Chapter 5

Investigation of Dopant Energetics and the Tuning of Charge Carrier Dynamics in Cu-doped CdSe Nanocrystals

5.1. Introduction

As mentioned in the introduction Cu-doped NCs are important as luminescent phosphors and understanding the basic photo-physics is required to attain better applications. In this chapter we report the electrochemical investigation of Cu-dopant energetics and the effect of Cu-doping on the charge carrier dynamics of CdSe NCs. Electrochemical measurement on doped NCs where the signal due to an electroactive dopant is traced to determine the energetics of the dopant relative to the NC host is rare. Electrochemical measurements based on cyclic voltammetry (CV) are one of the simplest ways to determine the band-edge parameters and trap along with mid-gap state energetics of NCs.\(^{14}\) Considering this the present study presents cyclic voltammetric measurements on Cu-doped CdSe NCs explicitly determining the dopant energy level and thus correlating the large Stokes shift and dopant emission energy with band-edge energies of CdSe NC host. Previously, few attempts were made for bulk materials in case of bulk ZnSe, CdSe, CdS, and CdTe crystals and in CdSe NCs through sophisticated ultraviolet photoelectron spectroscopy (UPS), however, determination of energy levels for the Cu-dopant in the NC host through electrochemical technique still remains elusive.\(^{5-9}\) Recently Fuhr et al. have determined the Cu-related defect state energy in CIS NCs through electrochemistry correlated with the PLE Stokes shift.\(^{10}\)

Moreover, the role of Cu dopant in affecting the exciton dynamics in ultrafast timescale for Cu-doped II-VI NCs has not been elucidated in detail so far. Earlier Gul et al. have reported charge carrier dynamics in nanosecond timescale for Cu-doped ZnSe NCs through measuring the effect of Cu-doping in the luminescence decay of the band-edge emission.\(^{11}\) However, to fully explore the opto-electronic properties the exciton dynamics needs to be investigated in picosecond to femtosecond timescale. The influence of Cu in the exciton dynamics will be particularly interesting to investigate as doping Cu in CdSe introduces states closer to the valence band (VB) which selectively localizes the hole making the electron and hole act differently.

To shed light on the fundamental aspects of energetics and dynamics Cu\(^+\)-doped CdSe NCs were synthesized in the low doping regime using colloidal hot injection
method with long lived red shifted Cu-related emission. Distinct oxidation and reduction features were identified in the cyclic voltammogram due to electroactive Cu-dopant along with the CdSe band-edge peaks. The Cu level was determined to be at \( \sim 5.09 \) V in the CdSe NC host which is very close to values reported for Cu in the bulk semiconductors.\(^{30-33}\) The emission maxima of 1.63 eV for the Cu-related emission was nicely correlated with the difference between conduction band-edge of CdSe NC and Cu-level. Moreover, the shape of the TA spectra remains unaltered upon Cu-doping as the low Cu concentration did not severely affect the electronic structure of the CdSe NC. Interestingly, Auger assisted electron cooling gets slower with increase in Cu concentration which can be explained in terms of decoupling the electronic wave function from hole since the Cu-dopant acts as an intrinsic hole trapping center. If the hole is quenched at the first place with amino phenols the dopant emission gets quenched, however, once the hole gets transferred to Cu\(^{+}\) activating it to Cu\(^{2+}\), then the Cu has a strong affinity for electrons and electron transfer to external electron quencher such as nitrophenols gets restricted.

