Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Self-assembly mesoporous $Ni_{0.85}Se$ spheres as high performance counter cell of dye-sensitized solar cells

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Experiments

Synthesis of $Ni_{0.85}Se$ *nanoparticles*

In a typical synthesis of $Ni_{0.85}Se$ nanoparticles, the original molar ratio of $NiCl_2 \cdot 6H_2O$ and selenium dioxide was selected to be 1:1. First, 0.714 g (3 mmol) $NiCl_2 \cdot 6H_2O$, 1 g sodium citrate and 0.3 g PVP 40000 were dissolved in 30 mL distilled water in Teflonlined autoclave of 50 mL capacity. After stirring for 20 min, 0.345 g (3 mmol) selenium dioxide was added to the above mixture. Then, 10 ml hydrazine hydrate was added dropwise. The resulting solution was sealed and heated at 180 ◦C for 15 h. Thereafter, the autoclave was allowed to cool to room temperature. The product was washed with water and absolute ethanol to remove impurities, and then dried at 60 ◦C.

Synthesis of GO nanosheets

Graphene oxide (GO) nanosheets were made by a modified Hummers method. In detail, graphite powder (2 g) was put into 100 mL of cooled (0 °C) concentrated H_2SO_4, followed by the slow addition of $KMnO_4$ (6 g), a slight exotherm may be produced in this process. The suspension was then stirred at 35 °C for 12–15 hours. Afterwards, 200 mL of distilled water was added and the temperature was kept at 96 °C for 2 h. The temperature was reduced to 60 °C, and H_2O_2 (30%, 10 mL) was injected into the suspension to completely react with the excess KMnO4, which yielded a bright yellow mixture. The solid product was separated by centrifugation, and then washed with HCl (5 %) several times and with water until the pH value of the supernatant was nearly 6, and graphene oxide was obtained. The collected precipitate was dispersed in water, then sonicated and subsequently concentrated to obtain a GO suspension, and kept at 50 °C for 10 h and GO powder was obtained.

SWCNT

SWCNT was purchased from Nanotech Port Co. (Shenzhen, Guangdong Province, China). On the basis of the information provided by the manufacturer, the carbon nanotubes were synthesized by a chemical vapor deposition method using cobalt, manganese, molybdenum, or nickel as catalysts. The SWCNT contained more than 90% (by volume) carbon nanotubes and less than 10% impurities, mainly amorphous carbon; the content of SWCNT with an outer diameter less than 2 nm was above 50% in this product. And the length of carbon nanotubes ranged from 5 to 15μm for both the SWNT.

Fabrication of Dye-Sensitized Solar Cells.

Mesoporous $Ni_{0.85}Se$ spheres or $Ni_{0.85}Se$ nanoparticles slurry was made in ethanol by mixing 0.1 g of $Ni_{0.85}Se$ powder with 0.025 g of PEG20000 and stirred continuously. Then a film was made by wiping $Ni_{0.85}Se$ slurry onfluorine-doped tin oxide (FTO) conductive glass (LOF, TEC-15, 15 W per square) with a doctor-blade. After the film was steady, the conductive glass with film was heated at 450°C for 2 h under the protection of argon to get the $Ni_{0.85}Se$ CEs. A commercial TiO_2 sol (Solaronix, Ti-Nanoxide T/SP) was used to prepare the TiO_2 film on FTO also by the aforementioned method, and the film was soaked in an N719 dye solution (in ethanol) for 24 h to obtain dye-sensitized TiO_2 electrodes. DSSCs were assembled by injecting the electrolyte into the aperture between the dye-sensitized TiO_2 electrode and the CE. The liquid electrolyte is composed of 0.05 MI_2, 0.1 M LiI, 0.6 M 1, 2-dimethyl-3-propylimidazolium iodide (DMPII), and 0.5 M 4-tert-butylpyridine with acetonitrile as the solvent. Surlyn 1702 was used as the spacer between the two electrodes. The two electrodes were clipped together with solid paraffin working as the sealant to prevent the electrolyte solution from leaking. The effective cell area was 0.25 cm^2. For comparison, other DSSCs were fabricated by mixing mesoporous $Ni_{0.85}Se$ spheres powder with different amount of RGO or SWCNT, and other procedures remained the same. The standard Pt CE was purchased from Dalian Heptachroma Solar Tech Co., Ltd.

