

Supporting Information

Copper Quantum Clusters in Protein Matrix: Potential Sensor of Pb^{2+} ion

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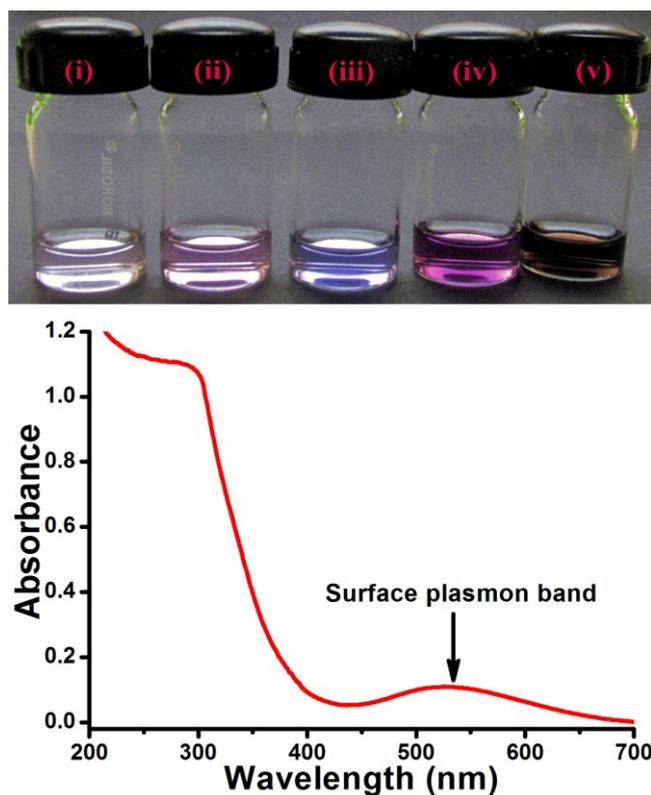


Figure S1: Photographs of the Cu_{QC}@ BSA under visible light keeping BSA concentration same i.e., 15 mg/ml. The final metal ion concentrations are (i) 0.57 mM, (ii) 1.43 mM, (iii) 2.86 mM, (iv) 5.71 mM and (v) 8.33 mM. It can be observed that as a function of metal ion concentration, different colors are observed. However, at higher concentration nanoparticles are seen. Absorbance spectrum of Cu_{QC}@ BSA with final metal ion concentration of 8.33 mM is shown in the lower panel. Surface plasmon band of the Cu nanoparticles are clearly seen from the spectrum.

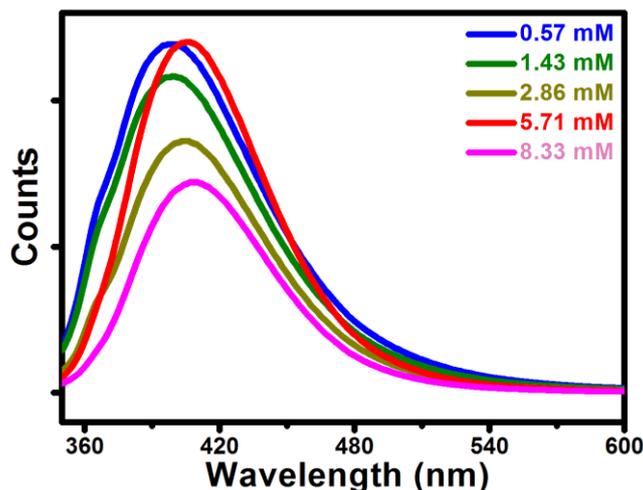


Figure S2: Photoluminescence spectrum ($\lambda_{ex} = 325$ nm) for Cu_{QC}@ BSA keeping BSA concentration same i.e., 15 mg/ml. The final metal ion concentrations are (i) 0.57 mM, (ii) 1.43 mM, (iii) 2.86 mM, (iv) 5.71 mM and (v) 8.33 mM. Results indicate that emission of clusters depends on various metal ion concentrations, and at higher metal ion concentration diminution of emission occurs as nanoparticles are formed.

