

Supporting Information:

Synthesis of Unstable Colloidal Inorganic Nanocrystals through the Introduction of a Protecting Ligand

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Materials

Nickel(II) stearate ($\text{Ni}(\text{St})_2$), lithium stearate (LiSt), sodium stearate (NaSt), stearate acid (HSt) and 1-octadecanol (ODA, 97%) were purchased from Alfa. Oleylamine (80-90%) and 1-octadecene (ODE, tech. 90%) were purchased from Acros Organics. Copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$) was purchased from J&K. Chloroform, hexane, methanol, ethanol and ethyl acetate were analytical grade reagents from Sinopharm Chemical (China). All chemicals were used as received.

Characterization techniques

FTIR spectra were recorded on a Bruker Tensor 27 spectrophotometer at room temperature. To monitor the reactions for the synthesis of oxide nanocrystals, the samples were prepared by directly spotting hot aliquots taken at different intervals onto CaF_2 substrates.

UV-Vis transmission spectra were obtained using a Shimadzu UV-3600 spectrometer.

XRD measurements were performed on a X'Pert PRO system operated at 40 keV and 40 mA with Cu KR radiation ($\lambda = 1.5406 \text{ \AA}$).

TEM images were recorded by using a JEOL JEM 1230 microscope operated at 80 keV.

HRTEM were performed on a FEI Tecnai G2 F20 S-TWIN microscope operated at 200 keV.

ICP-AES and **ICP-MS** analysis were carried out using an IRIS Intrepid II XSP

ICP-AES equipment and an XSENIES ICP-MS equipment, respectively. The purified NiO nanocrystal samples were dissolved in concentrated HCl solutions (36-38 %). The metal ions were transferred to aqueous phase by extraction twice with distilled water.

UPS analysis were recorded on a Thermo ESCALAB-250Xi spectrometer using a UV radiation source (21.2 eV) and applying a -8 V bias.

AFM measurements were performed on a Veeco Metrology Atomic Force Microscope.

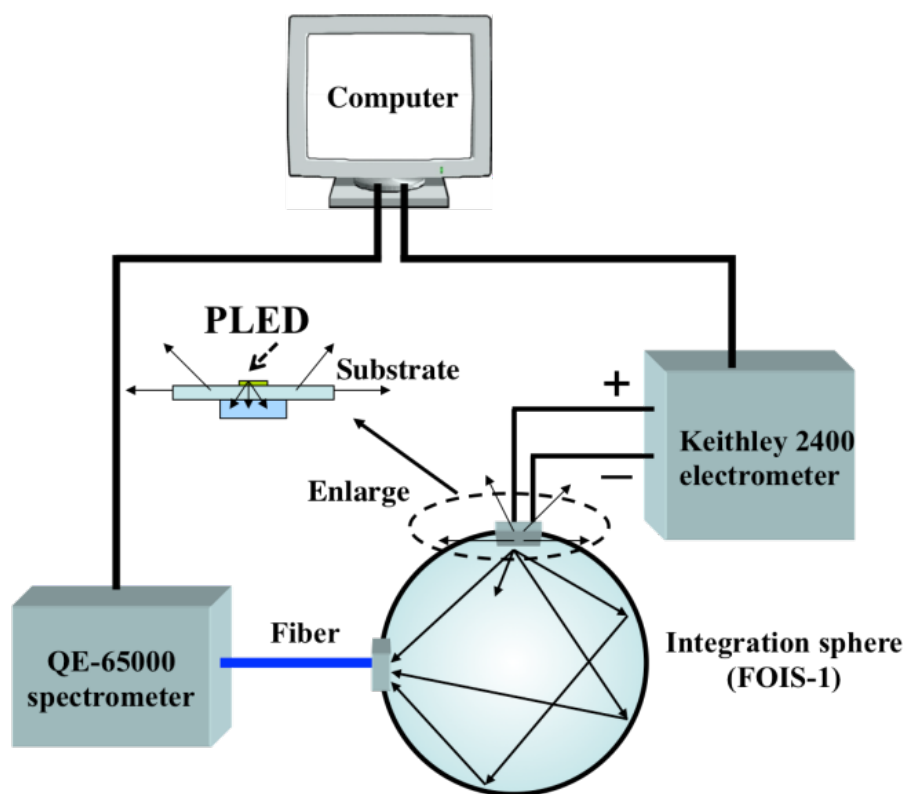
Device fabrication and characterization

Deposition of NiO nanocrystal thin films. ITO-coated glass substrates were cleaned by ultrasonication in acetone, deionized water and isopropyl alcohol, respectively, followed by UV-ozone treatment. Thin films were deposited by spin-casting a chloroform solution containing NiO nanocrystal (~ 5 mg/mL) at 4000 rpm for 60 s. Then the thin films were annealed at 130 °C for 1 h at ambient conditions, followed by UV-ozone treatment.

Organic solar cells were fabricated using a solution of TQ1:PC₇₁BM (9:27 mg/mL) in 1,2-dichlorobenzene. The blend was spin-cast onto the NiO nanocrystal thin films with a speed of 650 rpm for 60 s, followed by 3000 rpm for 30 s. Bi-layer top electrodes of LiF/Al (0.7/100 nm) were deposited by thermal evaporation under a base pressure of 6×10^{-7} Torr. The device area was 7.25 mm² defined by the overlapping of the ITO and top electrode. J-V characterization of the solar cells were

performed with a Keithley 2400 source meter controlled by a LabVIEW program under simulated AM 1.5 solar illumination (100 mW/cm^2). The light intensity was calibrated using a silicon reference cell.

