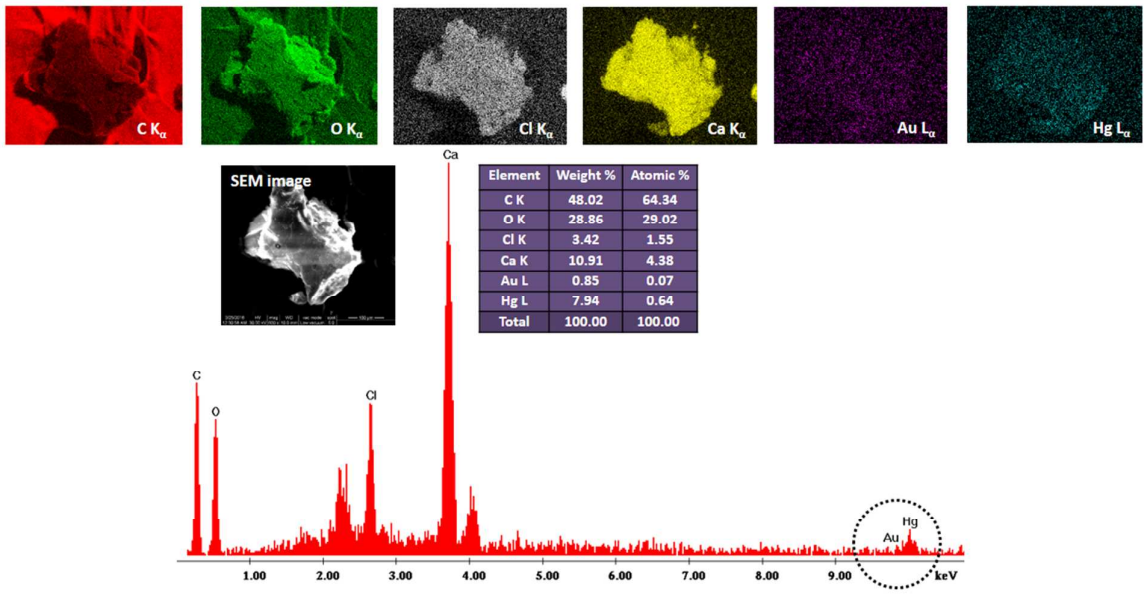


Figure S5. SEM-EDS elemental analysis and elemental mapping of Hg^{2+} saturated nanocomposite.

Supporting information 6: SEM–EDS characterization of the Cu^{2+} saturated nanocomposite

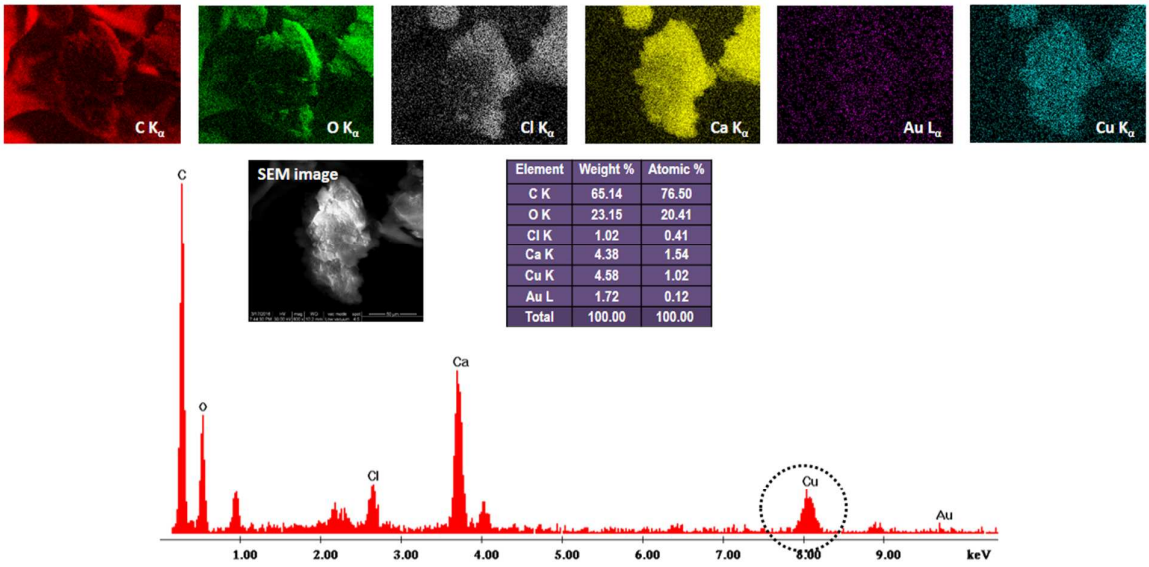


Figure S6. SEM-EDS elemental analysis and elemental mapping of Cu^{2+} saturated nanocomposite.

