Supporting information

## Solution-Processed Nickel Oxide Nanoparticles with NiOOH for Hole Injection Layers of High-Efficiency Organic Light-Emitting Diodes

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### • Additional optical transmittance data of NiO<sub>x</sub> NP layers



Fig. S1 Transmittance spectra of the  $NiO_x$  NP films with different thicknesses deposited on glass when bare glass is used as reference.

#### • XPS data analysis



**Fig. S2** XPS spectra of the prepared NiO<sub>x</sub> NP films on glass; (a) Ni  $2p_{3/2}$  and (b) O 1s of the NiO<sub>x</sub> NP film annealed in N<sub>2</sub>, (c) Ni  $2p_{3/2}$  and (d) O 1s of NiO<sub>x</sub> NP film annealed in air. The black dotted lines are the experimental data and the black solid lines are the fitted data. The XPS spectra were fitted for the NiO, Ni(OH)<sub>2</sub>, and NiOOH peaks. The broad peak (green dotted line) in the Ni  $2p_{3/2}$  spectrum has been ascribed to a shake-up process in the NiO structure.

Components	Ni 2p <sub>3/2</sub> binding energy (eV)	O 1s binding energy (eV)	Component ratio from Ni 2p <sub>3/2</sub> (%)	Component ratio from O 1s (%)
NiO	853.88	529.38	41.97	44.29
Ni(OH) <sub>2</sub>	855.48	531.08	34.98	34.53
NiOOH	856.68	531.98	23.05	21.18

Table S1 Binding energies and component ratios of Ni 2p<sub>3/2</sub> and O 1s signals from Fig. S2c-d.

• Additional data for energy level band diagram



Fig. S3 Absorbance spectra of the HAT-CN and PEDOT:PSS films on glass.



Fig. S4 Energy level band diagram of OLEDs using HAT-CN or PEDOT:PSS HIL.

### • A comparison of the electrical conductivity and the work function between airannealed NiO<sub>x</sub> and N<sub>2</sub>-annealed NiO<sub>x</sub>.

To investigate the electrical conductivity characteristics of NiO<sub>x</sub> NP layer depending on annealing environment, we fabricated hole only devices (HODs) using each NiOx layer. The structure of the HOD was ITO / NiO<sub>x</sub> NP (20 nm) / NPB (50 nm) / TCTA (10 nm) / Al. The charge transport in this kind of devices is possible solely by holes since the electron transport is blocked due to the large barrier between the work function of Al and lowest unoccupied molecular orbital (LUMO) of TCTA. The current density of HOD using air-annealed NiO<sub>x</sub> is higher by two orders of magnitude at 2.5 V which is near the turn-on voltage of the OLEDs, and over 1000 times higher at 6 V than that using N<sub>2</sub>-annealed one as shown in Fig. S5. This experimental data supports that air-annealed NiOx NP layer has higher conductivity. To compare work functions of each NiO<sub>x</sub>, we performed UPS analysis as shown in Fig. S6. The valence band edge of air-annealed NiO<sub>x</sub> NP layer (0.53 eV) is 0.15 eV lower than that of N<sub>2</sub>annealed one (0.68 eV). The work functions of air-annealed and N<sub>2</sub>-annealed NiO<sub>x</sub> is 4.86 eV and 4.67 eV, respectively. We also measured band gaps, but there is no difference between two. Considering these values, the energy band diagram of NiO<sub>x</sub> and NPB is as shown in Fig. S7. Air-annealed NiO<sub>x</sub> has substantially low injection barrier to the HOMO of NPB, and thus has enhanced hole transport characteristics.



Fig. S5 J–V characteristic of the hole only devices using NiO<sub>x</sub> depending on annealing environment



Fig. S6 UPS spectra of air-annealed NiO<sub>x</sub> and N<sub>2</sub>-annealed NiO<sub>x</sub>



Fig. S7 Energy band diagram of NiO<sub>x</sub> depending on annealing environment

# • Device performance of OLEDs using $NiO_x$ annealed at low temperature but longer time & FTIR measurement.

To verify that the low current density is due to the residual organic compounds in the HIL, we investigated the performance of OLEDs using NiO<sub>x</sub> annealed at low temperature but longer time. When the NiO<sub>x</sub> layer was annealed at 100 °C, we could observe that the current density increases distinctly for longer annealing time, as shown in Fig. S8. However, the current density of the OLEDs at the range of working voltage was saturated after 24 h annealing and the value was still too low.



Fig. S8 J–V characteristic of the OLEDs using NiO<sub>x</sub> annealed at 100°C for various times

When the NiO<sub>x</sub> layer was annealed at 200 °C, we also could observe that current density of the OLED apparently increases. However, in contrast to the case of 100°C annealing, the current density of the OLED using 200°C-36hr-annealed NiO<sub>x</sub> reached up to 1/10 of that using 270 °C-annealed NiO<sub>x</sub> as shown in Fig S9. These experimental data support the fact that the low device performance at lower annealing temperatures is attributed to residual organic compounds.