PLED devices were fabricated by spin-coating a chlorobenzene solution of MEH-PPV (8 mg/mL) onto the NiO nanocrystal thin films. Bi-layer top electrodes of Ca/Al (20/100 nm) were deposited by thermal evaporation under a base pressure of 6×10^{-7} Torr. The device area was 3.24 mm^2 defined by the overlapping of the ITO and top electrodes. Reference devices using PEDOT:PSS interlayers were also fabricated. The PEDOT:PSS layers were spin-coated at 4000rpm for 60 s and baked at 145°C for 20 min. For the PLED testing, we used a Keithley 2400 electrometer for J-V characteristics and a fiber integration sphere (FOIS-1) coupled with a QE-6500 spectrometer for light output measurements, as shown in Scheme S1. Note that the ITO glass substrate was in close contact with the input port of the integration sphere. The area of the PLED device was considerably smaller than that of the input port (9.5 mm in diameter) so that the coupling factor of PLED-to-integration sphere was unity.



Scheme S1. PLED measurement system.

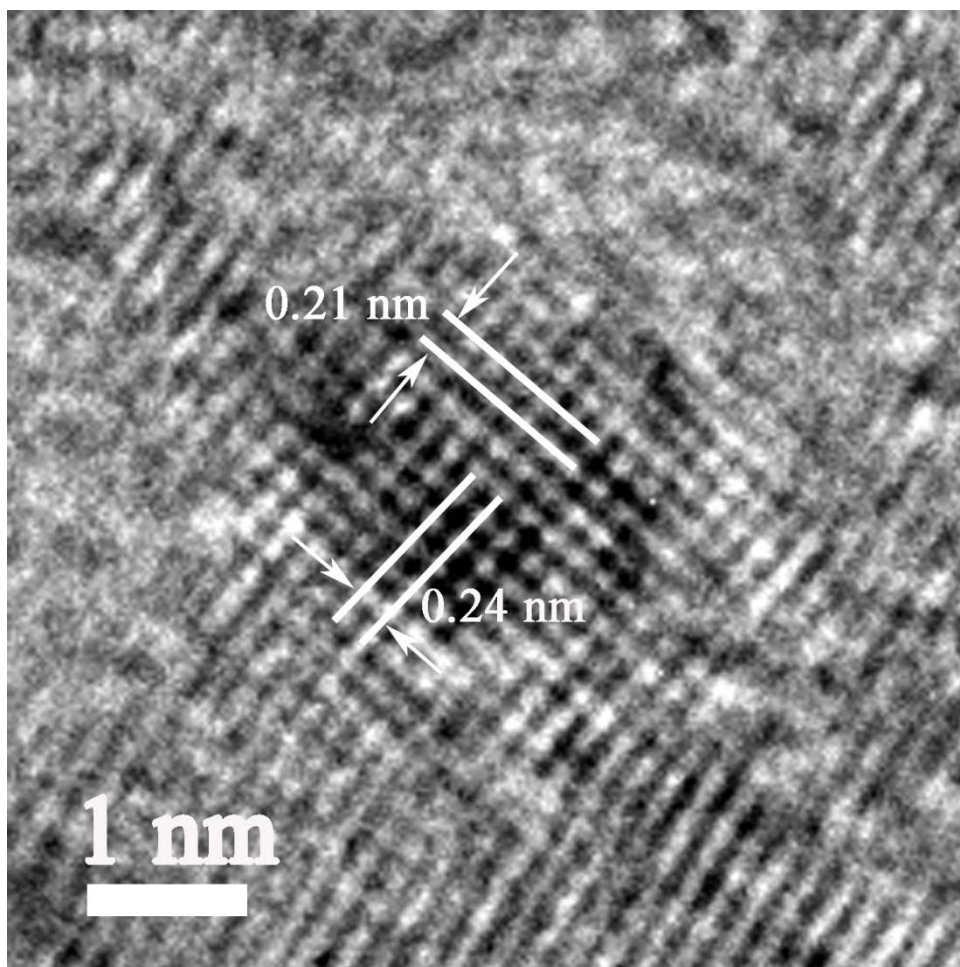


Figure S1. A typical HRTEM image of the irregular nanoparticles in the products from the reactions without the introduction of LiSt. The interplanar spacing of 0.21 and 0.24 nm corresponds to the {200} and {111} lattice planes of the rock salt structured NiO, respectively.

