In situ Electrochemical Organization of CdSe nanoclusters on Graphene during Unzipping of Carbon Nanotubes

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Detailed synthetic and Characterization Procedure:

In a typical preparation, single walled carbon nanotubes (SWCNTs) (obtained from Carbon Nanotechnologies Inc. and were purified according to the reported protocol¹) were unzipped according to our recent report.² Briefly, a thin coating of SWCNT was prepared on a Pt-electrode (2 mm diameter) using 0.05 wt% nafion. It was then unzipped to form graphene sheets in 0.5 M H₂SO₄ by first oxidizing at 0.8 V (vs mercury mercurous sulphate reference electrode for 6 h) followed by reduction at -0.7 V (for 6 h). At the end of reduction process, 10 mM CdSO₄ and 5 mM Na₂SeO₃ were added in the solution and the reduction process was continued for 5 min, 15 min and 1 h for CdSe formation. Samples were collected by sonication of the electrode in deionized water and washed several times before submitting for any characterization.

Powder X-ray Diffraction patterns were recorded on a Phillips PANalytical diffractometr with CuK α radiation ($\lambda = 1.5406$ Å), with a scan speed of 2° min⁻¹ and a step size of 0.02° in 20. For measurements samples were scratched out from the electrodes, dried and directly placed on the XRD plates. FTIR spectra were taken on a PERKIN ELMER FT-IR SPECTRUM (Nicolet) spectrometer. All Raman spectroscopy measurements were carried out at room temperature on an HR 800 Raman spectrophotometer (Jobin Yvon HORIBA, France) using monochromatic radiation emitted by a He–Ne laser (632.8 nm), operating at 20 mW. The experiment was repeated several times to verify the consistency of the spectra. Transmission Electron microscopy was carried out by a JEOL JEM 1200 EX operated at an accelerating voltage of 200 kV with a resolution of not less than 3-4 nm. Atomic Force Microscope (AFM) images of GNRs were carried out using digital instrument nanoscope-IV, multimode scanning probe microscope at ambient conditions in the tapping mode. UV-VIS spectra were recorded using Carry Win 50 (Agilent Tech.) after dispersing the materials in dimethylformamide (DMF). Steady-state photoluminescenc emission was carried out using a Fluorolog HORIBA Jobin Yvon fluorescence spectrophotometer. Measurements were made at 22.5° in front-face films (in soild state). EDAX analysis

Phoenix energy dispersive analysis of X-ray (EDX). Photoconductivity of the sample was measured by two probe method using KEITHLEY source meter and voltmeter in presence of 1.5 AM light source.

Section S2 Cyclic voltammetry before and after unzipping

Fig. S1 shows the cyclic voltammograms of SWCNTs (coated on a 2 mm Pt-disk electrode) before and after applying constant anodic bias (0.8 V vs MMS) for 10 h in 0.5 M H_2SO_4 . The couple A1/C1 is attributed to quinol-hydroquinone couple.¹ The capacitance increases significantly after applying positive potential, indicating the increase in overall surface area of the materials due to unzipping to form oxidized GNRs.



Figure S1: Cyclic voltammogram of SWCNTs on Pt-electrode in 0.5 M H₂SO₄ before and after oxidative unzipping of SWCNT at 0.8 V for 10 h.

Section S3 Theoretical Interpretation of *i-t* transient during CdSe deposition

Fig. 1(b) shows the chronoamperogram for the codeposition of CdSe during the reduction of oxidized GNRs at -0.7 V. Fig. S2(a) shows the linear dependence of portion I indicating instantaneous nucleation during deposition. Plot of two dimensionless numbers $(i/i_m)^2$ vs t/t_m for portion II gives information for the two types of nucleation mechanisms namely instantaneous and progressive. Equation 1 and 2 describe the instantenous and progressive mechanisms respectively according to the classical nucleation theory.³⁻⁵

$$(\frac{i}{i_m})^2 = \frac{1.9542}{\frac{t}{t_m}} \{1 - \exp[-1.2564\left(\frac{t}{t_m}\right)]\}^2 \dots (1)$$

$$(\frac{i}{i_m})^2 = \frac{1.2254}{\frac{t}{t_m}} \{1 - \exp\left[-2.3367\left(\frac{t}{t_m}\right)^2\right]\}^2 \dots (2)$$

Equation (1) is for instantaneous nucleation and (2) describes well the progressive nucleation mechanism during electrodeposition. Fig. S2(b) shows the good fitting of the experimental data with that with instantaneous plot (theoretically). This further confirms that the CdSe formation on GNRs occurs via instantaneous mechanism.



Figure S2: (a) current density vs $t^{1/2}$ during the initial stage of deposition and (b) dimensionless i-t transient for nucleation of CdSe on GNRs and corresponding theoretical curves for instantaneous and progressive nucleation.

Section S4 Powder X-ray Diffraction



Figure S3: Powder X-ray diffractograms of the CdSe-unzipped SWCNT composite prepared in situ.