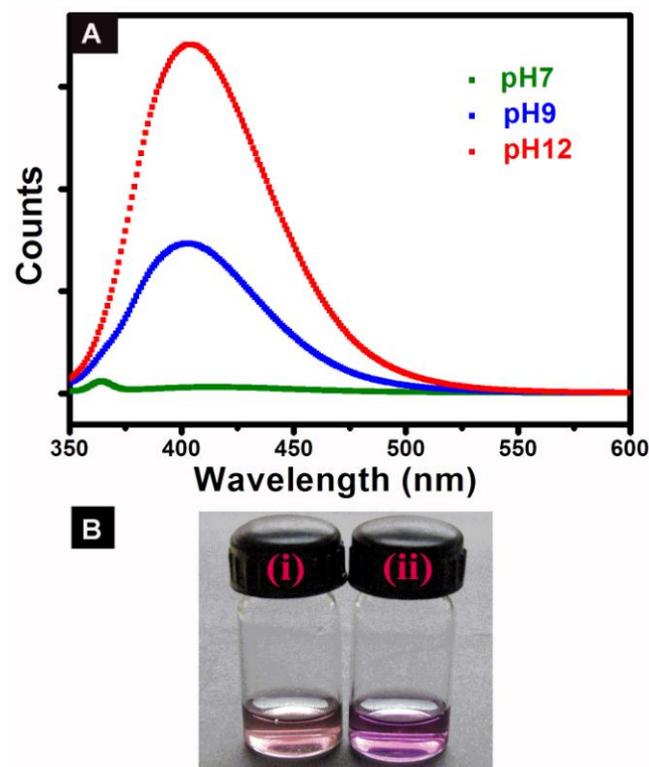


Figure S3: Photoluminescence spectrum ($\lambda_{\text{ex}} = 325 \text{ nm}$) for Cu_{QC}@ BSA synthesized at different pHs. Photographs under visible light for the Cu_{QC}@ BSA synthesized at (i) pH~9 & (ii) pH~12. At pH~7 no Cu QCs are formed as it can be seen from the panel A of figureS3.

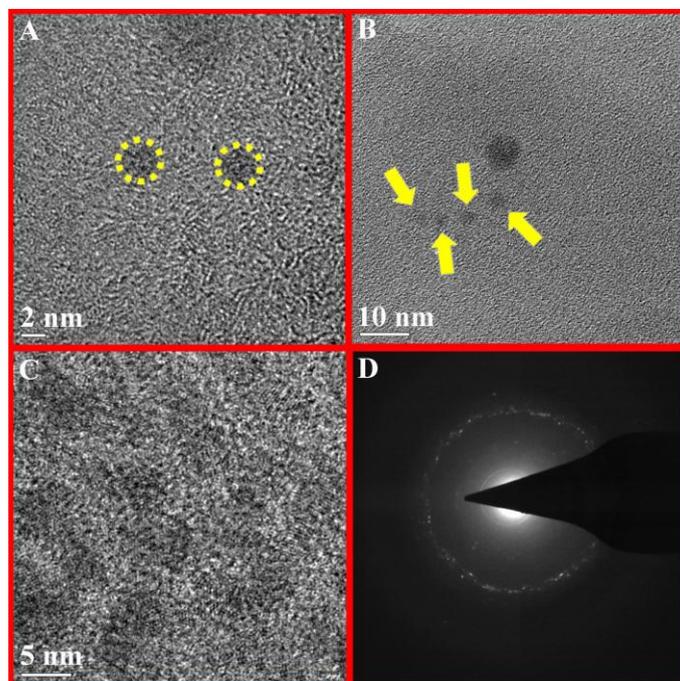


Figure S4: (A), (B) & (C) HRTEM images of Cu_{QC}@ BSA after being exposed to the strong electronic beam. Nanoparticles are marked with yellow circles (A) and arrows (B). (D) Selected area electron diffraction (SAED) pattern showing the crystalline structure of Cu_{QC}@ BSA.