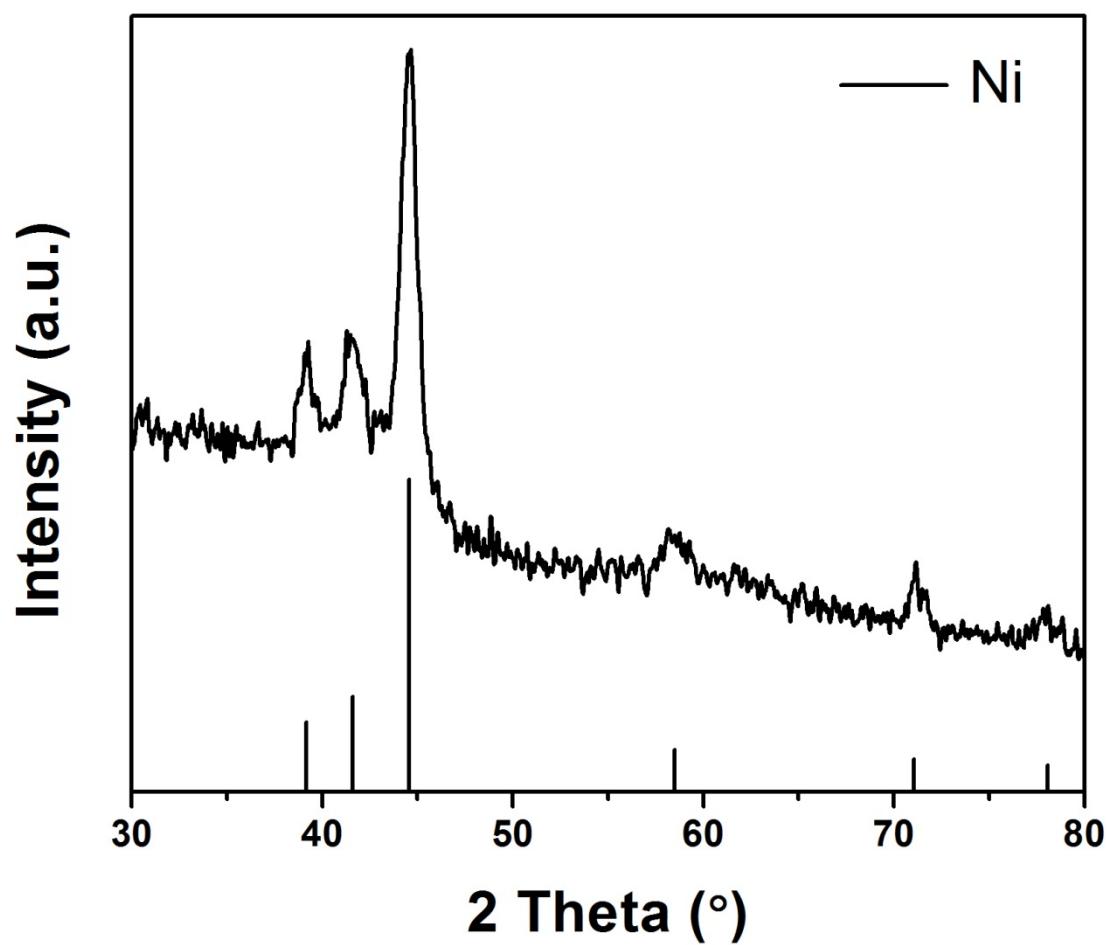


Figure S2. XRD profile of the products from the reactions without the introduction of LiSt. The reaction time was extended to 8 h.

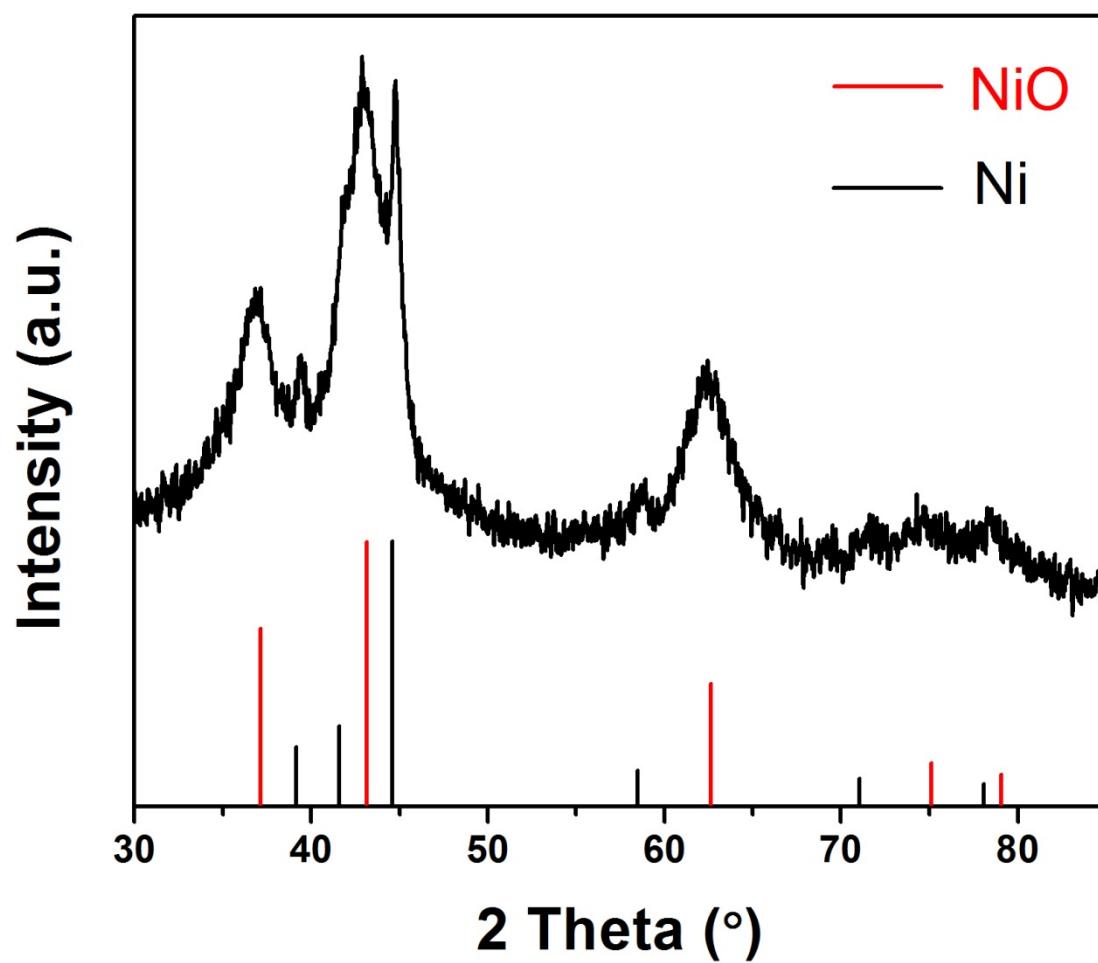


Figure S3. XRD profile of the products from the reactions without the introduction of LiSt. Additional free HSt (0.2 mmol) was introduced into the reaction system and all the other parameters were same.

