Supporting Information

Mo-doped NiSe hierarchical microspheres boosting triiodide evolution for dye-sensitized solar cells: Theoretical and experimental study

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1. Experimental details

1.1 Materials

All the chemicals and reagents were used as received. Nickel acetate tetrahydrate ($Ni(CH_3COO)_2·4H_2O$), sodium selenite (Na_2SeO_3), diethyltriamine (DETA), sodium molybdate dihydrate ($Na_2MoO_4·2H_2O$), N-methyl-2-pyrrolidone, acetonitrile, and polyvinylidene fluoride were purchased from the Aladdin Reagent Co., Ltd. The hydrazine hydrate ($N_2H_4·H_2O$), acetone and anhydrous ethanol were obtained from Tianjin Fuyu Chemical Reagent Co., Ltd. The conductive substrate is fluorine doped SnO_2 glass (FTO, 15 Ω/square, Nippon sheet glass, Japan). The used Ru complex dye was *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bistetrabutyl-ammonium (N719, Solaronix SA, Switzerland). The redox shuttle electrolyte was a blend of 0.1 M LiI (anhydrous, 99 %, Acros), 0.05 M I_2 (anhydrous, 99.8 %), 0.5 M tert-butylpyridine (99 %, Aldrich), 0.1 M guanidine thiocyanate (99 %, Aladdin Co.) and 0.6 M 1-propyl-2, 3-dimethylimidazolium iodide (99 %) in methoxyacetonitrile (99 %, Fluka). H_2PtCl_6 were purchased from the Sinopharm Chemical Reagent Co., Ltd.

1.2 Preparation of CEs

The obtained materials such as the $Mo_{0.05}$-NiSe, $Mo_{0.10}$-NiSe, and $Mo_{0.15}$-NiSe, (95 wt%) and polyvinylidene fluoride (5 wt%, binder) were mixed together with the certain amount of the N-methyl-2-pyrrolidone, followed by stirring and sonication to form the slightly viscous slurry. Then the uniform catalyst films were covered on the surface of a cleansed FTO glass by doctor-blade technique, and sintered in a tube furnace for 1 h at 400 °C under high purity N_2 atmosphere. For comparison, pyrolytic Pt CE was prepared by drop-casting H_2PtCl_6 (50 μL) in ethanol (5 mM) on the cleansed FTO glass and calcination at 400 °C for 30 min under air atmosphere.

1.3 Fabrication of DSSCs

The dye-sensitized TiO_2 photoanodes were prepared by the standard method. DSSCs assembled into a sandwich structure with the N719 loaded TiO_2 photoanode, iodine-based electrolyte containing redox couple (I_3^-/I^-), and CEs ($Mo_{0.05}$-NiSe, $Mo_{0.10}$-NiSe,

$Mo_{0.15}$-NiSe, and Pt). The redox shuttle electrolyte was injected into the space between the photoanode and CE. In order to prevent the electrolyte solution leakage, two electrodes were adhered together with thermoplastic hot-melted surlyn.

1.4 Characterizations and Measurements

X-ray powder diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku D/max-IIIB, Cu Kα, λ=1.5406 Å) at a scan rate of 10° min^{-1} in the range from 10° to 80°. X-ray photoelectron spectroscopy (XPS) was carried out by using a model of VG ESCALAB MK II with an Mg Ka (1253.6eV) achromatic X-ray source. Scanning electron microscopy (SEM) was carried out by using a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained from JEM-3010 (JEOL) with a voltage of 200 kV.