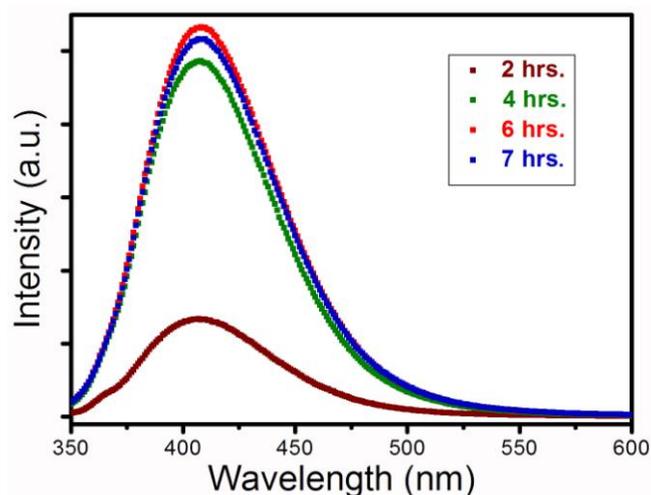


Figure S5: Time evolution of the photoluminescence spectrum ($\lambda_{\text{ex}} = 325 \text{ nm}$) for $\text{Cu}_{\text{QC}}@ \text{BSA}$ during the synthesis of cluster.

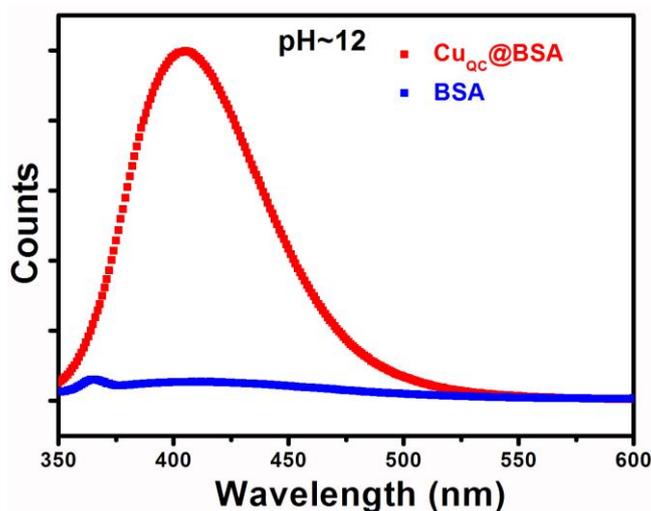


Figure S6: Photoluminescence spectrum ($\lambda_{\text{ex}} = 325 \text{ nm}$) of $\text{Cu}_{\text{QC}}@ \text{BSA}$ (red) and BSA (blue) at $\text{pH} \sim 12$. All the parameters are same in both cases.

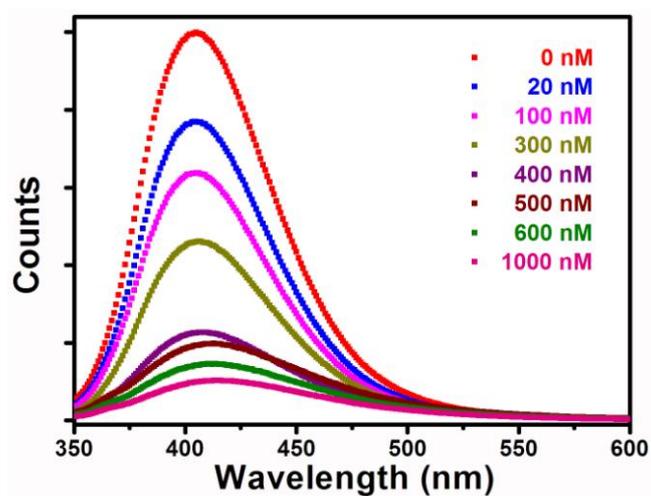


Figure S7: Photoluminescence spectrum ($\lambda_{\text{ex}} = 325 \text{ nm}$) of $\text{Cu}_{\text{QC}}@ \text{BSA}$ with the addition of H_2O_2 (0-1000 nM).