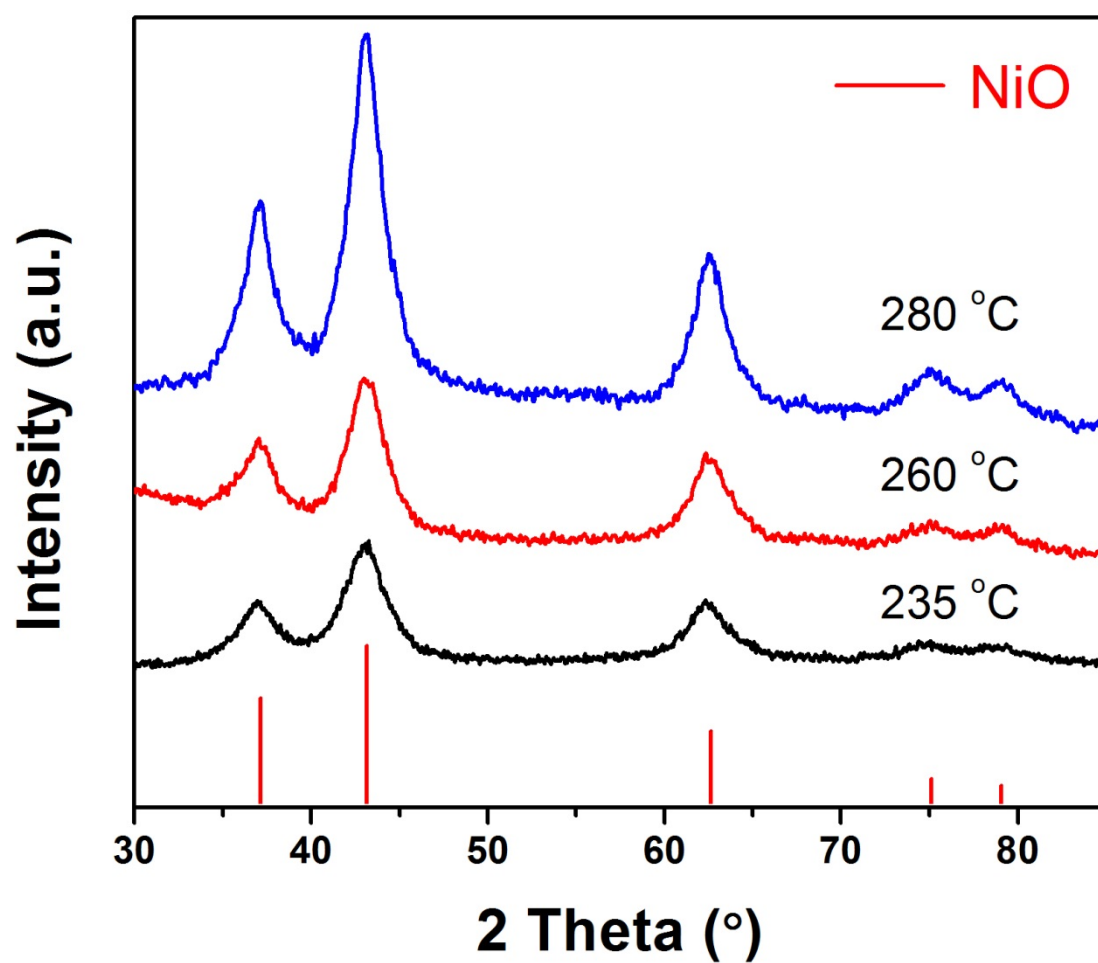


Figure S4. XRD characterizations on the products from the LiSt assisted reactions.

The reaction temperatures were varied from 235 to 280 °C and all the other reaction parameters were same.