The whole electrochemical tests were conducted on a CHI760E electrochemical workstation (Shanghai Chenhua Instrument Corp., Shanghai, China). The typical photocurrent density-voltage (J-V) data of the assembled DSSCs could be detected under AM 1.5 G illumination irradiation (100 mW cm^{-2}). The active size of DSSCs is 1.5 cm^2, and the irradiation area is 0.20 cm^2 with a photomask. Cyclic voltammetry (CV) was carried out in a three-electrode system. Specifically, the as-prepared materials and Pt CEs were worked as a working electrode, Pt plate was used as a CE, Ag/AgCl was used as a reference electrode. The supporting electrolyte was an anhydrous acetonitrile solution of 0.1 M $LiClO_4$, 10 mM LiI, and 1mM I_2, and the potential range was from -0.4 V to 1.0 V. Electrochemical impedance spectroscopy (EIS, bias voltage: 0 mV; frequency range: 0.01 Hz to 100 kHz; disturbance voltage: 10 mV) and Tafel polarization data were assembled as the style of the symmetrical cells which were full of the identical electrolyte. The obtained EIS data were fitted by the Z-View software in terms of appropriate equivalent circuits.

1.5 Computational method

All calculations based on DFT were carried out using the Vienna ab initio simulation package (VASP)[1, 2]. Perdew-Burke-Ernzerhof functional with a generalized gradient approximation (GGA-PBE)[3] form was adopted to deal with the exchange correlation energies of the systems. The plane-wave and pseudo-potential techniques were used[4], and the energy cutoff was 400 eV. To obtain a good numerical sampling of electron densities in Brillouin zone, a (3×3×1) Monkhorst-Pack mesh was applied to the $NiSe_2$ surface and a (5×5×1) one for the density of states calculation. The van der Waals (vdW) interactions were considered as the DFT-D2 method of Grimme for all the calculations[5]. The optimization procedure was repeated until the maximum residual force is less than 0.02 eV·Å^{-1} in any directions. During the calculations, a vacuum layer of 15 Å is used to avoid the fake interactions between periodic images along z axis.

2. Supporting data

Table S1 Adsorption data of I_3^- complex on metal sites of NiSe and Mo-NiSe.

	Metal sites	Adsorption energy (eV)
NiSe	Ni	-1.08
Mo-NiSe	Mo	-1.84
	Ni	-1.65

Table S2 EDS analysis of obtained samples with average value in random three spots.

Samples	Atom (%)		
	Mo	Ni	Se
$Mo_{0.05}$-NiSe	0.24	44.92	54.84
$Mo_{0.10}$-NiSe	0.44	44.58	54.98
$Mo_{0.15}$-NiSe	0.65	44.28	55.07

Table S3 Performance parameters of devices based on the different CEs.

CEs	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	R_s (Ω)	R_{ct} (Ω)
NiSe	0.761±0.005	16.03±0.31	0.62±0.01	7.51±0.13	32.43	17.62
$Mo_{0.05}$-NiSe	0.773±0.006	16.92±0.35	0.64±0.01	8.40±0.11	24.07	8.11
$Mo_{0.10}$-NiSe	0.768±0.004	18.07±0.28	0.64±0.01	8.92±0.09	23.17	3.67
$Mo_{0.15}$-NiSe	0.768±0.006	17.72±0.32	0.63±0.01	8.62±0.12	24.03	5.69
Pt	0.755±0.005	16.18±0.29	0.63±0.01	7.74±0.07	24.17	11.03