### 5.2. Results and Discussion

#### 5.2.1. Characterization of NCs and Steady State Optical Studies

Cu doped CdSe NCs (termed as Cu-CdSe) were synthesized by following previously reported procedure with required modifications.\(^{12-14}\) Two different doping concentrations of Cu were obtained by varying the amount of Cu-precursor; Cu-CdSe(1) and Cu-CdSe(2) with 0.66\% and 2\% of Cu as determined from elemental analysis through inductively coupled plasma mass spectrometry (ICP-MS). This translates to \( \sim 1.6 \) and \( \sim 5.3 \) Cu dopant atom per NC on average for the size of the NCs (discussed below) which is on the low doping regime where there will be no interaction between the dopants. Undoped CdSe NCs were also synthesized under similar conditions as a reference sample. The size of the NCs were calculated from the first excitonic maxima of the NCs using the CdSe sizing curve and determined 2.91 and 3.12 nm for Cu-CdSe(1) and Cu-CdSe(2), respectively.\(^{15}\) The size determined from transmission electron micrographs of Cu-CdSe(2) is 3.14±0.15 nm as shown in Figure 5.1 (A) in close
agreement with the size determined from the sizing curve of CdSe. Now, for Cu-CdSe(1), the NC volume \( V = \frac{4}{3} \pi r^3 = \frac{4}{3} \times 3.14 \times (1.46 \times 10^{-7})^3 \) is \( 1.30 \times 10^{-20} \text{ cm}^3 \). The mass of CdSe is \( 1.30 \times 10^{-20} \times 5.82 = 7.58 \times 10^{-20} \text{ gm} \) (density of CdSe = 5.82 gm/cm\(^3\)) which gives moles of CdSe = \( 7.58 \times 10^{-20} / 191 \times 3.97 \times 10^{-22} \) (molar mass of CdSe = 191 gm/mole). Therefore, number of Cd/NC = \( 3.97 \times 10^{-22} \times 6.023 \times 10^{23} \) = 239.14. As Cd: Cu ratio in Cu-CdSe(1) is 0.0066, the number of Cu/NC = 239.14 \times 0.0066 = 1.58. Similarly the number of Cu/NC in Cu-CdSe(2) can be calculated as \( \sim 5.3 \).

![Image of TEM and EPR spectra]

**Figure 5.1.** (A) TEM of Cu-CdSe(2) showing monodisperse spherical NCs with size 3.14±0.15 nm. (B) EPR spectra of Cu-CdSe(2). No Cu\(^{2+}\) characteristic EPR signal is present here. (C) XRD spectra of Cu-CdSe(2) depicting a zinc blend structure.

EPR measurement suggests presence of Cu\(^{2+}\) as paramagnetic signal originating from Cu\(^{2+}\) was absent (Figure 5.1(B)). Therefore, we can conclude that the Cu(II)-stearate precursor gets reduced in presence of TOP under nitrogen atmosphere. EPR has been extensively used as an evidence for the presence of Cu\(^{2+}\) in doped NC for similar Cu-doping concentrations. The X-ray diffraction (XRD) pattern also shown in Figure 5.1(C) indicates zinc blend structure formation in accord with literature.

Figure 5.2 shows the absorption and emission spectra of Cu-CdSe(2) NCs in comparison with undoped CdSe. In undoped CdSe the first excitonic absorption peak (Figure 5.2a) appears at \( \sim 550 \text{ nm} \) (2.25 eV) with a band-edge emission maxima (Figure 5.2b) at \( \sim 575 \text{ nm} \) (2.16 eV). On the other hand, the doped NCs have a sharp first excitonic absorption (Figure 5.2c) at \( \sim 555 \text{ nm} \) (2.23 eV) with a broad red-shifted...
emission (Figure 5.2d) centered at ~760 nm (1.63 eV) along with a weak band-edge emission (Figure 5.2e) maxima at ~ 570 nm (2.18eV). The excitation spectra measured for 760 nm emission closely matches with the absorption spectra (Figure 5.2f) implying the broad red shifted emission involves CdSe band-gap transition. This broad emission has been attributed to the metal to ligand (conduction band) charge transfer transition.

![Figure 5.2](image)

**Figure 5.2.** UV-vis absorption (a), emission (b) of undoped CdSe. UV-vis absorption (c), Cu-related emission (d), band-edge emission after 10X zoom (e) and excitation spectra measured at dopant emission maxima (f) for Cu-CdSe(2) NCs. The absorption 'foot' due to direct excitation of ML<sub>CB</sub>CT band in Cu-CdSe(2) is shown separately. (g) Cu-related emission spectra in presence of dodecanethiol (DDT). The emission gets quenched in presence of DDT suggesting the dopant in +1 oxidation state (Cu<sup>+</sup>).<sup>22</sup> If Cu was in +2 state the emission should have increased as pointed out by Viswanatha *et al.*<sup>22</sup> (Inset) Emission decay traces for band-edge emission in undoped CdSe (h). In case of Cu-CdSe(2) the decay traces for Cu-related emission at 760 nm (i) and band-edge emission at 570 nm (j).
(ML\textsubscript{CB}CT) involving the recombination of conduction band (CB) electron to the Cu-localized hole. The exact mechanism of this transition depends on the oxidation state of Cu.\textsuperscript{18,19,23-26} This broad emission involving Cu states gets quenched in presence of dodecanethiol (DDT) further suggesting presence of Cu\textsuperscript{*} as a dopant (Figure 5.2g).\textsuperscript{22} Moreover, the broad weaker absorption 'foot' tailing to longer wavelengths after the first excitonic IS peak (Figure 5.2c) corresponding to direct photoexcitation of the ML\textsubscript{CB}CT absorption band is also a characteristic feature of Cu\textsuperscript{+} doped CdSe NCs.\textsuperscript{13,27}