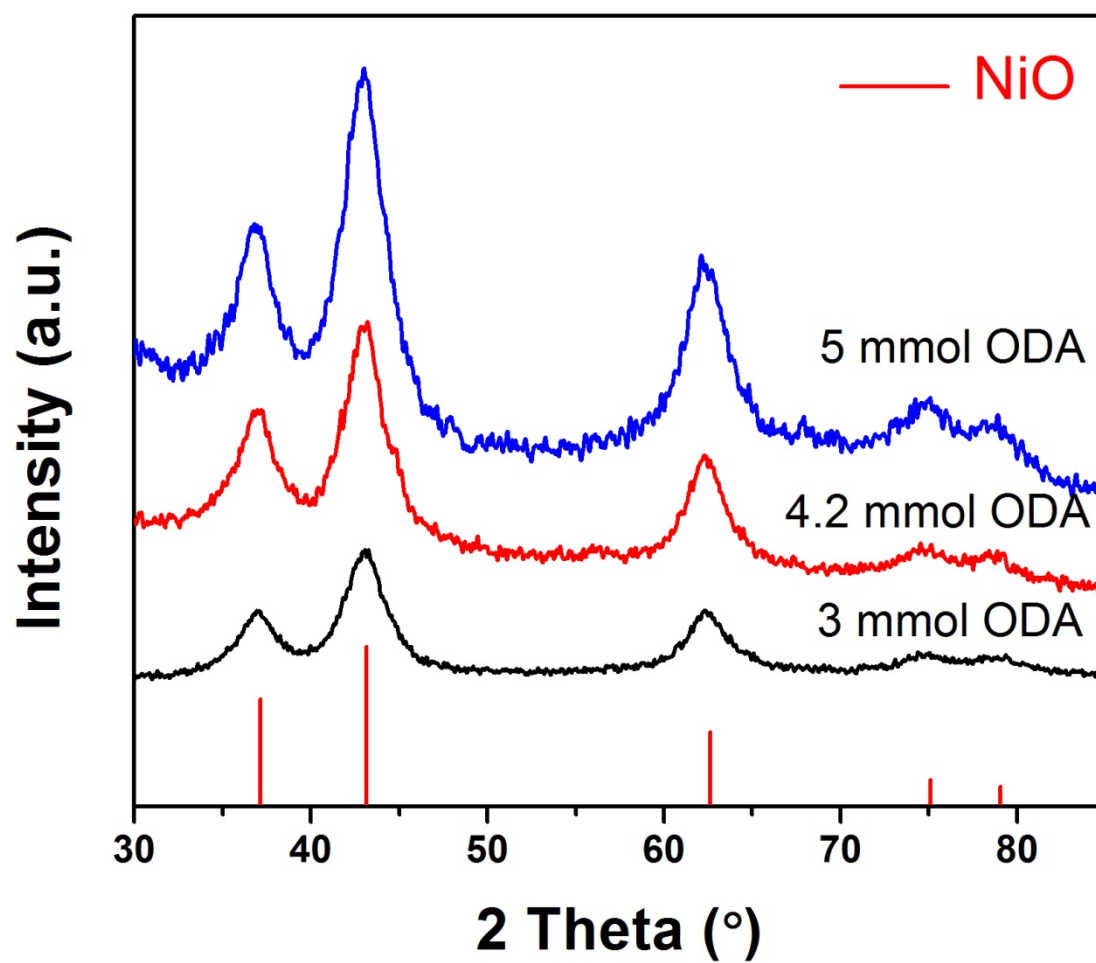


Figure S5: XRD characterizations on the products from the LiSt assisted reactions.

The molar ratios of ODA to $\text{Ni}(\text{St})_2$ were varied from 6:1 to 10:1 and all the other reaction parameters were same.

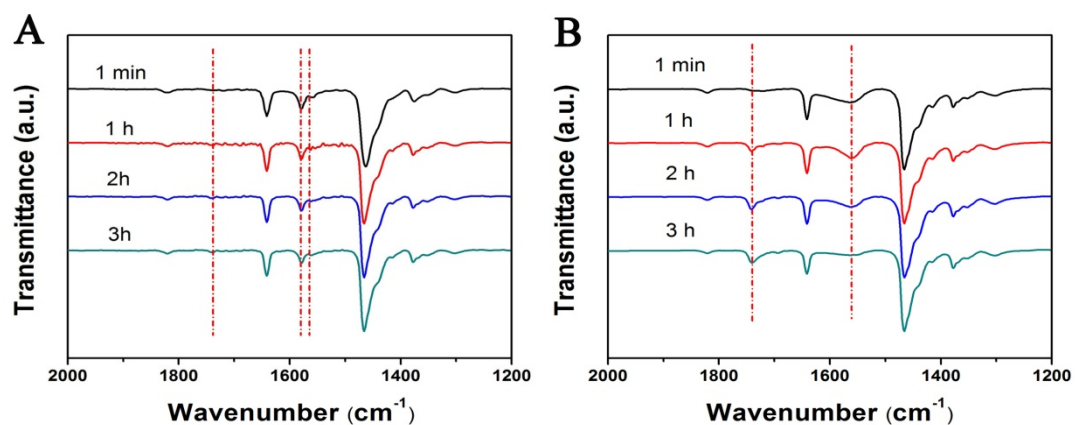


Figure S6. Temporal evolution of FTIR spectra for (A) a mixture of LiSt (0.5 mmol), ODA (3 mmol) and ODE (5 mL) heated to 235 °C and (B) a mixture of Ni(St)₂ (0.5 mmol), ODA (3 mmol) and ODE (5 mL) heated to 235 °C.

Table S1. Summary of FTIR assignments.

Sample	Characteristic peaks (cm ⁻¹)	Assignment
Oxide nanocrystals from the reaction without the introduction of LiSt	1550	Surface bound St ⁻
NiO nanocrystals purified by the first method	1550	Surface bound St ⁻
NiO nanocrystals purified by the second method	1550 & 1560	Surface bound St ⁻ & surface bound LiSt
Free LiSt	Doublet : 1580 (stronger) & 1560	Free LiSt

