Supporting information

Eco-friendly synthesis of SnSe nanoparticles: Effect of reducing agents on the reactivity of Se-precursor and phase formation of SnSe NPs

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1. Deposition of SnSe NPs thin films

The deposition of SnSe NPs absorber layer with smoother morphology as well as with well controlled and uniform film thickness is a challenging task due to different kinds of issues (see our recent review papers of Ref. [1,2] for more details). The preparation of SnSe NPs ink with suitable rheology plays a critical role in the process of film coating. For prompt dispersion of SnSe NPs, we used mixed solvent systems depending upon the film coating technique. In the present case, the deposition of SnSe NPs thin films were carried out using two different film coating techniques such as brush painting and spin coating.

(a) Brush painting: In this case, the as-synthesized SnSe NPs were dispersed in a mixed solvent of EG:MEA (5:1 vol./vol.) and brush painted onto molybdenum coated soda-lime glass substrates. The particular choice of combination of ethylene glycol (EG) and MEA are their suitable boiling points (B.P) and viscosity adjustments for brush painting. The B.P of EG is 197.3 °C with a viscosity of 16.9 cP, whereas for MEA, the B.P is 170 °C with a viscosity of 15.1 cP at 30°C. The SnSe NPs precursor films were dried at 180 °C after the brush coating. The SnSe NPs precursor films showed a thickness of ~2 µm. These precursor films were rapid thermal annealed at 500 °C for 5 min under Se-atmosphere (N_2 gas + Se) with 100 mTorr pressure. The resultant p-type SnSe NPs absorber layers showed a thickness of ~1.3 µm (see Fig. S3). The main advantage of brush painting is its simplicity, less material wastage, and lower cost.[3] However, this technique has lower controllability over the film thickness, lack of reproducibility, and needs expertization for casting the good

quality thin films. The heterojunction SnSe NPs solar cell fabricated by brush coating showed an efficiency of 0.054% without ZnO and Al-doped ZnO layers.

(b) <u>Spin coating</u>: In this case, the as-synthesized SnSe NPs were dispersed in a mixed solvent of En:MEA (5:5 vol./vol.) and spin coated (spin coater model: ACE-200) onto molybdenum coated soda-lime glass substrates. The B.P of En is 116 ^{o}C with a viscosity of 1.8 cP at 20^{o}C, whereas for MEA, the B.P is 170 ^{o}C with a viscosity of 15.1 cP at 30^{o}C. In this case, we used a combination of two solvents having low and high viscosities for easy and fast evaporation of them from the films. A total of 2.5 ml of SnSe NPs ink (0.1 M) was used in the spin coating. After each spin coating of 0.5 ml of SnSe NPs ink, the precursor films were dried at 350 ^{o}C for 1 min under air. In the subsequent steps, these precursor layers were rapid thermal annealed at 500 ^{o}C for 5 min under Se-atmosphere (N_2 gas + Se) with 100 mTorr pressure. The resultant p-type SnSe NPs absorber layers showed a thickness of ~0.9-1.0 µm (see Fig. S3). The main advantage of spin coating is the higher controllability on the film thickness and good reproducibility. However, in this technique, there is significant material wastage during the coating. The spin coated SnSe NPs solar cell showed an improvement of PCE to 0.43% with ZnO and Al-doped ZnO layers.

2. CdS buffer layer deposition by CBD

CdS buffer layer (thickness of ~70 nm) was deposited onto the p-type SnSe NPs absorber layer using chemical bath deposition (CBD). The deposition of CdS layer was carried out using a chemical bath as follows: First, 100 ml of $CdSO_4$ (0.0074 M) aqueous solution was mixed with 80 ml of 25% ammonia (NH_3(aq)) solution. To this mixture, 100 ml of thiourea (0.2M) ($SC(NH_2)_2$) aqueous solution was added. Finally, 120 ml of deionized water was added to the above solution mixture to make up a total volume of 400 ml chemical bath. Next, SnSe NPs thin films coated on Mo were immersed vertically in the bath to carry out deposition of CdS layers. The deposition of CdS was carried out at a bath temperature of 80 ^{o}C for 20 min. The temperature of the bath was kept constant at 80 ^{o}C with the help of a thermostated water bath. In the deposition process, NH_3 acts as ligand for Cd^{2+} ions as well as it also controls the hydrolysis of thiourea. In addition, it can also

etch the surface of SnSe NPs thin film just before CdS nucleation start.[4] After a deposition time of 15 min, the samples were taken out from the bath, rinsed with deionized water, and dried under N_2 stream.