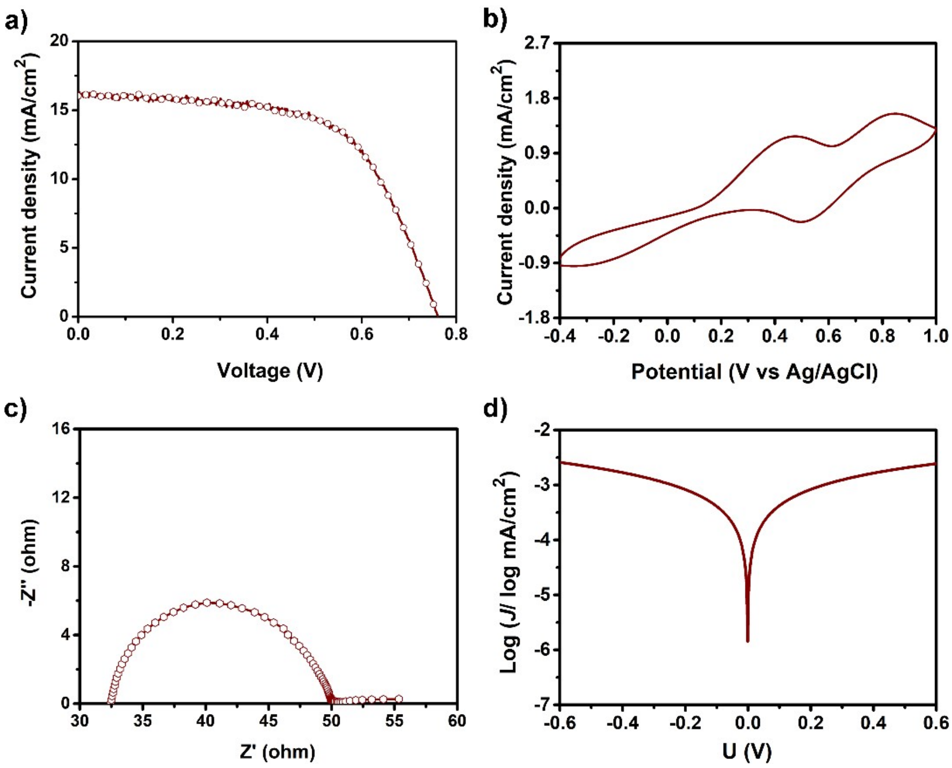

Fig. S1 J-V curve (a), CV curve (b), EIS (c), and Tafel polarization curves (d) based on the pure NiSe CEs.

Table S4 Photovoltaic parameters of DSSCs based on Ni-based selenide.

CEs	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF*	η (%)	η (Pt) (%)	Ref.
NiCoSe	18.5	0.71	0.66	8.19	6.53	6
NiSe-sb	15.90	0.62	0.69	6.75	6.18	7
NiSe-112	18.16	0.706	0.59	7.61	7.85	8
$NiSe_2$-180	15.49	0.756	0.66	7.78	8.07	9
$Ni_{0.85}Se$	16.67	0.74	0.64	7.85	6.18	10
6%GLW-NiCoSe	16.72	0.72	0.65	8.14	7.20	11
NiSe/$GN_{0.50}$	16.73	0.75	0.68	8.62	7.68	12
$NiCoSe_2$-150	17.82	0.77	0.63	8.76	8.22	13
$NiSe_2$-W	18.08	0.74	0.66	8.78	7.97	14
$Mo_{0.10}$-NiSe	**18.07**	**0.768**	**0.64**	**8.92**	**7.74**	**This work**

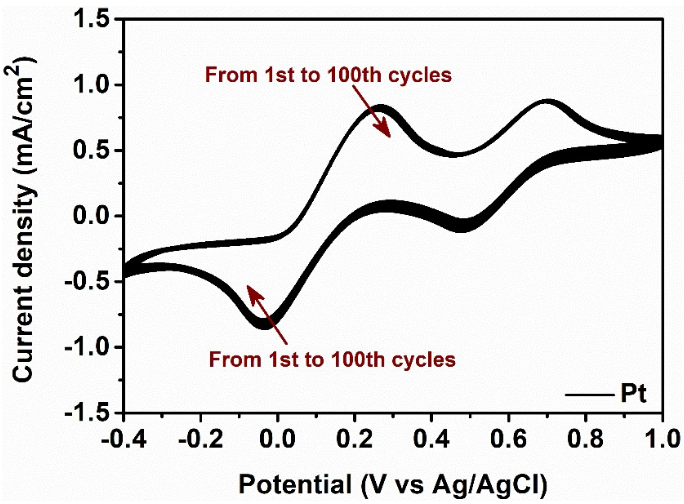

Fig. S2 100 consecutive CV curves of Pt CEs.

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