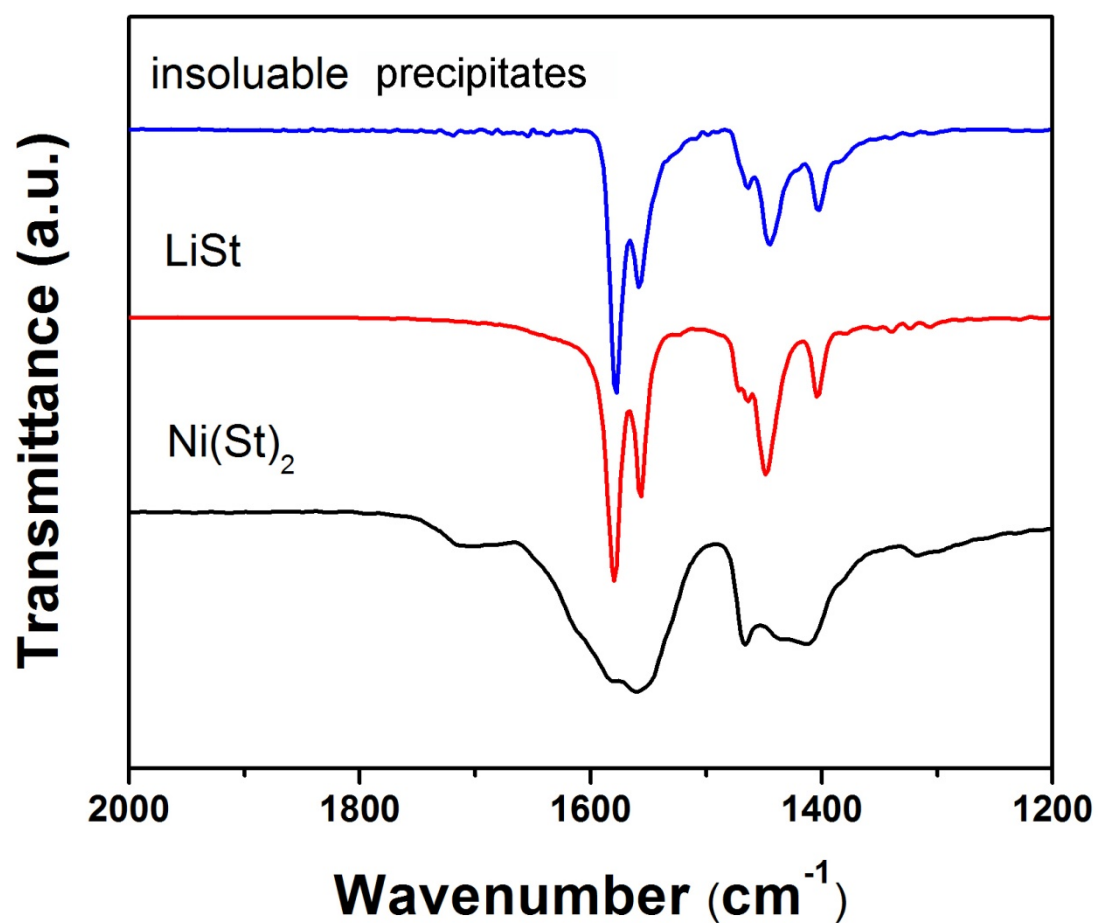


Figure S7. FTIR spectrum of the insoluble precipitates (top) that were separated from the hexane solution of nanocrystals by staying overnight. The FTIR spectra of LiSt (middle) and Ni(St)₂ (bottom) are also displayed.

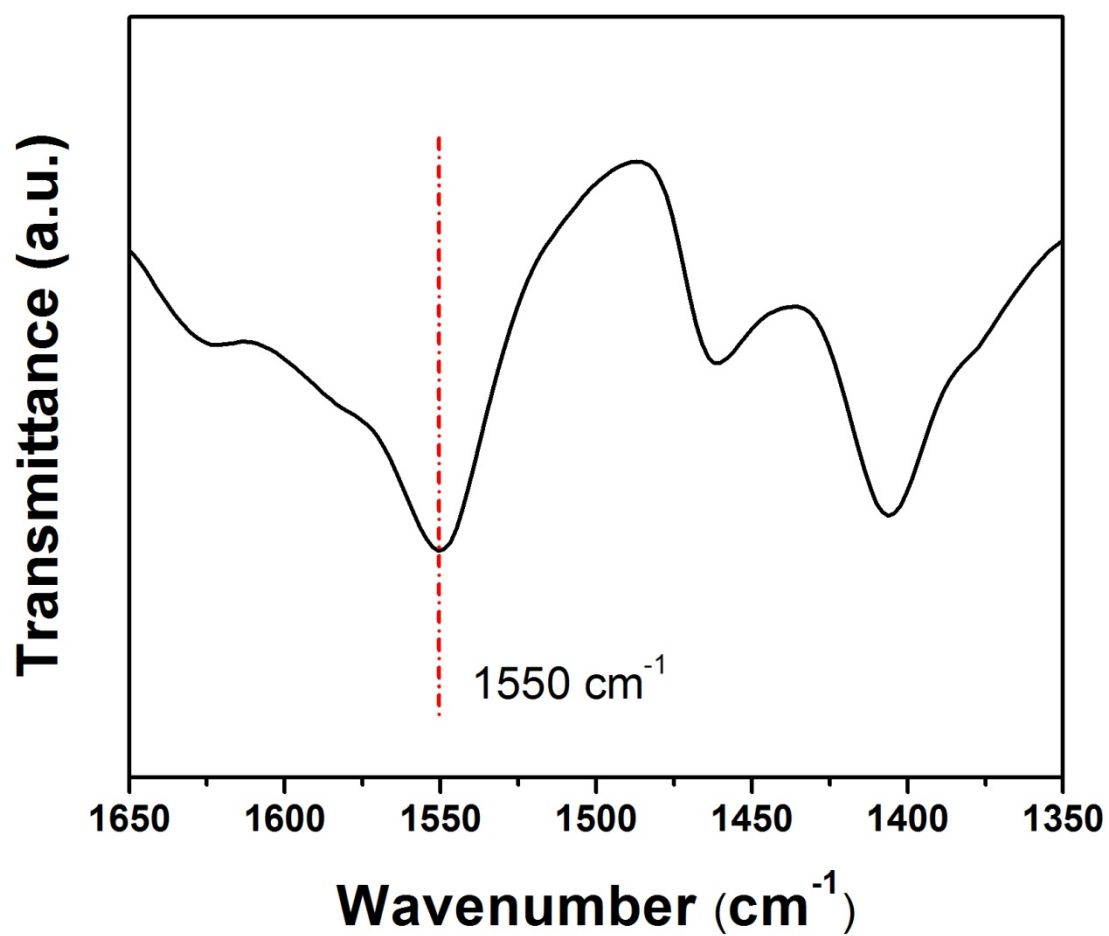


Figure S8. FTIR spectrum of the NiO nanocrystals purified by the second method and further intensively washed by hot methanol.