3. EDS mapping of SnSe NPs

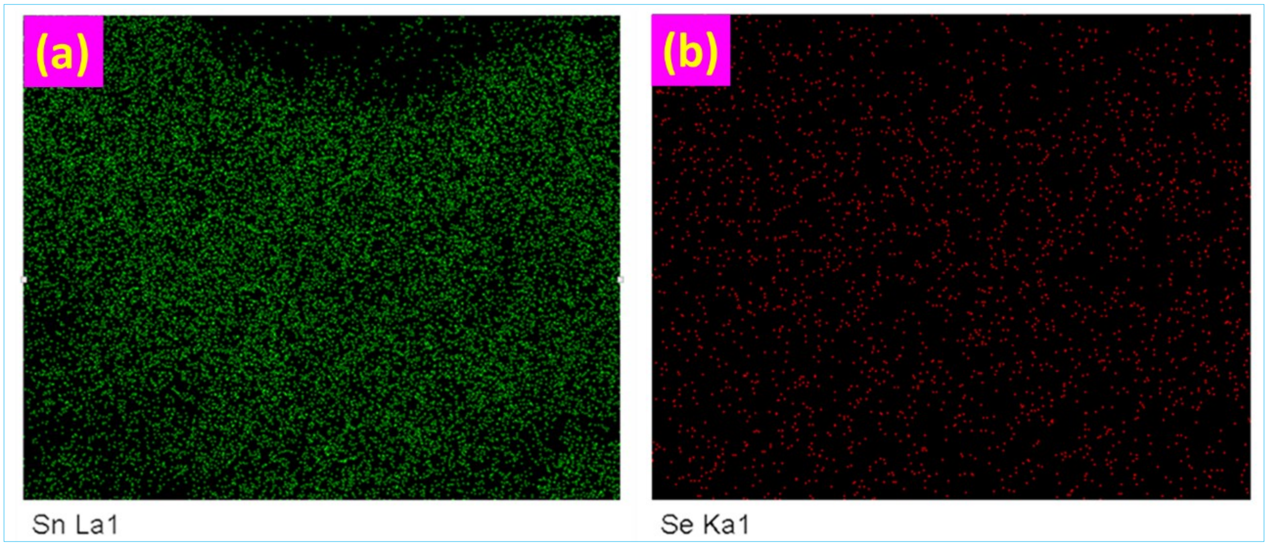

Fig. S1 (a-b) Elemental mapping of SnSe NPs grown in route-3.

4. Photovoltaic properties of SnSe NPs

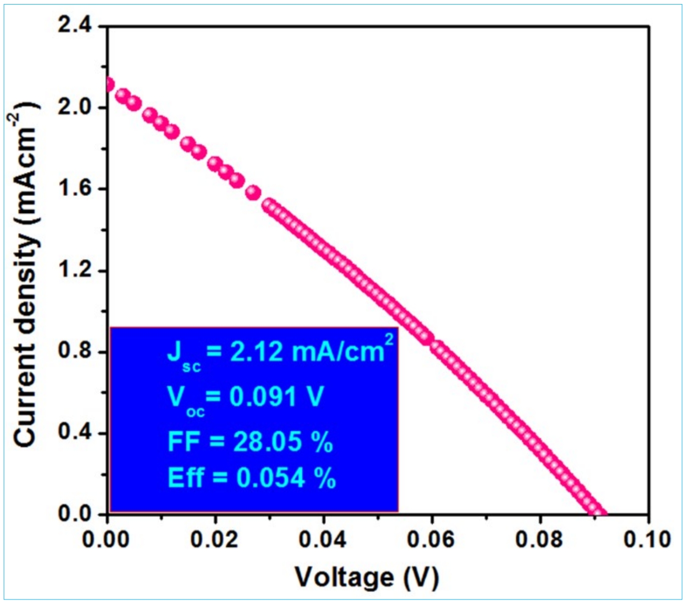

Fig. S2 J-V characteristic of SnSe NPs heterojunction solar cell, in which the absorber layer was coated by brush painting method.