Supporting information 7: Characterization of Au@BSA NCs

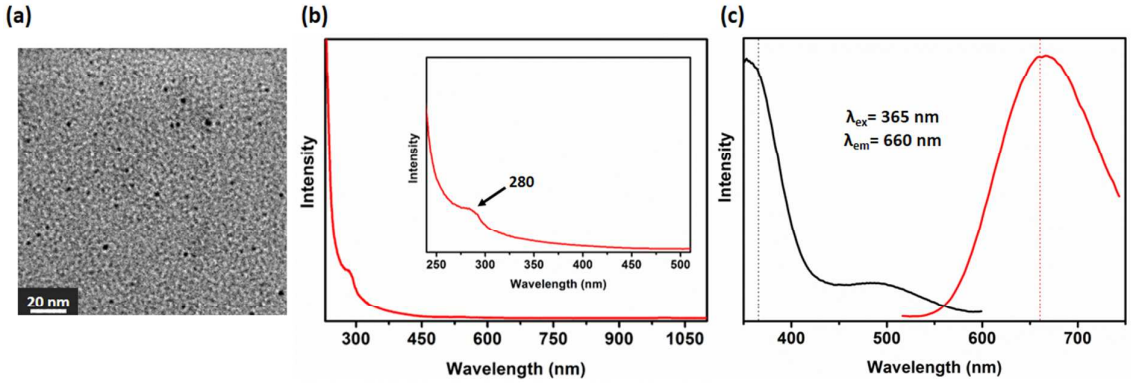


Figure S7. (a) TEM image (b) UV-Vis absorbance spectrum and (c) Photoluminescence spectra showing the excitation (black line) and emission (red line) peaks of Au@BSA NCs.

Supporting information 8: XPS characterization to study cluster quenching and Hg^{2+} binding mechanism

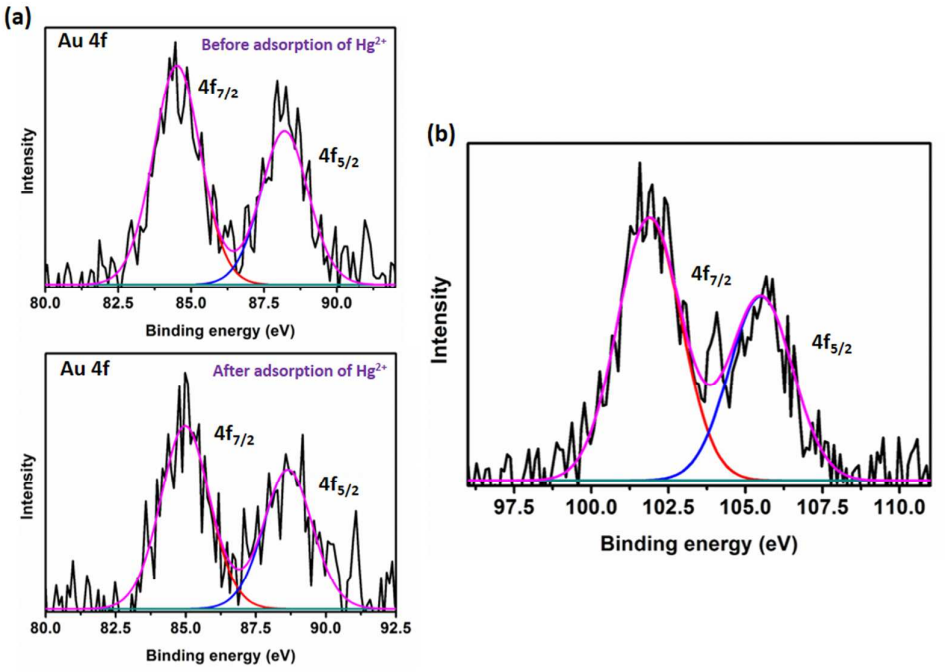


Figure S8. (a) XPS spectra of Au 4f region for the nanocomposite before (up) and after (down) Hg^{2+} adsorption. (b) XPS spectra of Hg 4f region of the nanocomposite after Hg^{2+} adsorption (Hg 4f data are given only after Hg^{2+} adsorption as the control nanocomposite does not have Hg^{2+}).

Supporting information 9: Red intensity profile for quenching experiment

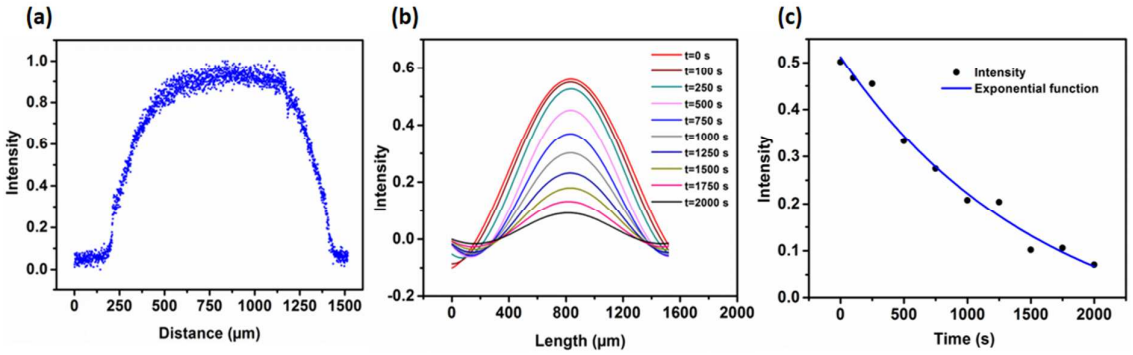


Figure S9. (a) Plot showing the variation in red intensity along the bead diameter at t = 100 s for 100 ppm concentration of Hg^{2+}. (b) Plot showing the fitting of the variation in red intensity for various time points to a sine curve. (c) Plot of the maximum intensity (taken from the centre of sine curve) plotted against time.