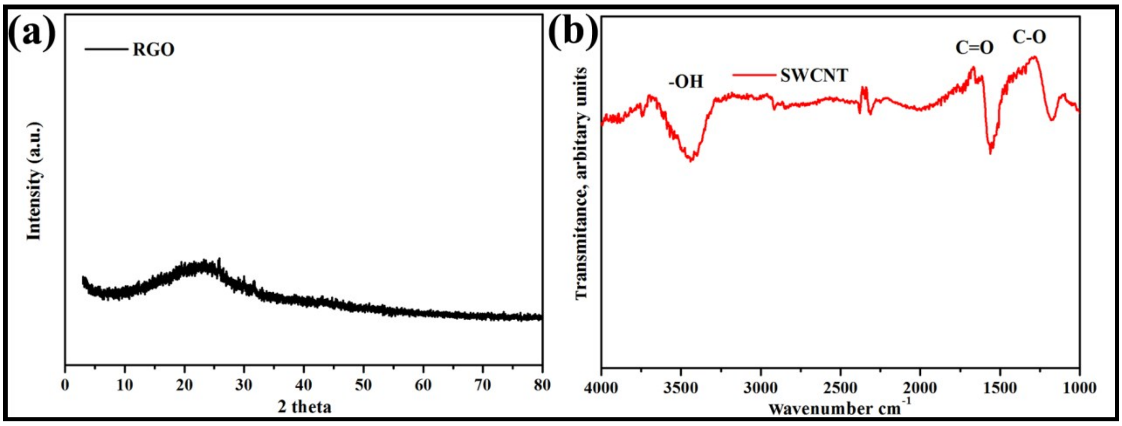

Fig. S1. XRD pattern of RGO (a) and Fourier transform infrared (FTIR) transmission spectra of SWCNT (b).