For Cu\textsuperscript{2+} (d\textsuperscript{9} system) the CB electron directly recombines with the optically active hole in Cu resulting the Cu-related emission. Conversely, Cu\textsuperscript{+} doping represents a filled shell d\textsuperscript{10} system which needs to be oxidized in order to accept electrons. After photoexcitation electron-hole pair is generated in the CdSe host. The hole from the VB rapidly (in ps timescale) localizes in Cu\textsuperscript{+} oxidizing it to Cu\textsuperscript{2+} followed by recombination of an electron from CB with the hole in the Cu\textsuperscript{2+}.\textsuperscript{12,19} This converts the Cu\textsuperscript{2+} again to the original Cu\textsuperscript{+} center capable of accepting the hole.

![Figure 5.3. Luminescence up-conversion decay traces of (a) CdSe and (b) Cu-CdSe(2) monitored at 570 nm. The NCs were excited at 400nm. The traces for CdSe can be fitted as 5 ps (59%), 35 ps (26%) and > 100ps (15%). The traces for Cu-CdSe(2) can be fitted as 600fs (45%), 5 ps (38%), 30 ps (12%) and >100ps (5%).](image)
5.2.2. Time Resolved Emission Experiments

Since in the Cu-doped CdSe the CB electron delocalized over the whole NC recombines with a hole localized in the Cu-center the Cu-emission has a very long lifetime (300-500 ns) compared to CdSe band-edge emission.\textsuperscript{8,13,19,22,24} In our case the exciton lifetime ($\tau_{\text{PL}}$) of pure CdSe (Figure 5.2h) was found to be 12.1 ns (1.1 ns, 35%; 7.8 ns, 36%; 30.4 ns, 29%) whereas the $\tau_{\text{PL}}$ at 760 nm for Cu-CdSe(2) was single exponential (Figure 5.2i) having $\tau_{\text{PL}}$ of $\sim$350 ns which is in accord with the literature mentioned above. Interestingly, the weak band edge emission in the doped NC gets quenched (Figure 5.2j) with $\tau_{\text{PL}}$ of 0.69 ns (0.27 ns, 84% and 2.98 ns, 16%) due to fast hole localization in Cu from the VB of CdSe. To find out the hole transfer time accurately luminescence up-conversion measurements were carried out monitoring the PL decay at 570 nm as represented in Figure 5.3. The appearance of an additional fast $\sim$600 fs component for Cu-CdSe(2) can be attributed to hole transfer from VB of CdSe to Cu-center. This time scale is analogous to the flattening distortion of $[\text{Cu(dmphen)}_2]^+$ associated with the hole transfer from ligand $\pi^*$ orbital to Cu$^+$.\textsuperscript{28,29}

![Figure 5.4](image.png)

**Figure 5.4.** (A) Cyclic voltammogram of (a) CdSe and (b) Cu-CdSe(1) NCs. (Inset) (A) UV-vis absorption (d), emission (e) and excitation spectra (f) measured at dopant
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emission maxima for Cu-CdSe(1) NCs. (B) Cyclic voltammograms of (a) CdSe and (g) Cu-CdSe(2) NCs. The arrows denote the anodic and cathodic current, respectively due to the Cu dopant. The red dotted arrow denotes the VB-edge peak.

