[Electronic Supplementary Information]

Structure of Ni(OH)₂ Intermediates Determines The Efficiency of NiO-based Photocathodes – A Case Study Using Novel Mesoporous NiO Nanostars

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A. Synthesis and Possible Formation Mechanism of NiO Nanoflakes and NiO Nanoparticles

Synthesis of NiO nanoflakes (NF) was carried out by dissolving 2.5 g NiSO₄ and 0.5 g potassium persulfate into 200 mL distilled water and subsequent stirring at 50°C for 15 mins. An amount of 2.5 mL NH₄OH was then added drop wise into the solution. The possible reaction mechanism to yield Ni(OH)₂ is described as follows:

The preformed NiO, that is either $M(OH)_2$ or MOOH might be the brucite crystals showing weak interaction between layers (formation of flakes) and the strong binding within the layered planes.

Synthesis of compact NiO nanoparticles (NP) was carried out by preparing 0.1 M of Ni(CH₃COOH)₂.2H₂O in diethylene glycol (DEG) and heating at 180°C. Once the reaction temperature reached 150°C, 10 mL of distilled water was injected and the solution was stirred for 2h. A green solution was obtained and cooled down in a flask and centrifuged. The reaction solution was annealed at 450°C for 2h to obtain NiO NP. The possible reaction mechanism to yield Ni(OH)₂ is described as follows:

Ni (CH₃COO)₂+ H₂O \rightarrow Ni(OH) (CH₃COO) + CH₃COOH.

Condensation between the hydrolyzed Ni(CH₃COO)(OH) yields a Ni–O–Ni bond

Ni (CH₃COO)₂+ Ni(OH) (CH₃COO)→Ni₂(O) (CH₃COO)₂+ CH₃COOH

Ni(OH) (CH₃COO) + Ni(OH) (CH₃COO) \rightarrow Ni₂(O) (CH₃COO₂)+ H₂O.

Following the Raman analysis for NiO NS to track the intermediates during synthesis, Raman spectra of intermediates during synthesis of NiO NP and NiO NF are recorded (Fig. S1). The assignment of Raman bands of intermediates, e.g. Ni(OH)(CH₃COO), Ni(OH)₂ in α or β phase, and [Ni(H₂O)_{6-x}(NH₃)]²⁺, is based on the Raman spectra reported in literature.¹⁻³



Fig. S1. Raman spectra of reaction solution containing intermediates during the synthesis of (a) NiO NP and (b) NiO NF.



Fig S2. (a) TEM image of intermediate product during synthesis of NiO NS and the corresponding SAD at position No. 2. HRTEM images and FFT analysis of intermediate product of NiO NS at position (c,d) No. 3 and (e,f) No. 4.



Fig. S3 FTIR spectra of the NiO with different nanostructures including nanoflakes, nanoparticles, and nanostars, prepared at different temperatures: 100°C (black), 200°C (red), 300°C (blue), and 400°C (green).



Fig. S4 Raman spectra of the preform $Ni(OH)_2$ (grey) and NiO (black) with different nanostructures including nanoflakes, nanoparticles, and nanostars.

In order to assess the Ni(OH)₂ polymorph prior to transform into pristine NiO, FTIR measurements were carried out. Theoretical calculation and experimental data of the IR vibrational mode of α - and β -Ni(OH)₂ have been reported in literatures.¹⁻⁶ In general, a broad peak between 3500 and 3200 cm⁻¹ is attributed to the O–H stretching of free H₂O originating from either α -or β -Ni(OH)₂. Therefore, assignment in this frequency range is not considered. IR bands of Ni(OH)₂-NF in the range of 1600 – 900 cm⁻¹ are spectrally matched with the lattice OH and O-H bend vibration as well as the lattice mode of α -Ni(OH)₂. In contrast, the IR bands of Ni(OH)₂-NS in the similar frequency ranges are spectrally matched with the β -Ni(OH)₂ showing O-H bend vibration and E_u (LO, longitudinal optical phonon) at 1638 cm⁻¹; E_g and A_{2u} (TO, transverse optical phonon) combination at 1384 cm⁻¹; and E_u(LO) O-H bend vibration at 1045 cm⁻¹. Vibrational spectrum of Ni(OH)₂-NP shows IR bands which combine the IR bands for both α - and β -Ni(OH)₂.