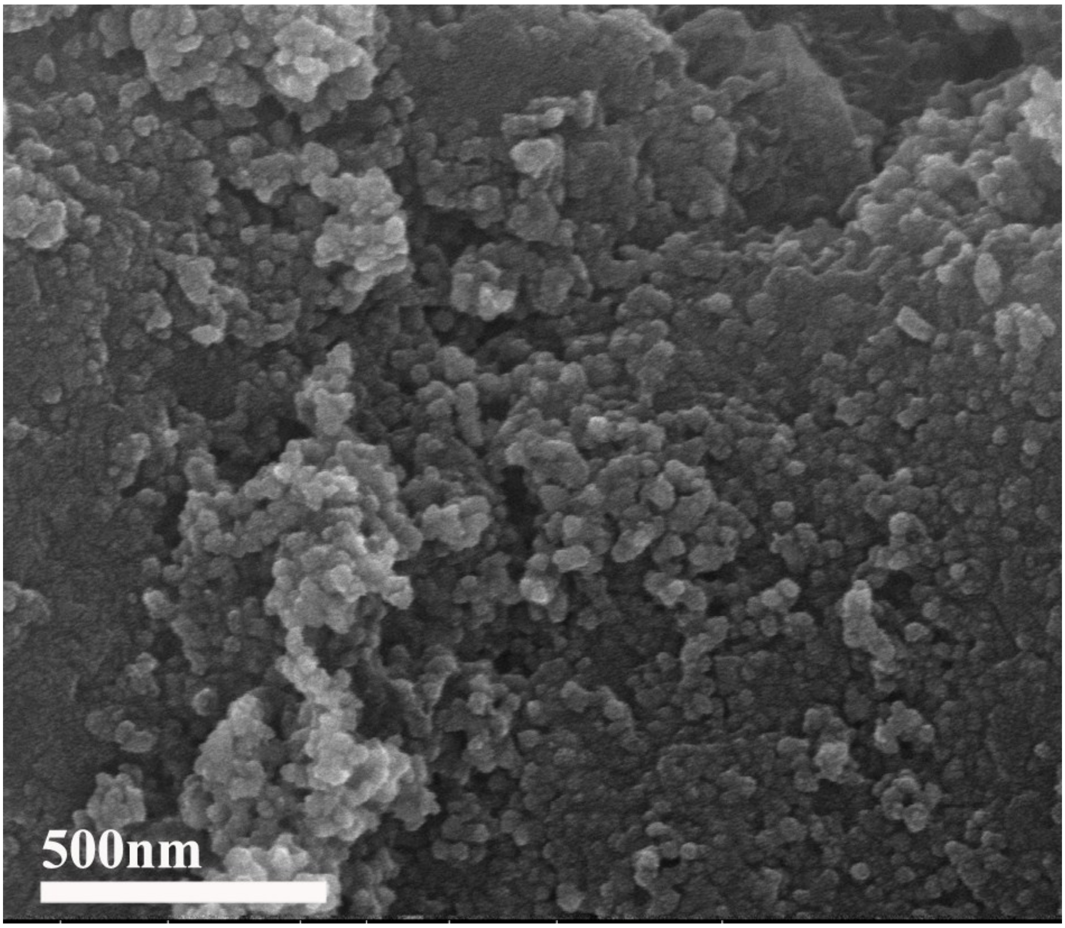

Fig. S2. Typical SEM image of $Ni_{0.85}Se$ nanoparticle.

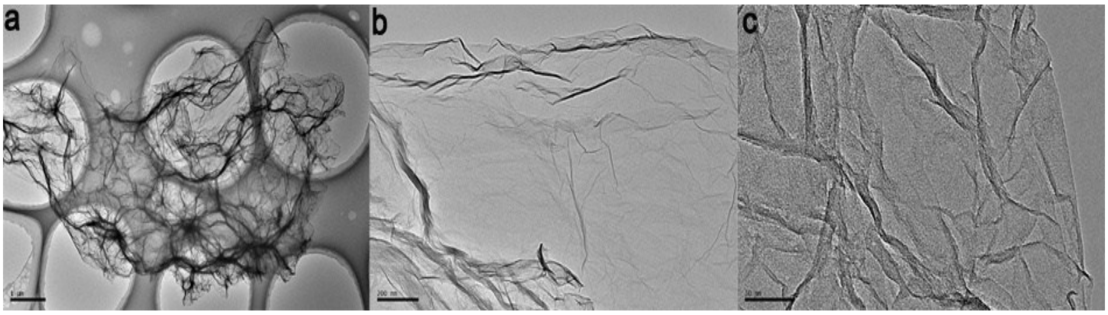

Fig. S3. TEM images of as-prepared GO (a, b, and c).

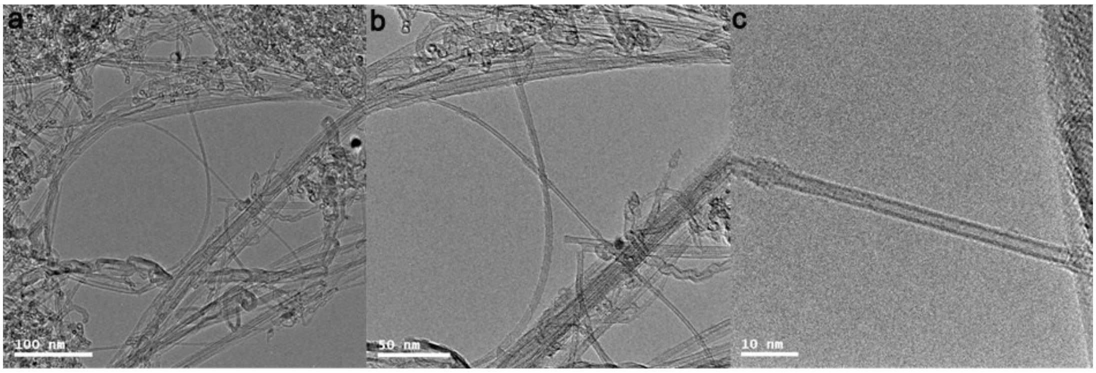

Fig. S4. TEM images of SWCNT (a, b, and c).