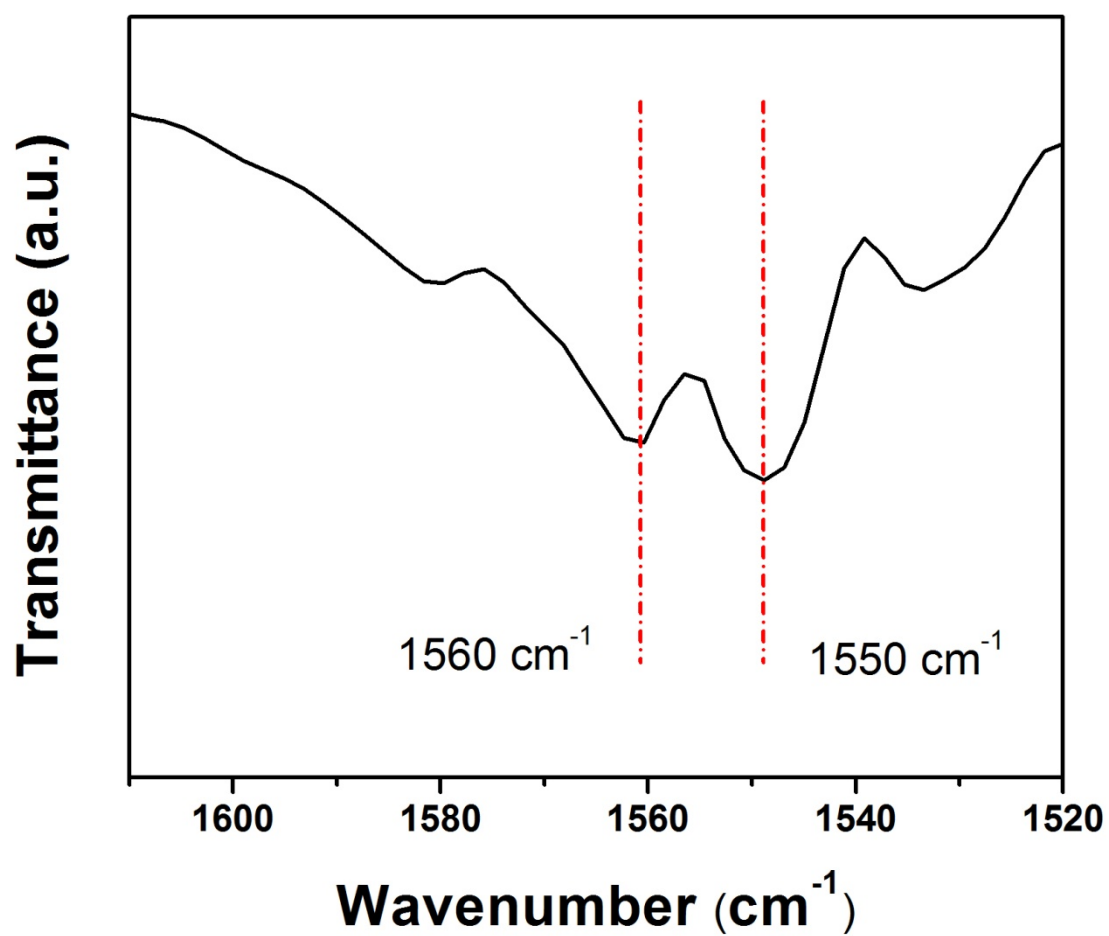


Figure S9. FTIR spectrum of the sample prepared by refluxing the NiO nanocrystals purified by the first method in a mixture of LiSt (0.2 mmol) and ODE (5 mL).