In a good agreement with DSC analyses described in the main paper, the results from XRD measurement confirm that NiO crystalline can be obtained by minimum annealing temperature of 300°C for NiO NP and NiO NF. Broad peak of crystal plane reveals implicitly the effect of crystal defects and dislocation, further verified by PL emission. According to the Scherrer's estimation the average crystallite size is 2.4 and 2.7 nm for NiO NF annealed at 300°C and 400°C, respectively, while NiO NP has crystallite size of 28.8 nm.



Fig. S5. X-ray diffraction pattern of Ni(OH)₂ (black) and NiO (red) of (a) NiONF, (b) NiO NS, and (c) NiO NP. The right panel shows the electron density map of NiO NS and NiO NF derived from the Fourier analysis of X-ray diffraction pattern. The Ni and O atoms in the electron density map are placed in the corner of figures (Ni: bottom-left and top-right, while O: top-left and bottom-right).

B. Optical and Physical Properties of NiO Nanostructures

Optical properties is assessed from the UV/vis absorption and emission measurement. Absorption band in the range of 370 - 390 nm is observed at room temperature and the absorption onset is systematically red-shifted upon higher annealing temperature. The pronounced red-shift is owing to quantum confinement effect altering the energy band of NiO. The estimated energy gap of NiO nanoparticles, nanoflakes and nanostars is 3.755 - 3.7654 eV, 3.781-3.789 eV and 3.815 - 3.816 eV, respectively. This calculated energy gap is consistent with earlier findings.⁴⁻⁶ Photoluminescence (PL) emission spectra of NiO were obtained at room temperature with an excitation wavelength of 310 nm. The PL emission is generally divided into near band edge (NBE) UV emission, indicated by the arrow, and deep level (DL) defect related visible emission.⁷⁻⁹ The UV emission is attributed to the direct recombination of excitons

through an exciton-exciton scattering. The visible emission of NiO originates from the radiative recombination of a photo-generated hole with an electron occupying the oxygen vacancy.⁷



Fig. S6 Absorption spectra of NiO nanoparticles (a), nanoflakes (b) and nanostars (c) at annealing temperature of 100, 200, 300 and 400 °C. (d) the Tauc-plot ($(\alpha hv)^2$ vs hv) with extrapolated linear curve determining the optical band gap of NiO.



Fig. S7 Photoluminescence emission spectra of NiO nanoparticles (a), nanoflakes (b) and nanostars (c) at annealing temperature of 300 and 400 °C.

The physical properties, particularly the surface area and the pore distribution, is assessed by BET measurements (Fig. S8). For NiO NP and NiO NF, N₂ adsorption-desorption curves shows typical type IV isotherm curves indicating the both NiO structures possess mesoporous structures (verified by BJH pore distribution showing peak pore distribution at 1.882 nm). For NiO NF, the presence of type H2 hysteresis loop at higher pressure shows disordered materials with unwell defined pore size and shape distribution as also observed in SEM images. Nonetheless, from BET calculation the specific surface area of NiO NF is 121.9 m²/g, which is a class of large surface area p-type semiconductor. Meanwhile, the specific surface area of NiO NS and NiO NP is 44.9 and 21.2 m²/g, respectively.



Fig. S8 N_2 adsorption and desorption curves of (a) NiO NS and (c) NiO NP. BJH pore distribution of (b) NiO NS and (d) NiO NP determined from the isotherm desorption curves.

C. Electrochemical Characterization of NiO Nanostructures

To investigate the effect of defects and trapping states on the performance of NiO nanostructures as a photocathode material in DSSCs, NiO NS, NiO NP, and NiO NF are deposited on FTO glass and annealed at a certain heat treatment to avoid surface cracks (Fig. S9).



Fig. S9 The heat treatment scheme to prepare NiO photocathode using NiO NS, NiO NP, and NiO NF.

Cyclic voltammetry and impedance measurement of NiO were carried out using computer controlled potentiostat-galvanostat (Princeton Applied Research VersaSTAT) in three electrode system using 0.2 M KCl as the supporting electrolyte and 0.01 M KH₂PO₄ and 0.01 M K₂HPO₄ as the buffer. The working electrode was NiO deposited on thin film Pt coated FTO glass whiles Pt disk and Ag/AgCl (saturated) electrode were used as counter and reference electrode, respectively. To obtain cyclic voltammogram, the scan rate was set to 100 mV/s.