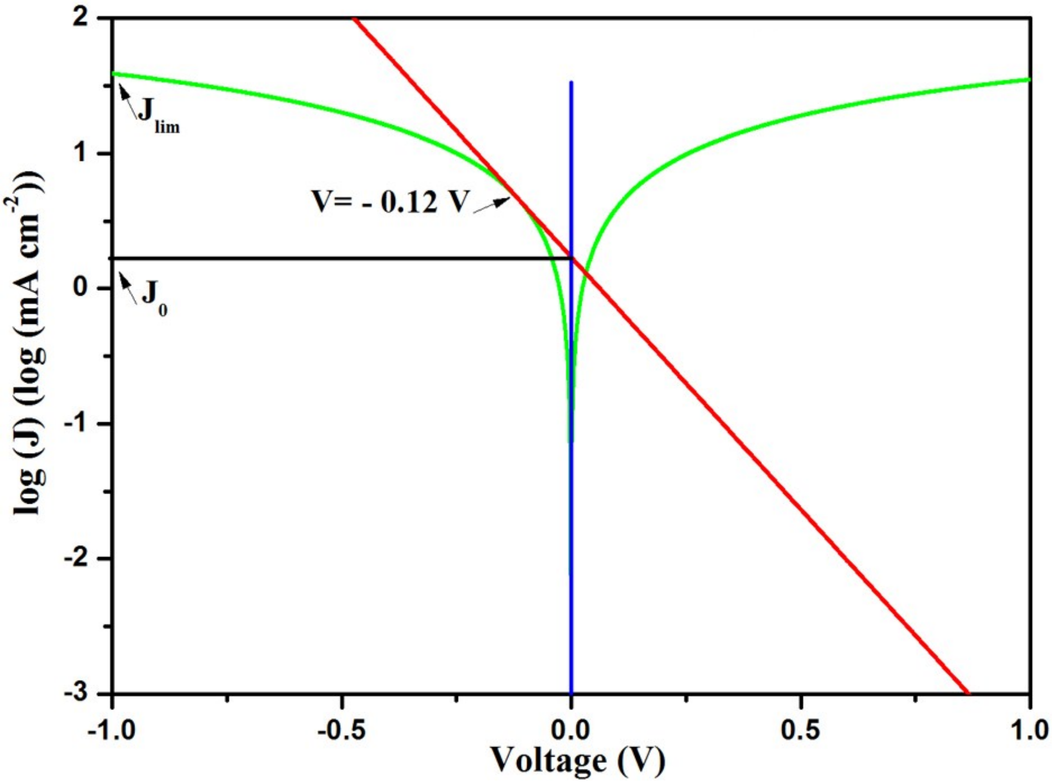

Fig. S5. Annotations of getting J_0 and J_{lim} from the Tafel curves.

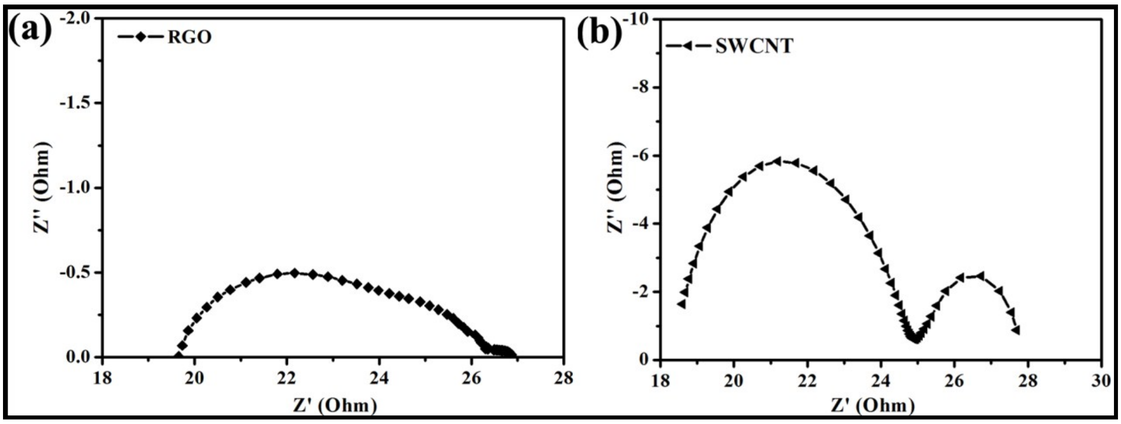

Fig. S6. Nyquist plots for symmetric cells fabricated with (a) RGO and (b) SWCNT.