5.2.3. Cyclic Voltammetric Experiments

As Cu is well-known electro active material we investigated if Cu states have any role to play in cyclic voltammetric measurements. We compare both the Cu-CdSe NCs and undoped CdSe of similar size as depicted in Figure 5.4. For CdSe prominent oxidation (anodic) and reduction (cathodic) peaks are observed at -5.54 V and -3.34 V (vs. local vacuum), respectively (Table 5.1). For Cu-CdSe(1) the anodic and cathodic peaks are at very similar positions of -5.52 V and -3.28 V, respectively. Similarly for Cu-CdSe(2) the anodic and cathodic peaks are observed at -5.53 V and -3.38 V, respectively. The anodic peak potential corresponds to the removal of electron from the VB-edge and the cathodic peak potential represents addition of electron to the CB-edge of NCs.

Table 5.1. The conduction band edge, valence band edge of CdSe, Cu-CdSe(1) and Cu-CdSe(2) NCs. For Cu-CdSe the Cu related values are also given. Values are with respect to both vacuum and NHE.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size (nm)</th>
<th>Optical band-gap (eV)</th>
<th>CB-edge (V) Vs. Vac/(Vs. NHE)</th>
<th>VB-edge (V) Vs. Vac/(Vs. NHE)</th>
<th>Quasi particle gap (V)</th>
<th>Cu-peak (V) Vs. Vac/Vs. NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe</td>
<td>3.0</td>
<td>2.25</td>
<td>-3.34/(-1.16)</td>
<td>-5.54/(1.04)</td>
<td>2.20</td>
<td>-</td>
</tr>
<tr>
<td>Cu-CdSe(1)</td>
<td>2.91</td>
<td>2.28</td>
<td>-3.28/(-1.22)</td>
<td>-5.52/(1.02)</td>
<td>2.24</td>
<td>~ -5.16/(0.66)</td>
</tr>
<tr>
<td>Cu-CdSe(2)</td>
<td>3.12</td>
<td>2.23</td>
<td>-3.38/(-1.12)</td>
<td>-5.53/(1.03)</td>
<td>2.15</td>
<td>~ -5.02/(0.52)</td>
</tr>
</tbody>
</table>

The determined VB and CB-edges for both CdSe and Cu-CdSe match reasonably well with literature as compared in Figure 5.5 (A). For Cu-CdSe(1) a prominent peak ~ -5.16
V was observed (Figure 5.4 (A)) which we attribute to Cu-oxidation peak as it was not present in the undoped CdSe. Therefore, the Cu-related state is located ~ 5.16 eV. Interestingly, Cu-CdSe(2) shows additional oxidation-reduction peaks corresponding to ~5.16 V and ~ 4.88 V, respectively in the CV data as shown in Figure 5.4 (B). The anodic peak at ~5.16 V and cathodic peak at ~4.88 V are again attributed to the oxidation of Cu$^+$ dopant to Cu$^{2+}$ followed by the subsequent reduction of Cu$^{2+}$ to Cu$^+$. Therefore, we attribute the Cu related level has energy of $(E_{\text{ox}} + E_{\text{red}})/2 = -5.02$ V (as tabulated in Table 5.1). The position and intensity of the band-edge peaks and Cu-related peaks are independent of scan direction (Figure 5.6) confirming credibility of the positions determined. The anodic oxidation peak due to Cu is more intense compared to the cathodic reduction peak mostly due to irreversibility of this redox cycle within the CdSe NC host. Comparing Cu-CdSe(1) and Cu-CdSe(2) the Cu-related state has energy ~ 5.09 eV on average. The UV-vis absorption spectra remain very similar before and after CV experiments suggesting negligible degradation of the NCs (Figure 5.6). The Cu-level in case of bulk semiconductors has been reported to be ~0.65 eV above the VB level of CdSe$^7$, ~ 0.68 eV above the VB in ZnSe$^6$, at ~0.15 eV over the VB in CdTe$^9$ and at 1.2 eV above the VB in CdS.$^5$

![Figure 5.5. (A) Comparison of CdSe CB and VB energy levels of CdSe and Cu-CdSe NCs synthesized in this study with present literatures.$^{2,4,30,31}$ (B) Compilation of literature for Cu-energy level in bulk semiconductors.$^{5-7,9}$]({})
The compilation of the literature values as depicted in Figure 5.5 (B) translates to ~5.1 (±0.05) eV for the Cu related atomic like state which is in very close agreement with the value determined from CV experiments. Our measured potential also match reasonably well with the reported redox potential of Cu$^{1+/2-}$ couple under different chemical environments$^{32-34}$ and with the recently reported energy of the Cu-defect state (~5.54 eV) in copper indium sulfide (CIS) NCs.$^{10}$ Moreover, the difference of 1.64 V between the CB edge (-3.38 V) and Cu-level (-5.02V) is in good agreement with the emission maxima of 1.63eV for Cu-related emission in Cu-CdSe(2). The Stokes shift of 0.6 eV is also correlative with the difference between VB-edge (-5.53 eV) and Cu-state (-5.02 eV) of 0.51 eV.

