Electronic Supplementary Information

Photoinduced 2-way Electron Transfer in Composites of Metal Nanoclusters and Semiconductor Quantum Dots

Navendu Mondal, Sneha Paul and Anunay Samanta*

School of Chemistry, University of Hyderabad, Hyderabad-500 046, India

*Corresponding author: anunay@uohyd.ac.in

Figure S1. Absorption spectra of CdTe QDs with addition of Au$_{25}$(BSA).

Figure S2. Emission spectra ($\lambda_{ex} =$ 550 nm) of CdTe QDs with addition of Au$_{25}$(BSA).

Figure S3. Emission decay profiles of CDTe QDs with increase in concentration of Au$_{25}$(BSA).

Figure S4. (A) Bleach formation kinetics of QDs in presence and absence of Au$_{25}$(BSA), (B) TA spectrum of Au$_{25}$(BSA) alone at 480 nm excitation.

Figure S5. Absorption and emission spectra of QDs with addition of Au$_{10}$(His)

Figure S6. Absorption and emission spectra of QDs with addition of Au$_{25}$(GSH)

Figure S7. Comparison of bleach recovery kinetics of QDs with addition of Au$_{25}$(GSH) and Au$_{10}$(His).

Table S1. PL decay parameters of QDs with increase in concentration of Au$_{25}$(BSA).

Table S2. Bleach recovery parameters of QDs for all the three nanocomposites.
Figure S1. Changes in the absorption spectra of CdTe QDs (0.2 μM) on addition of Au$_{25}$(BSA) (0 to 10 μM)

Figure S2. PL spectra ($\lambda_{ex} = 550$ nm) of the QDs as a function of the concentration of Au$_{25}$(BSA) (0, 2.5, 5, 7.5, 10, 12.5 μM)
Figure S3. Emission ($\lambda_{\text{ex}} = 440$ nm) decay profiles of CdTe QDs (0.2 $\mu$M) monitored at 609 nm for different concentration of Au$_{25}$(BSA) (0, 3.3, 6.6, 10 $\mu$M) at. Black dashed line represents the instrument response function.

Figure S4. (A) Bleach formation dynamics (at 585 nm) of the QDs in the absence and presence of Au$_{25}$(BSA), and (B) Transient absorption spectra of Au$_{25}$(BSA) NC (0.3 mM) in aqueous medium at 480 nm excitation.
Figure S5. Absorption (A) and photoluminescence ($\lambda_{\text{ex}} = 440$ nm) (B) spectra of CdTe QDs (0.45 $\mu$M) with increase in concentration of Au$_{10}$ (His) (0, 4, 6, 8 $\mu$M).

Figure S6. Absorption (A) and photoluminescence ($\lambda_{\text{ex}} = 440$ nm) (B) spectra of CdTe QDs (0.35 $\mu$M) with increase in concentration of Au$_{25}$ (GSH) (0, 7.5, 25, 45 $\mu$M).
Figure S7. Comparison of the bleach recovery kinetics monitored at 585 nm of (A) QDs and QD-Au_{25}(GSH), and (B) QDs and QDs-Au_{10}(His) (concentration of Au NC was used 0.3 mM in both cases) (λ_{ex} = 480 nm).

Table S1. PL decay parameters of the CdTe QDs as a function of the concentration of Au_{25}(BSA).

<table>
<thead>
<tr>
<th>Au_{25}(BSA) [µM]</th>
<th>( \tau_1(a_1) ) [ns]</th>
<th>( \tau_2(a_2) ) [ns]</th>
<th>( \tau_3(a_3) ) [ns]</th>
<th>(&lt;\tau_{\text{int}}&gt;^\dagger) [ns]</th>
<th>(&lt;\tau_{\text{amp}}&gt;^\ddagger) [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.03 (0.18)</td>
<td>24.50 (0.12)</td>
<td>0.44 (0.69)</td>
<td>18.88</td>
<td>4.01</td>
</tr>
<tr>
<td>3.3</td>
<td>3.07 (0.12)</td>
<td>22.80 (0.06)</td>
<td>0.34 (0.82)</td>
<td>15.96</td>
<td>2.00</td>
</tr>
<tr>
<td>6.6</td>
<td>2.59 (0.10)</td>
<td>22.30 (0.05)</td>
<td>0.29 (0.85)</td>
<td>15.42</td>
<td>1.53</td>
</tr>
<tr>
<td>10</td>
<td>2.34 (0.09)</td>
<td>21.20 (0.04)</td>
<td>0.29 (0.87)</td>
<td>13.91</td>
<td>1.27</td>
</tr>
</tbody>
</table>

\(^\dagger\) \(<\tau_{\text{int}}>= (a_1\tau_1^2+a_2\tau_2^2+a_3\tau_3^2)/(a_1\tau_1+a_2\tau_2+a_3\tau_3), \pm \text{ and } ^\ddagger\) \(<\tau_{\text{amp}}>= (a_1\tau_1+a_2\tau_2+a_3\tau_3)/(a_1+a_2+a_3)\)

\(^\ddagger\) \(<\tau> = \pm 5\%\)
Table S2. Bleach recovery kinetic parameters of the QDs for the three nanocomposites.

<table>
<thead>
<tr>
<th>Quencher</th>
<th>$\tau_1(a_1)$ fs</th>
<th>Decay components</th>
<th>$\tau_2(a_2)$ ps</th>
<th>$\tau_3(a_3)$ ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_{25}$(BSA)</td>
<td>206±31 (8%)</td>
<td>2.05±0.06 (74%)</td>
<td>24.5±1.5 (18%)</td>
<td></td>
</tr>
<tr>
<td>Au$_{10}$(His)</td>
<td>1300±500 (30%)</td>
<td>5.75±1.3 (30%)</td>
<td>50±4.1 (40%)</td>
<td></td>
</tr>
<tr>
<td>Au$_{25}$(GSH)</td>
<td>---</td>
<td>3.34±0.09 (60%)</td>
<td>53.7±2.2 (40%)</td>
<td></td>
</tr>
</tbody>
</table>

Bleach recovery in QD-Au$_{25}$(GSH) could not be fitted to a tri-exponential decay function like in the case of other two nanocomposites. Therefore, as the bleach recovery kinetics of this nanocomposite is very similar at shorter time-scale with the QD-Au$_{10}$(His) nanocomposite, indicating very similar electron transfer time in both cases.