To estimate the valence band edge of NiO, impedance measurement was carried out using a computer-controlled potentiostat-galvanostat (Princeton Applied Research VersaSTAT). The amplitude of ac potential was 10 mV and the applied frequency was 1 kHz. The selected potential range was based on the current-voltage measurement where the flat current was obtained using LSV (linear scan voltammetry) technique. Capacitance (C) of NiO was extracted by fitting the impedance data (Nyquist and Bode plot) using modified Randle circuit as equivalent circuit model, *i.e.* the ideal capacitor was replaced with constant phase element (pseudocapacitor).¹¹ The extrapolation of plot C⁻² vs. electrode potential of NiO to x-axis (Fig. S10) reflects the flat band potential which is close to valence band edge of NiO.



Fig. S10 Plot of C⁻² [(capacitance)⁻²] vs. electrode potential of NiO deposited on thin film Pt/FTO substrate in 0.2 M KCl with potassium phosphate buffer (pH 7).

To obtain the trapping state density, open-circuit voltage decay (OCVD) measurements were carried out. The NiO photocathode are sensitized with the commercial organic dye, P1, and assembled into DSSCs employing an iodine-based electrolyte. The photoelectrochemical properties were characterized under irradiation provided by a solar simulator with an intensity of 100 mW·cm⁻² to obtain OCVD. The transient open-circuit voltage (V_{OC}) decay are evaluated (Fig. S11) with bi-exponential fitting function resulting in two different lifetimes (τ_n) corresponding to hole lifetimes at the bulk traps and surface states/traps. To analyze the distribution of bulk traps and surface traps qualitatively, log response time vs voltage curves are presented. The OCVD curves (log response time vs voltage) is fitted according to the electrochemical model¹² as follow:

• The response time as function of voltage decay is presented as:

$$\tau_n = -\frac{k_B T}{e} \left(\frac{dV_{OC}}{dt}\right)^{-1}$$

where k_B is Boltzman constant, T is absolute temperature, e is elementary charge, V_{oc} is open circuit voltage.

• The response time as function of chemical capacitance of trapping states and conduction band state is presented as:

$$\tau_{n} = \frac{C_{\mu}^{vb} + C_{\mu}^{bt} + C_{\mu}^{st}}{C_{\mu}^{vb} \frac{1}{\tau_{vb}} + C_{\mu}^{st} e_{red}(E_{F})}$$

where τ_{VB} is valence band lifetime, E_F is Fermi potential, e_{red} is transition probabilities, $C_{\mu}^{(vb,bt,st)}$ is chemical capacitance of valence band state^(cb), surface traps^(st) and bulk traps^(bt).



Fig. S11 Transient open circuit voltage decay of (a) NiO NS, (b) NiO NP, and (c) NiO NF measured under Xe-lamp irradiation in DSSC assembly.



Fig. S12 Cathodic photocurrent densities recorded for commercial NiO electrode (Dyenamo©) in the presence of $[Co(NH_3)_5Cl]Cl_2(20 \text{ mM})$ as IEA. The measurements were carried out in acetate buffer 0.1 M (pH 4.5) at an applied potential of 0 V *vs*. Ag/AgCl.

NiO structure ¦	Dye	J-V				
		Jsc / mA·cm ⁻²	Voc / V	FF	μ/%	Γ / mA·nmol
NS	Ru2	3.72	0.129	0.32	0.144	0.181
	P1	3.95	0.121	0.31	0.145	0.096
	C343	2.50	0.105	0.30	0.078	0.170
NP	Ru2	0.49	0.125	0.31	0.018	0.039
	P1	0.64	0.115	0.32	0.023	0.042
	C343	0.16	0.091	0.24	0.002	0.022
NF	Ru2	0.21	0.141	0.33	0.010	0.030
	P1	0.34	0.156	0.28	0.015	0.043
	C343	0.28	0.228	0.38	0.024	0.090

Table S1 Photoelectrochemical properties of DSSCs using different NiO photocathodes and different

 dyes derived from current-voltage measurement under 1 sun irradiation.

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