5.2.4. Ultrafast Transient Absorption Spectroscopy

TA measurement was utilized to reveal the role of Cu dopant in the exciton dynamics after exciting the NCs dispersed in chloroform with 400 nm pulsed laser (fwhm ~120fs) and probing the photo-induced changes in the absorption ($\Delta$OD=OD$_{\text{pump on}}$-OD$_{\text{pump off}}$) in the entire visible region.

![Figure 5.6. Cyclic voltammograms for Cu-CdSe(2) NCs with different scan directions. The scan directions are marked with an arrow. (Inset) UV-vis spectra before (c) and after](Image)

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(d) CV experiments (after 15 cycles). There is no obvious change in peak position in UV-Vis spectra of the NCs during CV experiments. This suggests there is no severe aggregation or change in NC size during CV and the NCs are stable during CV measurements.

Recently, Yang et al have utilized TAS to investigate the exciton dynamics in heavily Cu-doped III-V low band-gap InAs NCs where number of Cu per NC varies from 12 to 500 and the role of Cu is fundamentally different from II-VI semiconductors.\textsuperscript{35}

**Table 5.2.** Multiexponential fitting parameters for CdSe, CuCdSe(1) and Cu-CdSe(2) at their ground state bleach positions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavelength (nm)</th>
<th>$\tau_1^\text{e}$ (ps)</th>
<th>$\tau_2^\text{e}$ (ps)</th>
<th>$\tau_1'$ (ps)</th>
<th>$\tau_2'$ (ps)</th>
<th>$\tau_3'$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe</td>
<td>555</td>
<td>$&lt;1000fs$ (75%)</td>
<td>0.40 (25%)</td>
<td>20 (55%)</td>
<td>120 (21%)</td>
<td>$&gt;400$ (24%)</td>
</tr>
<tr>
<td>Cu-CdSe(1)</td>
<td>545</td>
<td>$&lt;1000fs$ (70%)</td>
<td>0.50 (30%)</td>
<td>20 (63%)</td>
<td>120 (17%)</td>
<td>$&gt;400$ (20%)</td>
</tr>
<tr>
<td>Cu-CdSe(2)</td>
<td>555</td>
<td>$&lt;1000fs$ (70%)</td>
<td>0.70 (30%)</td>
<td>20 (62%)</td>
<td>120 (20%)</td>
<td>$&gt;400$ (18%)</td>
</tr>
</tbody>
</table>