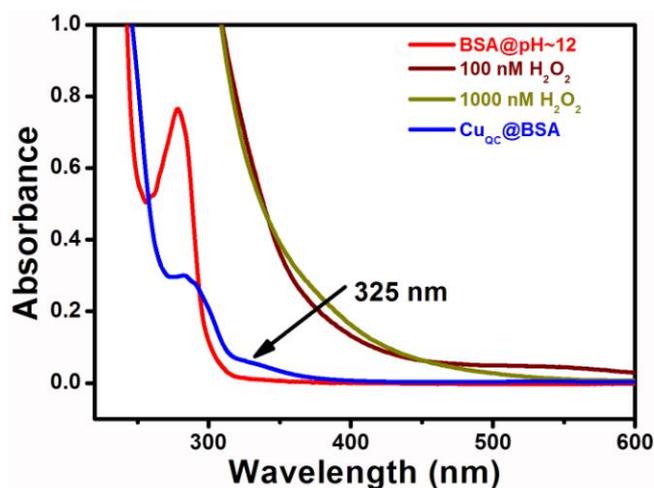


Figure S8: Absorbance of copper cluster after addition of H_2O_2 . The result indicates that the prominent absorption shoulder at 325 nm in $\text{Cu}_{\text{QC}}@ \text{BSA}$ (blue). The spectrum of $\text{Cu}_{\text{QC}}@ \text{BSA}$ in presence of H_2O_2 , does not show clear disappearance of the absorption shoulder at 325 nm because of the very large absorption at this wavelength-region after addition of H_2O_2 .

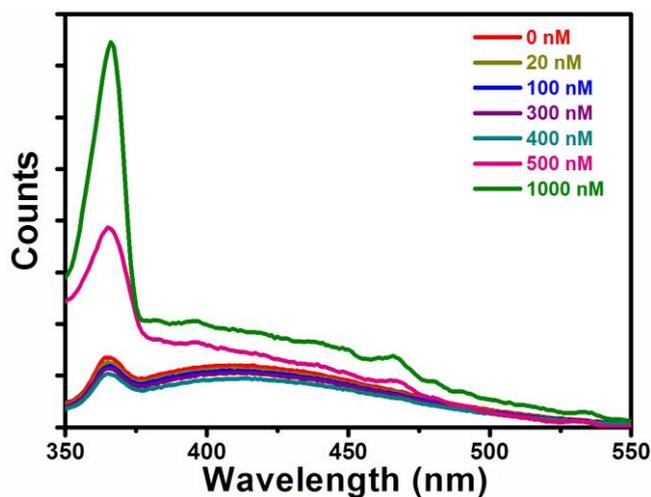


Figure S9: Photoluminescence spectra ($\lambda_{\text{ex}} = 325 \text{ nm}$) of BSA with the addition of H_2O_2 (0-1000 nM). A Raman peak at 363 nm is clearly visible from the spectra.