Fig. S9 (a) J–V characteristics of the OLEDs using (a)  $NiO_x$  annealed at 200°C for various times. (b) Comparison of J–V characteristics

However, this data cannot tell which organic components (i.e. solvent or surfactant) actually remains at lower annealing temperature. Thus, to further examine the ground of this phenomena, we performed FTIR measurement for 270°C-10min, 200°C-1hr, 200°C-36hr

annealed NiO<sub>x</sub> samples, as presented in Fig. S10. Distinct differences in the vibration modes in the FTIR spectra of 200°C-1hr NiO<sub>x</sub> were observed in the ranges of ~3400, 2850–3000 and ~1600 cm<sup>-1</sup>, which corresponds to N–H stretch mode, C-H stretch mode, and N–H bending mode, respectively.<sup>1</sup> Considering 1) the organic compounds we used to synthesize the NiO<sub>x</sub> NP ink and 2) two N–H modes in the FTIR spectrum, we can tell that oleylamine (C<sub>18</sub>H<sub>37</sub>N), at least, remains in the NiO<sub>x</sub> layer possibly as a surfactant of the nanoparticle. Since C–H stretch mode can be detected from both the ink solvent (tetradecane, C<sub>14</sub>H<sub>30</sub>) and oleylamine, we cannot tell at this time if tetradecane also remains in the 200°C-1hr NiO<sub>x</sub> layer.



Fig. S10 FTIR spectra of NiO<sub>x</sub> annealed at different conditions

• Effects of thickness variation of NiO<sub>x</sub> NP layers on OLED performances



**Fig. S11** Device performance of the OLEDs using 20–45-nm-thick NiO<sub>x</sub> NP layers. (a) J–V–L characteristics and (b) current efficiency–luminance and power efficiency–luminance characteristics.



**Fig. S12** Device performance of the OLEDs using 45–145-nm-thick NiO<sub>x</sub> NP layers. (a) J–V–L characteristics and (b) current efficiency–luminance and power efficiency–luminance characteristics.



**Fig. S13** Performance of OLEDs using 20–45-nm-thick NiO<sub>x</sub>. (a) Normalized EL spectra of OLEDs under an identical brightness of 10 000 cd m<sup>-2</sup>, (b) lifetime ( $L_{90}$ ) with an initial luminance  $L_0 = 1000$  cd m<sup>-2</sup>, and (c) luminance-current density characteristics.

**Table S2.** Device performance of OLEDs using NiO<sub>x</sub> NP of different thickness. The turn-on ( $V_T$ ) and driving voltages ( $V_D$ ) are obtained at a luminance of 1 and 1000 cd m<sup>-2</sup>, respectively. Current and power efficiency values of the OLEDs at the maximum, at 1000 cd m<sup>-2</sup>, and at 10 000 cd m<sup>-2</sup>.

			Maximum		at 1000 cd m <sup>-2</sup>		at 10 000 cd m <sup>-2</sup>	
NiO <sub>x</sub> NP	V <sub>T</sub> (V)	V <sub>D</sub> (V)	Current efficiency (cd A <sup>-1</sup> )	Power efficiency (lm W <sup>-1</sup> )	Current efficiency (cd A <sup>-1</sup> )	Power efficiency (lm W <sup>-1</sup> )	Current efficiency (cd A <sup>-1</sup> )	Power efficiency (lm W <sup>-1</sup> )
20 nm	2.53	4.14	71.37	84.60	68.53	51.98	62.93	31.86
30 nm	2.54	4.21	71.27	85.31	68.44	51.13	61.94	30.05
45 nm	2.54	4.27	72.43	86.52	68.16	50.91	62.38	28.93

### • Additional performance data of OLEDs with various HILs

**Table S3.** Device performance of OLEDs with various HILs. The turn-on  $(V_T)$  and driving  $(V_D)$  voltages are obtained at a luminance of 1 and 1000 cd m<sup>-2</sup>, respectively.

HILs	$V_{T}(V)$	$V_D(V)$	Luminance at 8 V (cd m <sup>-2</sup> )
HAT-CN	2.52	3.97	40680
PEDOT:PSS	2.50	3.86	58750
NiO <sub>x</sub> NP	2.46	3.67	82750



**Fig. S14** Histograms of the maximum current and power efficiencies of OLEDs with various HILs. Twenty one devices were fabricated and characterized; (a) OLEDs with HAT-CN, (b) OLEDs with PEDOT:PSS, and (c) OLEDs with NiO<sub>x</sub> NP. The average current and power efficiency values are 68.69 cd A<sup>-1</sup> and 82.52 lm W<sup>-1</sup> for OLEDs with HAT-CN, 55.42 cd A<sup>-1</sup> and 57.41 lm W<sup>-1</sup> for OLEDs with PEDOT:PSS, and 73.44 cd A<sup>-1</sup> and 88.32 lm W<sup>-1</sup> for OLEDs with NiO<sub>x</sub> NP, respectively. The solid lines in the graphs are Gaussian fittings.



Fig. S15 The average values of the turn-on voltages, the driving voltages, the maximum current and power efficiencies, the current and power efficiencies at 1000 cd m<sup>-2</sup> and 10 000 cd m<sup>-2</sup> of 21 OLEDs using each HIL.

### • Performance comparison of OLEDs with various HILs

HILs		V <sub>D</sub> (V)	Maximum		at 1000 cd m <sup>-2</sup>		
	V <sub>T</sub> (V)		Current efficiency (cd A <sup>-1</sup> )	Power efficiency (lm W <sup>-1</sup> )	Current efficiency (cd A <sup>-1</sup> )	Power efficiency (lm W <sup>-1</sup> )	Ref
NiO <sub>x</sub> NP	2.5	3.7	73	88	69	59	This work
NiO <sub>x</sub> (sol–gel)	2.6	6.0	70	75	40	21	2
WO <sub>3</sub>	2.7	N/A	46	52	44	26	3
$V_2O_5$	3.0	5.1	N/A	N/A	65	35	4
MoO <sub>x</sub>	3.0	N/A	56	55	45	28	5
CuSCN	2.7	N/A	51	55	47	22	6

**Table S4** Summary of the performance of green phosphorescent OLED with different types of metal– oxide or metal-based HILs.

### References

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