In that case the density of dopant related states increase near the CB-edge resulting an impurity sub-band at significantly higher doping concentrations. Here, we have employed TAS to reveal the role of Cu dopant on the exciton dynamics in II-VI CdSe NCs in the low doping regime where Cu-related single atomic alike state appear to be within the band gap of CdSe NC. Figure 5.7 (A) shows the TA spectra at different time intervals for CdSe and Cu doped CdSe NCs. The shape of the TA spectra is very similar for both doped and undoped NCs which are quite expected as the doping does not drastically change the shape of the linear absorption spectra. The bleach around $\sim555$ nm is the ground state 1S excitonic bleach attributed to $1S_\text{e}(e) - 1S_{3/2}(h)$ electronic transition. However, the bleach dynamics as depicted in Figure 5.7 (B) manifested by the bleach growth and recovery are quite different in the doped NCs. The bleach growth and
recovery kinetics essentially represents the population and de-population of the electron in the CB state for II-VI semiconductors and the contribution of hole in the bleach signal is insignificant due to higher density of hole states dispersing the hole population over many adjacent levels.\textsuperscript{36,37} For undoped CdSe the bleach growth has pulse width limited (<100fs, 75%) component along with a 0.4 ps (25%) component representing hot electron cooling time. The subsequent recovery of the 1S bleach is multi-exponential where the fast 20 ps (55%) and intermediate 120 ps (21%) components represent carrier trapping and the long >400ps component is due to radiative recombination and non-radiative electron trapping process. All the multi-exponential fitting parameters are tabulated in Table 5.2. As the NCs are excited with energy (400 nm, 3.1 eV) higher than the band-edge of the NCs (~555 nm, 2.23 eV), the photoexcited hot electron cools down to band-edge state (path q, figure 3C) within the first few picoseconds manifested by the bleach growth. In CdSe NCs the CB electronic states are apart by hundreds of meV which is quite large compared to typical phonon energies of ~20meV.\textsuperscript{36,38,39} Therefore, cooling of excited electron is unfavorable through phonons. Subsequently, an Auger assisted electron cooling mechanism was proposed and later experimentally verified where the electron cools down by transferring its energy to valence band hole which relaxes through dense phonon modes.\textsuperscript{38-40} This Auger-type energy transfer is strongly size dependent,\textsuperscript{41} however as we are using NCs of similar size (~3 nm) we can exclude any size dependence for the observed cooling process. Moreover, this electron-hole energy transfer process depends on the wave function overlap of both the charge carriers, if the charge carriers are decoupled the electron cooling time increases.\textsuperscript{39,40} Once decoupled from the hole the hot electron can relax through ligand vibrations. We also exclude the effect of surfactants or ligands in the relaxation process as both the doped and undoped NCs were synthesized under identical conditions. In Cu-doped NCs the Cu\textsuperscript{+} acts as a hole trapping center by capturing the hole and thus diminishing the electron-hole overlap integral. Therefore, as the amount of Cu increased we envision slower electron cooling of 0.5 ps in Cu-CdSe(1) and 0.7 ps in Cu-CdSe(2) due to decoupling of electron-hole wave functions.
Figure 5.7. (A) TA spectra for (a) CdSe, (b) Cu-CdSe(1) and (c) Cu-CdSe(2) upon 400nm photo-excitation. (B) Kinetics of ground state (1S) bleach recovery for (d) CdSe, (e) Cu-CdSe(1) and (f) Cu-CdSe(2). There is break between 2 ps and 2.01 ps in the figure. (C) Schematically depicting all the processes in undoped and Cu-doped CdSe. By monitoring at the 1S bleach position we are looking at the population and depopulation of the electron in the 1S state. Upon photo-excitation (p) electron-hole pair is generated and the electron resides in an upper excitonic state as the pump energy (3.1 eV) is higher than 1S transition (2.25 eV). The electron dissipates its excess energy through Auger assisted cooling (q) which depends on electron-hole wavefunction overlap. The electron cooling is depicted through the growth of the 1S bleach. Once the electron reaches 1S state the electron can depopulate (reflected by the recovery of the bleach) through radiative recombination (r) or trapping (s). In case of Cu-doped CdSe due to fast hole transfer (~600 fs) to Cu⁺ (t) the CB electron gets decoupled from hole resulting slower electron cooling. After hole transfer the oxidized Cu²⁺ accepts the CB electron to have the characteristic dopant PL. Therefore, the Cu creates an additional pathway (u) for electron depopulation from the 1S state, leading to marginally faster recovery of the 1S bleach. As
the electron transfer to Cu from CB is a slower process the recovery becomes slightly faster at longer time scale.

This is in contrast to heavily Cu-doped InAs NCs where the hot electron relaxation became faster with doping concentration as the impurity sub-band near the CB facilitates electron relaxation. In Cu doped CdSe, Cu introduces an atomic like state near the VB of CdSe and the cooling mechanism is fundamentally different as discussed above. Moreover, the recovery of IS bleach is marginally faster in case of Cu-CdSe NCs. In case of undoped CdSe the electron de-populates from the IS state though trapping and recombination with hole (path r and s, Figure 5.7 (C)). In Cu-doped CdSe the Cu-center upon capturing the hole recombines with the CB electron providing extra pathway for electron de-population (path u, figure 7C). As the electron (CB)-Cu$^{2+}$ recombination is a slow process, the recovery becomes marginally faster at longer time scales.