Section S5 FTIR Analysis

Fig. S4 is the representative FTIR spectra of p-SWCNT and un-SWCNT-CdSe composite showing structural changes on SWCNT surface due to electrochemical oxidation. The peak originating at 1614 cm⁻¹ is attributed to the stretching frequency of -COO⁻ from -COOH group upon the electrochemical oxidation. The bands at 1146, 1038 and 856.4 cm⁻¹ are due to the C=C backbone of p-SWCNT. The broad band between 3000-4000 cm⁻¹ is indicative of adsorbed atmospheric moisture and aerial oxidation of SWCNT surface. All peaks match well with that of the reported values for similar functional groups.⁶ It is however, noteworthy that absorption peaks corresponding to other oxygen functionalities like epoxy, carboxylic acids etc. are either absent or present in a very insignificant amount. This may be attributed to the fact that during the electrochemical reduction cycle, most of the oxygenated functional groups get reduced leaving behind very less number of such groups which further act as anchoring sites for the CdSe nanoparticles during their formation by electrochemical reduction.



Figure S4: FTIR spectra of SWCNT and unzipped SWCNTs.

Section S6 UV-VIS analysis

Figure-5 represents the absorbance spectra of pristine SWCNT (p-SWCNT) as well as graphene nanoribbons (formed from electrochemical unzipping of SWCNT) decorated with 4-5 nm CdSe nanoparticles (formed during the last 5 min reduction process of unzipping). The small peaks between 400 – 800 nm are characteristics of pristine SWCNTs and originate due to the presence of van Hove's singularities. After unzipping and CdSe organization on GNRs, these peaks disappear and absorption due to CdSe NPs emerges at around 576 nm.



Figure S5: UV-VIS spectra of pristine SWCNT (p-SWCNT) and CdSe on GNRs (unSWCNT). Spectra were taken after dispersing the materials in DMF with ultrasonication.

Section S7 Photoluminescence study



Figure S6: Photoluminescence of oleic acid capped CdSe NPs and CdSe NPs bonded to GNRs (both CdSe NPs have similar sizes). The spectra were recorded by exciting the suspension of the samples at 500 nm for comparison.

Section S8 EDAX Analysis



Figure S7: Rrepresentative EDAX spectrum of the composite showing the presence of Cd and Se in ~1:2 ratio.

One of the intermediates during electrodeposition of CdSe is H_2Se , which reacts further with Cd to form CdSe. Once formed, some part of H_2Se reacts with H_2SeO_3 to generate free Se according to the parasitic reaction,

 $2Se + 4H^{+} + 4e \longrightarrow 2H_2Se$ $2H_2Se + Na_2SeO_3 + 2H^{+} \longrightarrow 3Se + 3H_2O + 2Na^{+}$

This free Se then gets deposited on the preformed CdSe and also on the graphene. Hence, there is always some excess selenium during the electrodeposition of CdSe (please see ref. 7 in the ESI). However, this excess Se is not harmful for the performance of the hybrid material and can be avoided by changing the mode of electrodeposition from potentiostatic (in the present case) to potentiodynamic, where the excess Se is consumed in the subsequent step to form stoichiometric CdSe NPs. But, in our case, we mostly relied on potentiostatic deposition in order to ensure simultaneous reduction of oxidized graphene nanoribbons as well as CdSe formation

Section S9 Photoconductivity measurement

Photoconductivity of the hybrid (5 min CdSe deposition) shows almost double increment in conductivity on irradiating with 1.5 AM light. However, the increment is not very high because of less time of deposition and less concentration of the precursors, which together result in comparatively lower amount of CdSe nanoparticles on the GNRs. Effect of increasing precursor concentrations as well as other factors controlling the higher density of CdSe nanoparticles on GNRs is under investigation.



Figure S8: I-V characteristic of the composite CdSe-GNR formed during electrochemical unzipping process. The current increases significantly on irradiation with 1.5 AM light.

Section S10 TEM for different deposition times

Fig. S9(a) shows pristine SWCNTs before unzipping showing bundling and average diameter 0.7 to 1.2 nm. Fig. S9(b) is for 15 min deposition and (c) is for 1 h deposition. Clearly the particle size increases with increasing deposition time and eventually after 1 h covers the whole unzipped SWCNT surface.



Figure S9: Low resolution TEM images of (a) pristine SWCNT before unzipping showing bundling (b) after CdSe deposition for 15 min and (c) for 1 h.

Section S11 Calculation of SWCNT Diameter from RBM position

According to Araujo et al.⁸ the position of RBM band of SWCNTs varies with the diameter as follows, $\omega_{RBM} = 217.8/d_t + 15.7$ where ω_{RBM} is the frequency or position of RBM band and d_t is the diameter of the SWCNTs.

From fig. 2, the position of RBM is 210.48 cm⁻¹. Hence, from the above equation, the diameter of the SWCNTs is ~ 1.1 to 2 nm.

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