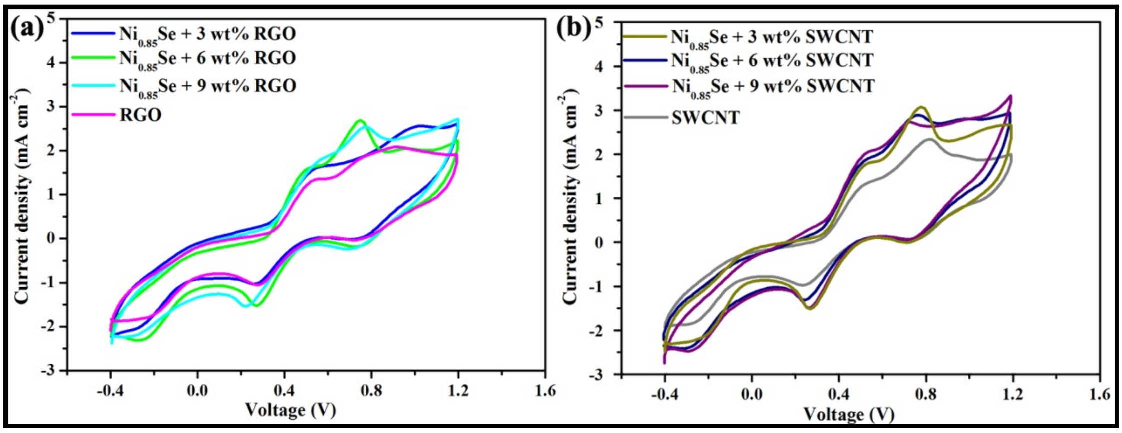

Fig. S7. Cyclic voltammograms of I_3^-/I^- symmetrical cells based on (a) NRCs and (b) NSCs.

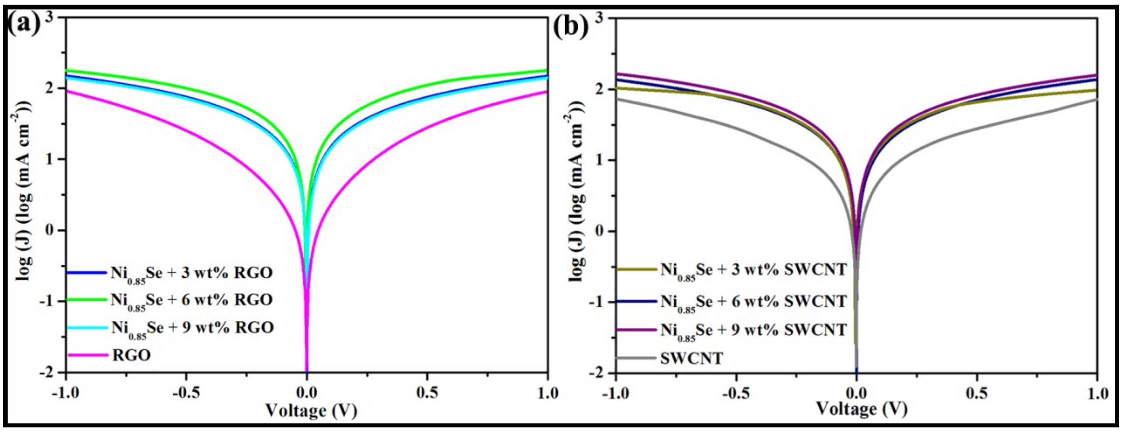

Fig. S8. Tafel polarization curves of I_3^-/I^- symmetrical cells based on (a) NRCs and (b) NSCs.