5.2.5. Effect of External Quencher Molecules on Exciton Dynamics

Following this the aim of the current investigation is to decipher the effect of Cu$^{+}$ center on the charge transfer dynamics to an external molecule with different anchoring groups. As stated earlier, Cu$^{+}$ oxidation state Cu acts as a hole trapping center located intrinsically within the NC. Therefore, it will be interesting to see the effect of external molecules either electron or hole acceptors on the dopant PL.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.8}
\caption{CV spectra of (A) ortho-Nitophenol and (B) ortho-Aminophenol. The arrows indicate the LUMO of ortho-nitrophenol and HOMO of ortho-aminophenol. (C) The band-edge positions and Cu-level of Cu-CdSe(2) as determined from CV experiments are...}
\end{figure}
shown. The HOMO-LUMO of ortho amino phenol (o-AP) and ortho nitro phenols (o-NP) relative to the vacuum as determined from cyclic voltammetry experiments in context of Cu-CdSe(2).

Two substituted phenols with electron rich amino functional group (o-AP) and with electron withdrawing nitro group at ortho position (o-NP) were chosen to elucidate their role in Cu-related emission. It is known in literature that depending on the energetics amino substituted molecules act as hole quenchers whereas nitro substituted molecules are typical electron quenchers for CdSe NCs.\textsuperscript{42-44} From CV measurements (Figure 5.8) we also found the lowest unoccupied molecular orbital (LUMO) of o-NP can energetically accept electrons, while the o-AP has suitable highest occupied molecular orbital (HOMO) level for capturing the hole from Cu-CdSe (Figure 5.8(C)). The absorption spectra of Cu-CdSe(2) remains similar upon addition of both the phenols as shown in Figure 5.9. Interestingly, for both the phenols the broad dopant emission gets quenched; however, the quenching propensity is quite different as depicted in the Stern-Volmer plots (Figure 5.9). Between o-AP and o-NP, the later is a weak quencher as higher concentrations of o-NP is required to have the same quenching effect. To further confirm this trend we have carried out time-resolved emission measurements (TCSPC) by monitoring the decay of Cu-related emission (∼760 nm) in presence of phenols which are shown in Figure 5.10 (A). For o-AP (0.25mM) the PL decay becomes tri-exponential (0.44 ns, 74%; 7.87 ns, 13% and 69.2 ns, 13%) with an initial fast component of 0.44 ns indicative of thermodynamically viable hole transfer process to the HOMO of the o-AP. On the other hand, for o-NP even at very high concentrations (2.5mM) the PL decay becomes bi-exponential (14.42 ns, 18% and >100ns, 82%) without any appreciable quenching. This excludes minimum possibility of electron transfer to the LUMO of o-NP. The multi-exponential fitting parameters for PL decay are shown in Table 5.3.
Figure 5.9. (A) Absorption of Cu-CdSe(2) in absence (a) and presence of (c) ortho-nitrophenol, (b) absorption spectra of pure ortho-nitrophenol. (B) Absorption of Cu-CdSe(2) in absence (a) and presence of (e) ortho-aminophenol, (d) absorption spectra of pure ortho-aminophenol. (C) Stern-Volmer plot (F₀/F vs. [Ligand]) for (f) ortho-aminophenol and (g) ortho-nitrophenol where F₀ and F are the PL intensity in absence and presence of quencher, respectively and [Ligand] is the quencher concentration. The ligand concentration is in log scale, therefore ortho-nitrophenol requires much higher concentration than ortho-aminophenol to have the same quenching effect.

Table 5.3. TCSPC Fitting Data for Cu-CdSe(2) in presence of ortho-aminophenol (o-AP) and ortho-nitrophenol (o-NP).

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Conc.(mM)</th>
<th>(\tau_1) (ns)</th>
<th>(a_1)</th>
<th>(\tau_2) (ns)</th>
<th>(a_2)</th>
<th>(\tau_3) (ns)</th>
<th>(a_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-AP</td>
<td>0.25</td>
<td>0.44</td>
<td>0.74</td>
<td>7.87</td>
<td>0.13</td>
<td>69.21</td>
<td>0.13</td>
</tr>
<tr>
<td>o-NP</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>14.42</td>
<td>0.18</td>
<td>&gt;100</td>
<td>0.82</td>
</tr>
</tbody>
</table>