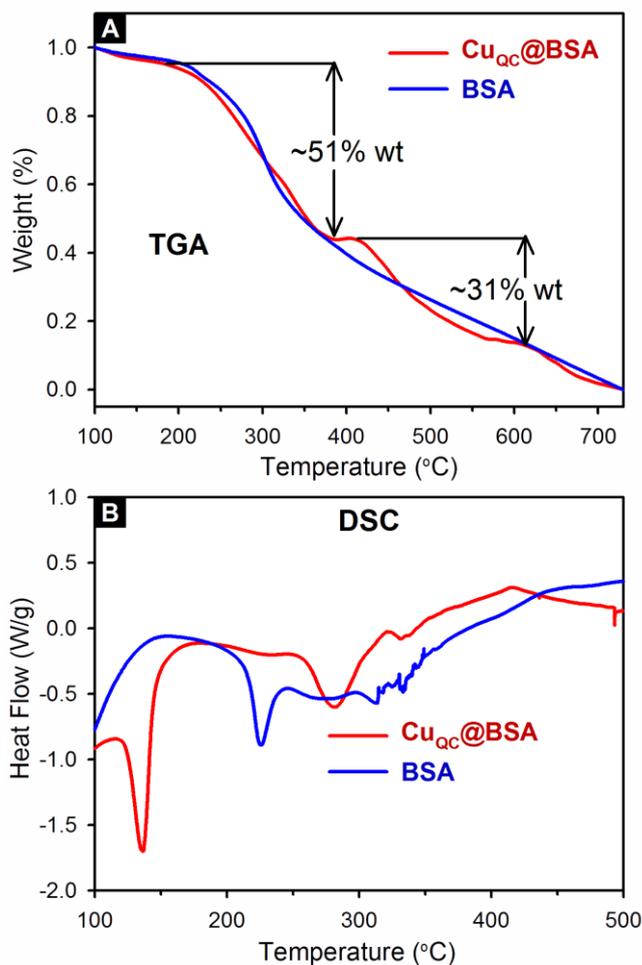


Figure S10: (A) Thermo gravimetric analysis (TGA) of Cu_{QC}@ BSA (red) and BSA (blue) performed under N₂. Mass loss below 150 °C is attributed to water. Protein mass loss is seen only above 200 °C. (B) This is also reflected in the DSC spectra.

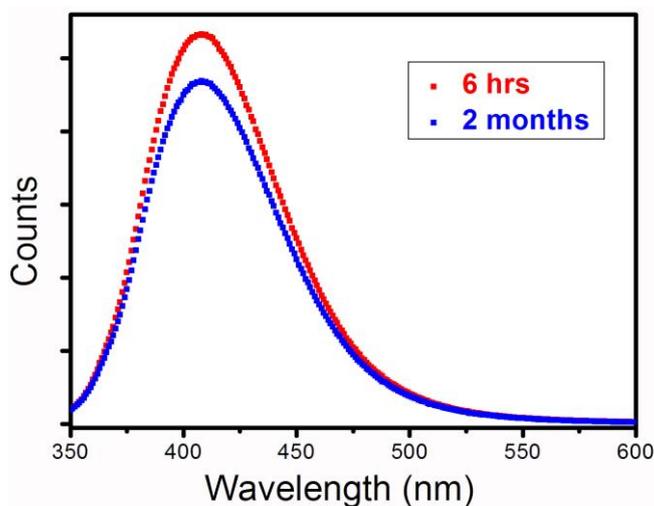


Figure S11: Photoluminescence spectra of Cu_{QC}@ BSA at different time indicating the high stability of clusters.

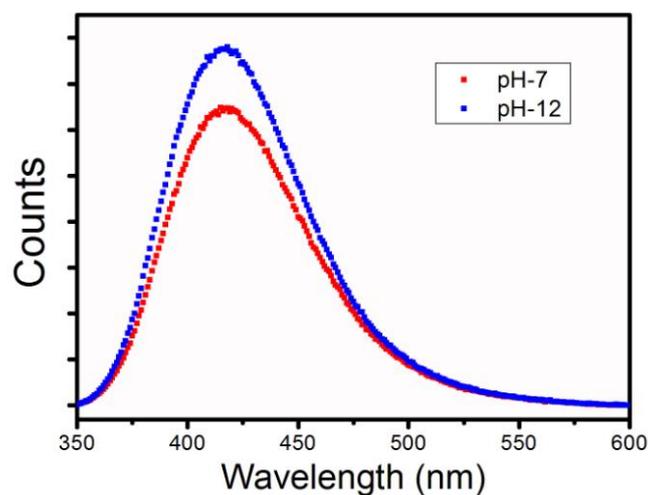


Figure S12: Photoluminescence spectra of Cu_{QC}@ BSA at different pH indicate the high stability of the clusters.