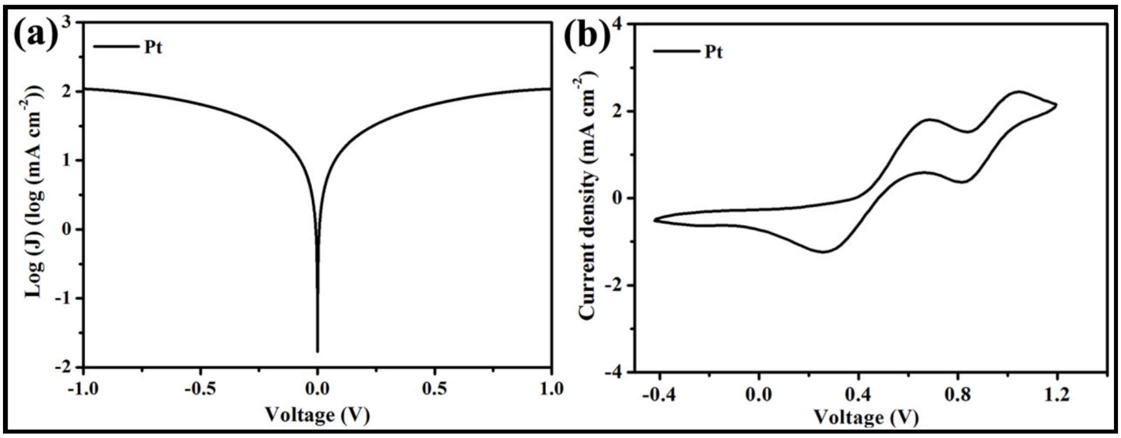

Fig. S9. (a) Nyquist plots and (b) cyclic voltammograms of I_3^-/I^- symmetrical cells based on Pt

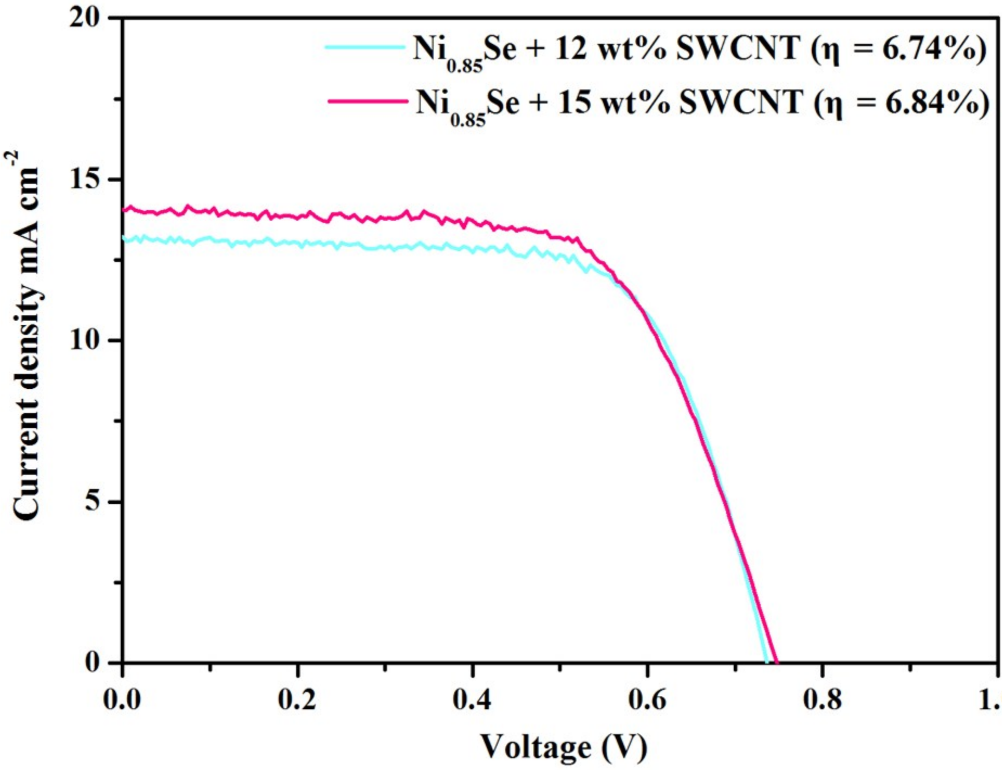

Fig. S10. Photocurrent density–voltage characteristics of DSSCs with $Ni_{0.85}Se$ + 12 wt% SWCNT, and $Ni_{0.85}Se$ + 15 wt% SWCNT.