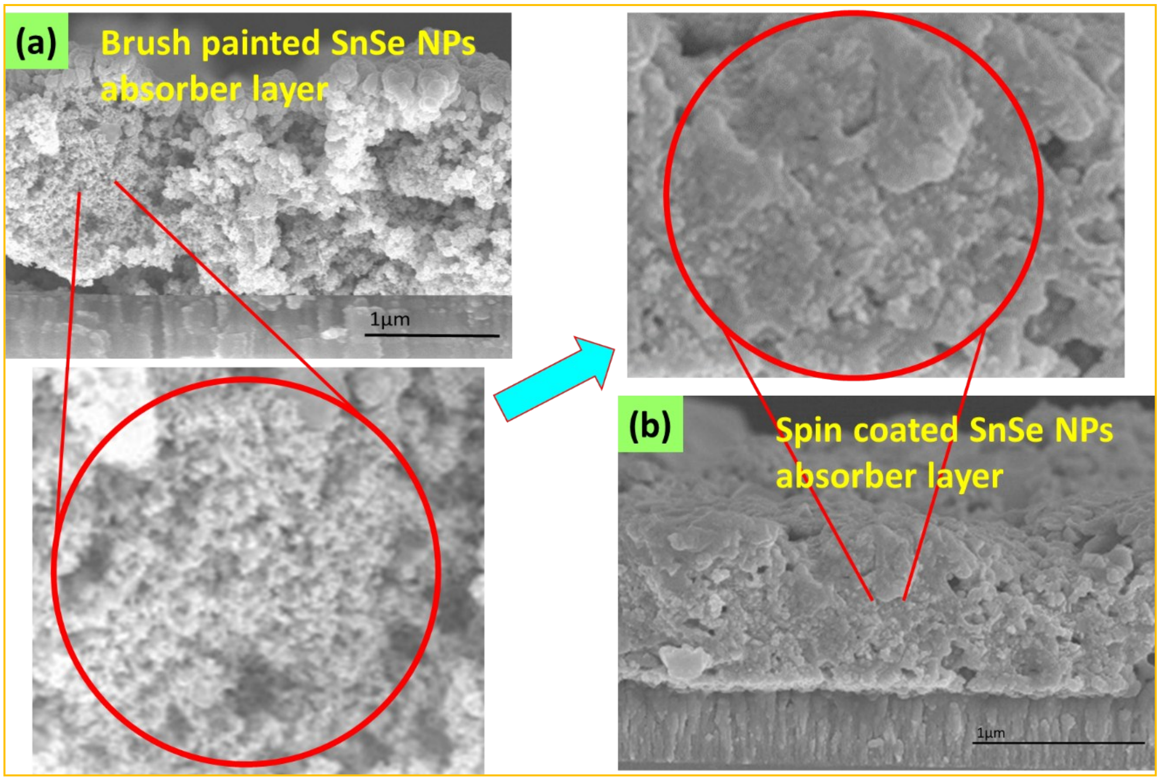

Fig. S3 Cross sectional SEM images of SnSe NPs absorber layer coated by brush painting (a), and spin coating (b).

Table S1. Photovoltaic performance of different type of SnSe solar cells

1. Inorganic SnSe thin film solar cells							
Device structure	**Absorber layer coating Method**	**V_{oc} (mV)**	**J_{sc} (mA/cm^2)**	**FF (%)**	**η (%)**	**E_g (eV)**	**Ref.**
***TEC-15/CdS/SnSe/carbon-paint**	**Electrodeposition**	**140**	**0.70**	**31**	**0.03**	**1.10**	[5]
TEC-15/CdS/SnSe/carbon-paint	**Chemical bath**	**215**	**1.70**	**26**	**0.10**	**0.96**	[6]
ITO/CdS/SnSe/Au	**Electrodeposition**	**370**	**5.37**	**30**	**0.80**	**1.2**	[7]
Glass/Ag/CdO:Sn/SnSe/Ag	**Thermal evaporation**	**273**	**0.99**	**69**	**0.59**	**1.71**	[8]
Glass/Mo/SnSe/CdS/i-ZnO/Al:ZnO/ Ni/Ag	**Thermal co-evaporation**	**76**	**8.34**	**33.8**	**0.215**	**1.17**	[9]
Glass/Mo/SnSe/CdS/i-ZnO/Al:ZnO/ Ni/Ag		**299**	**11.60**	**41**	**1.42**	**1.00**	[10]
2. Organic and dye sensetised/hybrid SnSe NPs solar cells							
ITO/MoO3/SnSe:PVP/PTCDI/LiF/Al	**Spin-casting**	**480**	**0.39**	**36**	**0.06**	**1.71**	[11]
ITO/PEDOT:PSS /P3HT:SnSe/LiF /Al	**Drop-casting**	**540**	**0.046**	**35**	**0.01**	**1.12**	[12]
FTO/TiO2/SnSe/Pt-FTO	**Dip coating**	**490**	**0.95**	**70**	**0.33**	**0.99**	[13]
3. Inorganic SnSe nanoparticle thin film solar cells							
SLG/Mo/ SnSe NPs/CdS/Ag	**Brush painting**	**91**	**2.12**	**28.05**	**0.054**	**1.1**	**Present work**
SLG/Mo/ SnSe NPs/CdS/i-ZnO / Al:ZnO /Ni/Ag	**Spin coating**	**350**	**3.63**	**34**	**0.43**	**1.1**	**Present work**

***TEC-15: SnO_2:F transparent conductive oxide (TCO) coated 3 mm glass**

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