Electronic Supplementary Information

Nanoscale Connectivity in a TiO$_2$/CdSe Quantum Dots/Functionalized Graphene Oxide Nanosheets/Au Nanoparticles Composite for Enhanced Photoelectrochemical Solar Cell Performance

Remya Narayanan, Melepurath Deepa, and Avanish Kumar Srivastava

Figure S1. (a) EDS plot and (b) Raman spectrum of ionic liquid functionalized graphene oxide.

The elemental composition of ionic liquid functionalized graphene oxide (FGO), in terms of atomic percentages are as follows: C: 43.8 %, N: 28.2 %, O: 14.7 %, F: 13.1 % and S: 0.3 %. The EDS (energy dispersive X-ray analysis) pattern of FGO is shown in Figure S1a. It is apparent that the ionic liquid 1-Butyl-3-methyl imidazolinium trifluoromethanesulfonate is incorporated between the graphene oxide nanosheets, for otherwise signals due to N, S and F would not have arisen.
The ionic liquid: 1-butyl-3-methyl-imidazolium (BMIM) trifluoromethanesulfonate, is mixed with water and used for exfoliating graphite rods. As suggested previously, for another water soluble tetrafluoroborate based ionic liquid, here also, upon application of dc potential (E = +15 V), at the anodic graphite rod, water molecules easily undergo oxidation to yield free radicals which, in turn lead to the formation of oxygen containing functional groups, on the graphene nanosheets, as shown through equation (1).

\[(C)_m + H-O\cdot\cdot\cdot H \rightarrow C_{m-1}C-OH + e^- + H^+ \text{ (at the anode)} \] (1)

These nanosheets are exfoliated from the anodic rod, upon action of water and potential, which act cumulatively to remove layers of graphene that collapse into the solution. Thus the graphene generated in the ionic liquid medium also has an oxidized graphene component. Simultaneously, at the cathode, the imidazolium ions can also undergo reduction, and form free radicals which, are easily entrapped by the graphene nanosheets generated in solution from the anode, as shown through equations (2) and (3). Such a mechanism has been proposed earlier for graphene functionalized with di-alkyl-imidazolium tetrafluoroborate / hexafluorophosphate.2

\[(BMIM)^+ + e^- \rightarrow (BMIM)^* \text{ (at the cathode)} \] (2)

\[(BMIM)^* + (C)_m \rightarrow (C)_m-(BMIM) \text{ (in the solution)} \] (3)

Non-covalent or \(\pi-\pi\) interactions can also form between the imidazolium cation and the graphene nanosheets suspended in the ionic liquid, as shown through equation (4).

\[(C)_m + (C_{11}H_{21}N_2)^+(CF_3SO_3)^- \rightarrow (C)_m-(C_{11}H_{21}N_2)^+(CF_3SO_3)^- \text{ (in the solution)} \] (4)

But all the aforementioned reactions (1-4), are rather speculative.

The Raman spectrum of FGO nanosheets (shown in Figure S1b) was recorded on a Bruker Senterra Dispersive Raman Microscope spectrometer, the laser excitation wavelength was fixed at 785 nm. It shows broad D and G bands. The G peak is seen at 1582 cm\(^{-1}\) and
arises from the in-plane vibration of sp² hybridized carbon atoms. The D band due to surface defects on graphene sheets is observed at 1310 cm⁻¹.

Figure S2. (a) Bright field image of neat TiO₂, (b) lattice scale image of TiO₂, with an interplanar spacing of 0.17 nm, corresponding to <105> reflection (JCPDS: 89-4921) of the tetragonal body centered lattice of TiO₂, (c) TiO₂/CdSe composite film and (d) Neat CdSe QDs of ~3.9 nm dimensions. Insets of (a) and (d) show the FFT images of TiO₂ and CdSe respectively.

The image of TiO₂/CdSe (Figure S2c) is fuzzy in comparison to neat TiO₂ (Figure S2a), indicating the presence of the bulky TOPO ligands surrounding the CdSe QDs. The uniformity of the glazy contrast in the low magnification image of TiO₂/CdSe (Figure S2c); for the faceted grains do not appear to have very distinct boundaries, also indicates that the
The TiO\textsubscript{2} surface is well covered by CdSe QDs, by means of the carboxylate groups on mercaptopropionic acid, the molecular linker.

![Graph showing absorption spectra](image)

**Figure S3** Main edge absorption spectra plotted as (a) \((\alpha h\nu)^2\) and (b) \((\alpha h\nu)^{1/2}\) vs. photon energy \((h\nu)\) for CdSe QDs and TiO\textsubscript{2} respectively.

Band gaps were determined from Tauc plots, wherein, absorption coefficient varies as a function of frequency, according to

\[ \alpha h\nu \propto (h\nu - E_g)^n \]

where \(h\nu\) is the photon energy and \(E_g\) is the band gap, and \(n = 2\), for indirect transitions, as in TiO\textsubscript{2} and \(n = \frac{1}{2}\) for direct transitions, as in CdSe. The absorption coefficient was determined from the absorption plots using the relation:
\[ \alpha = \frac{1}{d} \{A(\lambda)\} \]

where \( d \) is the thickness / path length of the film / solution and \( A \) is the absorbance. Band gaps of TiO\(_2\) and CdSe were 3.2 and 2.02 eV respectively, obtained from the intercepts of Tauc plots.

![Absorption quenching of a Au NPs colloid (4 mM) as a function of increasing CdSe QDs (3 mM) in toluene, added in steps of 50 µL and measured in the wavelength range of 300 – 700 nm.][1]

Figure S4. Absorption quenching of a Au NPs colloid (4 mM) as a function of increasing CdSe QDs (3 mM) in toluene, added in steps of 50 µL and measured in the wavelength range of 300 – 700 nm.

Starting from a solution of pure Au NPs (4 mM) in toluene, the direction of non-radiative charge transfer from the semiconductor CdSe QDs to the metallic Au NPs, was followed by first examining the progressive quenching of the plasmonic absorption peak of Au, as a function of increasing but quantified colloid loadings of CdSe QDs (3 mM). The total volume of the dispersion (be it neat Au NPs or neat CdSe QDs or CdSe QDs + Au NPs) was always fixed at 3000 µL, as can be seen in Figure S4. The systematic decay of the
absorption of Au NPs, with increasing CdSe QD content, at any particular volume ratio of CdSe QDs : Au NPs, is an indicator of electron transfer from the conduction band of the CdSe QDs to the Fermi level of the Au NPs.

Figure S5. Time resolved fluorescence decay profile of a TiO$_2$/CdSe composite film, measured at $\lambda_{ex} = 370$ nm and $\lambda_{em} = 570$ nm. The solid line represents the best fit obtained by deconvolution, assuming bi-exponential decay.

References