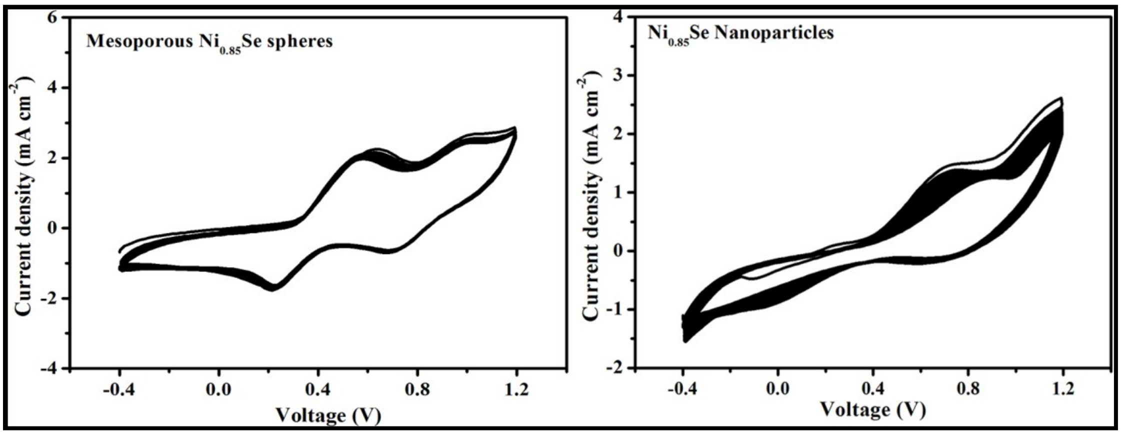

Fig. S11. Consecutive 50 cyclic voltammograms for mesoporous Ni$_{0.85}$Se spheres and Ni$_{0.85}$Se nanoparticles CEs at a scan rate of 50 mV s^{-1}.

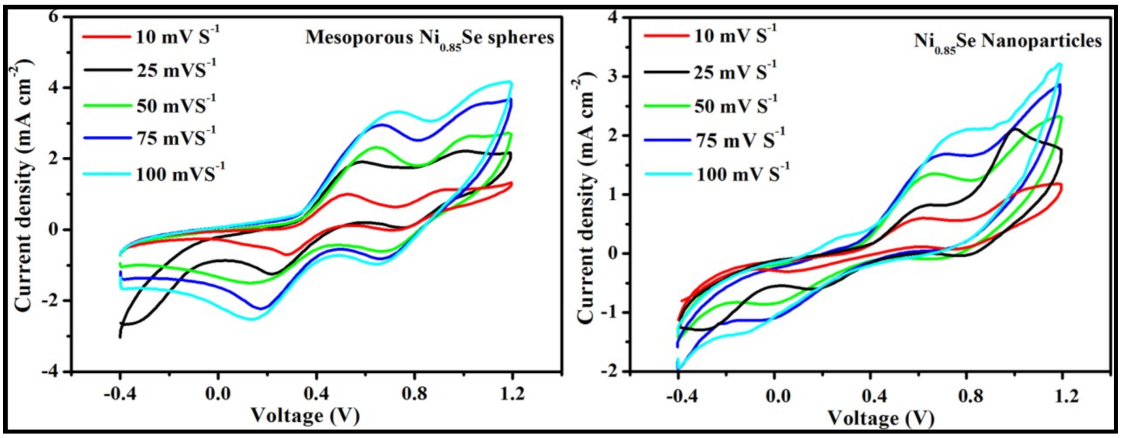

Fig. S12. Cyclic voltammograms of for the I_3^-/I^- redox species recorded at an increasing scan rate from 10 to 100 mV s^{-1}.