Supporting information 10: R-code to obtain the variation of red intensity along the bead diameter

```
library(jpeg)
readJPEG("/Users/Romy/Downloads/Quenching30.jpg")
r <- readJPEG("/Users/Romy/Downloads/Quenching30.jpg")
Red <- as.data.frame(r[,,1])
Green <- as.data.frame(r[,,2])
Blue <- as.data.frame(r[,,3])
center_red <- as.data.frame(Red[1024,])
center_green <- as.data.frame(Green[1024,])
center_blue <- as.data.frame(Blue[1024,])
center_red <- as.data.frame(t(center_red))
center_green <- as.data.frame(t(center_green))
center_blue <- as.data.frame(t(center_blue))
for (i in 1:nrow(center_red))
{
      center_red[i,2] <- i
      center_green[i,2] <- i
      center_blue[i,2] <- i
}
colnames(center_red) <- c("intensity","pixel.no")
colnames(center_green) <- c("intensity","pixel.no")
colnames(center_blue) <- c("intensity","pixel.no")
center_red[,3] <- "RED"
center_blue[,3] <- "BLUE"
center_green[,3] <- "GREEN"
center_pixels <- rbind(center_red,center_blue,center_green )
library(plotly)
plot_ly(center_pixels, y = intensity, color = V3, type = "Scatter",mode =
"markers")
```

Supporting information 11: Error calculation for diffusion coefficient estimation

$$\mathbf{D} = \frac{\mathbf{l}^2}{\boldsymbol{\pi}^2\boldsymbol{\tau}}$$

To calculate error,

$$\boldsymbol{\Delta D} = \frac{\mathbf{l}(2\boldsymbol{\tau}\boldsymbol{\Delta}\mathbf{l} + \boldsymbol{\Delta}\boldsymbol{\tau}\mathbf{l})}{\boldsymbol{\pi}^2\boldsymbol{\tau}^2}$$

Here:

τ = 1594 s,

l = 0.126 cm,

Δl = 0.75 x 10^{-4} cm (size of one pixel) and

$\Delta\tau$ = 478.7 sec (error from fitting the decay equation)

Substituting this in the equation, we get:

$$\boldsymbol{\Delta D = 0.3 \times 10^{-6}\ cm^2/sec}$$

Supporting information 12: Stability of the freeze dried nanocomposite hydrogel beads

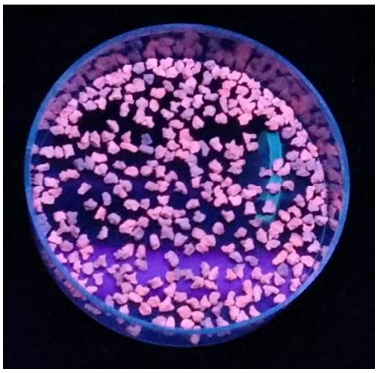


Figure S12. Photograph of the freeze dried nanocomposite hydrogel beads which have been stored for more than 6 months, under UV light.

Supporting information 13: Binding affinity of Hg^{2+} ions with Au@BSA NCs and Au@BSA NCs CNC-ALG nanocomposite

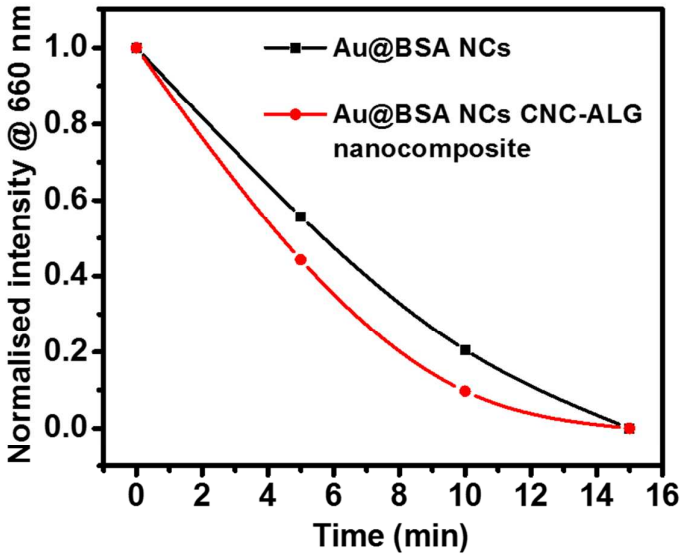


Figure S13. Normalized fluorescence intensities of Au@BSA NCs and Au@BSA NCs CNC-ALG nanocomposite after binding with Hg^{2+} ions at regular time intervals.