To understand the paradoxical behavior of nitro and amino phenols to quench the dopant emission and confirm charge transfer processes TAS measurements were carried out in presence of phenols. In case of hole quenching ligands the ground state bleach recovery tends to become slower due to decoupling of hole from the electron. For o-AP we do envision slower bleach recovery indicating energetically favorable hole transfer from Cu-CdSe to HOMO of o-AP as shown in Figure 5.10 (B) (the multi-
exponential fitting parameters are tabulated in Table 5.4). On the other hand, in case of electron quenchers the bleach recovery becomes faster due to fast depopulation of the CB electron to the LUMO of quencher.\textsuperscript{43,45,47}

Interestingly, from TAS we do not find any evidence of electron transfer from doped CdSe to o-NP as the ground state bleach recovery remains similar in presence of o-NP as shown in Figure 5.10 (B). This surprising behavior can be explained considering the mechanism of Cu-related emission as depicted in figure 8(C). As the Cu dopant is in the +1 oxidation state hole localization in Cu is the primary step for dopant emission. Therefore, once the hole is captured through o-AP the dopant emission gets drastically quenched.

![Figure 5.10](image)

**Figure 5.10.** (A) PL decay traces for Cu-related emission and (B) Kinetics of the ground state bleach dynamics for (a) Cu-CdSe(2), in presence of (b) o-AP, (c) o-NP.

On the other hand, once hole gets localized on Cu$^{+1}$, the oxidized Cu$^{2+}$ develops strong affinity towards the CB electron. Therefore, in presence of electron quenching o-NP electron transfer does not occur. The quenching at higher concentrations occurs through dynamic quenching mechanism involving collision of the o-NP with NCs. Our findings are corroborative with Sarkar et al. who also observed very slow reduction of nitrophenol in Cu-doped ZnS NCs compared to undoped ZnS NCs.\textsuperscript{44} As the Cu-dopant strongly interacts with the exciton the transfer of CB electron to external quenchers get retarded.
Table 5.4. Fitting TA data for Cu-CdSe(2) at the ground state bleach position with different phenols.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_{i}$ (ps)</th>
<th>$\tau_{j}$ (ps)</th>
<th>$\tau_{k}$ (ps)</th>
<th>$\tau_{l}$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-AP</td>
<td>&lt;100fs (65%)</td>
<td>0.7 (35%)</td>
<td>20 (46%)</td>
<td>150 (27%)</td>
</tr>
<tr>
<td>o-NP</td>
<td>&lt;100fs (70%)</td>
<td>0.7 (30%)</td>
<td>20 (64%)</td>
<td>120 (17%)</td>
</tr>
</tbody>
</table>

Therefore, in our investigation we have addressed two important aspects of energetics and dynamics in Cu-doped CdSe NCs. The Cu-dopant related oxidation-reduction peaks in the cyclic voltammogram have been correlated to its exact energy level. Moreover, the role of Cu as an strong internal hole sensitizer has been established through TAS where electron cooling slowed down 1.75 times in presence of 2% Cu. The hindrance of electron transfer to external electron quenchers further elucidates the role of Cu in the charge transfer dynamics.

5.3. Conclusions

In summary, Cu-doped CdSe NCs were synthesized and the dopant was characterized as Cu$^+$. The broad dopant related emission with large Stokes shift was attributed to hole localization from the VB in the Cu$^+$ state followed by capture of the CB electron as established in literature. The optical properties were compared with the CV measurements where additional oxidation-reduction peaks arise due to the electroactive Cu dopant electrochemically confirming the Cu energy level within the doped NC. The Cu related red shifted emission energy was well correlated with the Cu level determined from CV measurements. Moreover, the hot electron cooling time to the $1S_e$ state slows down with increase in Cu concentration due to localization of the hole in the Cu eventually reducing the electron-hole wave function overlap. In presence of external hole accepters (aminophenols) the dopant emission gets quenched due to hole transfer, however electron transfer was not operative with electron accepters (nitrophenols). This
surprising observation was attributed to the mechanism of Cu emission with Cu$^+$ as a dopant and strong affinity of Cu towards electron once it is oxidized to Cu$^{2+}$ with the VB hole. Thus our study provides fundamental information about the electrochemistry and exciton dynamics of Cu-doped CdSe NCs which pave the way for better understanding of the dopant-exciton interaction.

5.4. References


(33) Sanz, L.; Palma, J.; García-Quismondo, E.; Anderson, M. J. *Power Sources* 2013, 224, 278.