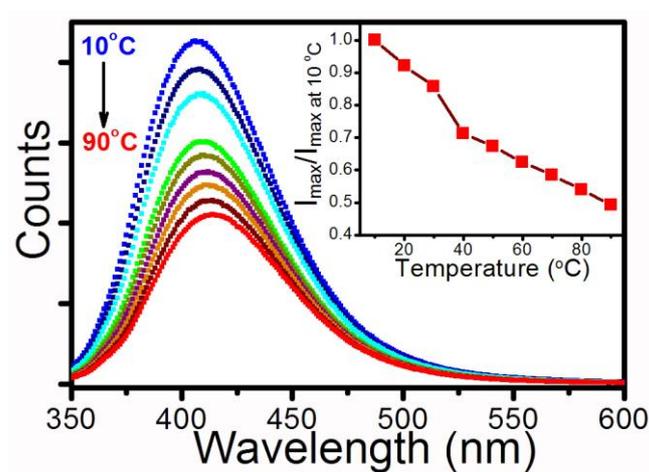


Figure S13: Steady-state Photoluminescence spectra of Cu_{QC}@ BSA recorded at different temperatures. Inset: Plot of temperature versus maximum fluorescence intensity of the cluster with respect to I_{\max} at 10 °C.

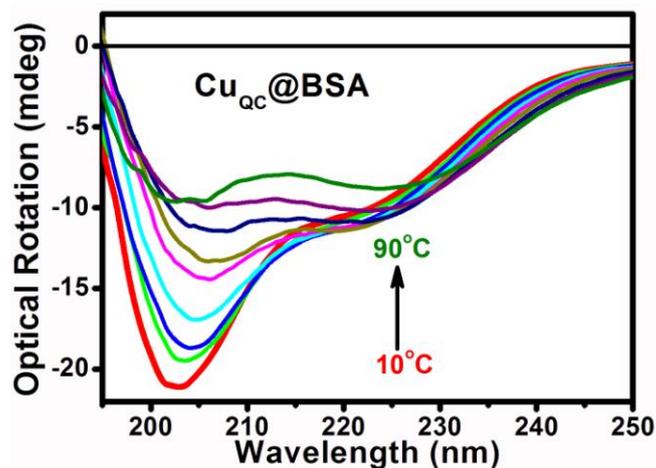


Figure S14: Circular Dichroism spectra of Cu_{QC}@ BSA recorded at different temperatures indicating the perturbation of the secondary structure of the protein.

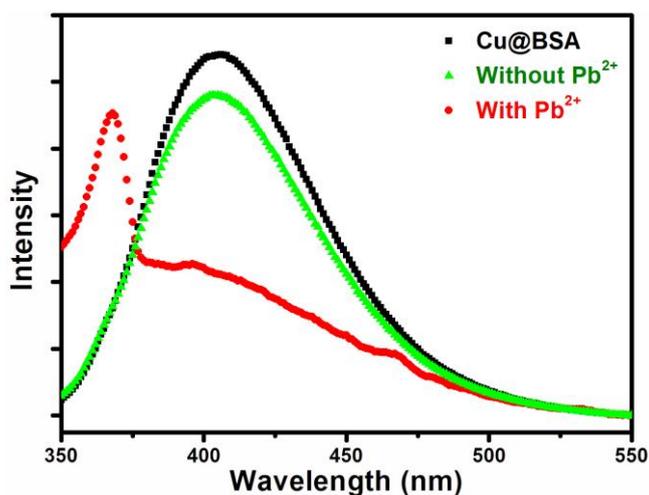


Figure S15: Steady-state Photoluminescence spectra of Cu_{QC}@ BSA (black), Cu_{QC}@ BSA with metal ions without Pb²⁺ ion (green) and Cu_{QC}@ BSA with metal ions as well as Pb²⁺ ion (red). A clear Raman peak at 363 nm is clearly visible from the spectrum.