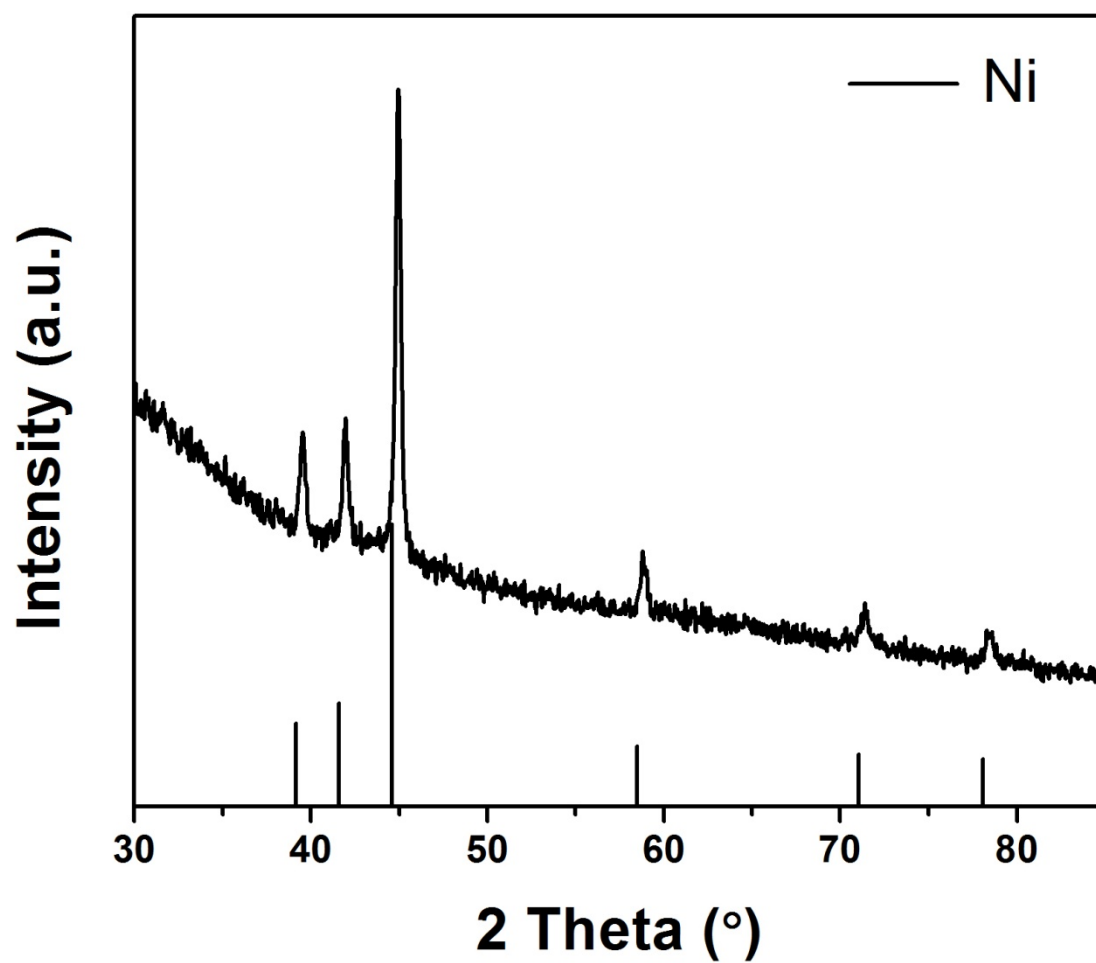


Figure S10. XRD pattern of the products from the reactions of refluxing the de-protected NiO nanocrystals in a mixture of ODE (5 mL) and ODA (3 mmol) at 235 °C.

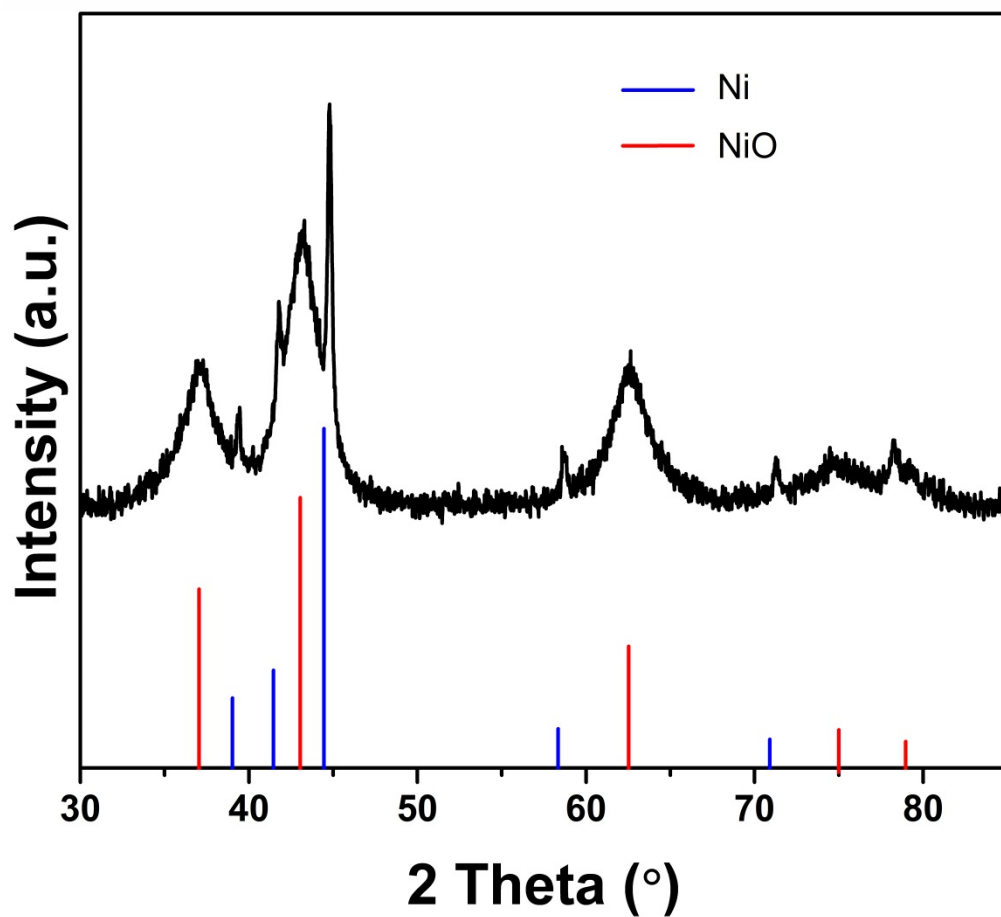


Figure S11. XRD pattern of the products from the reactions with the introduction of inert n-octadecane (0.2 mmol).

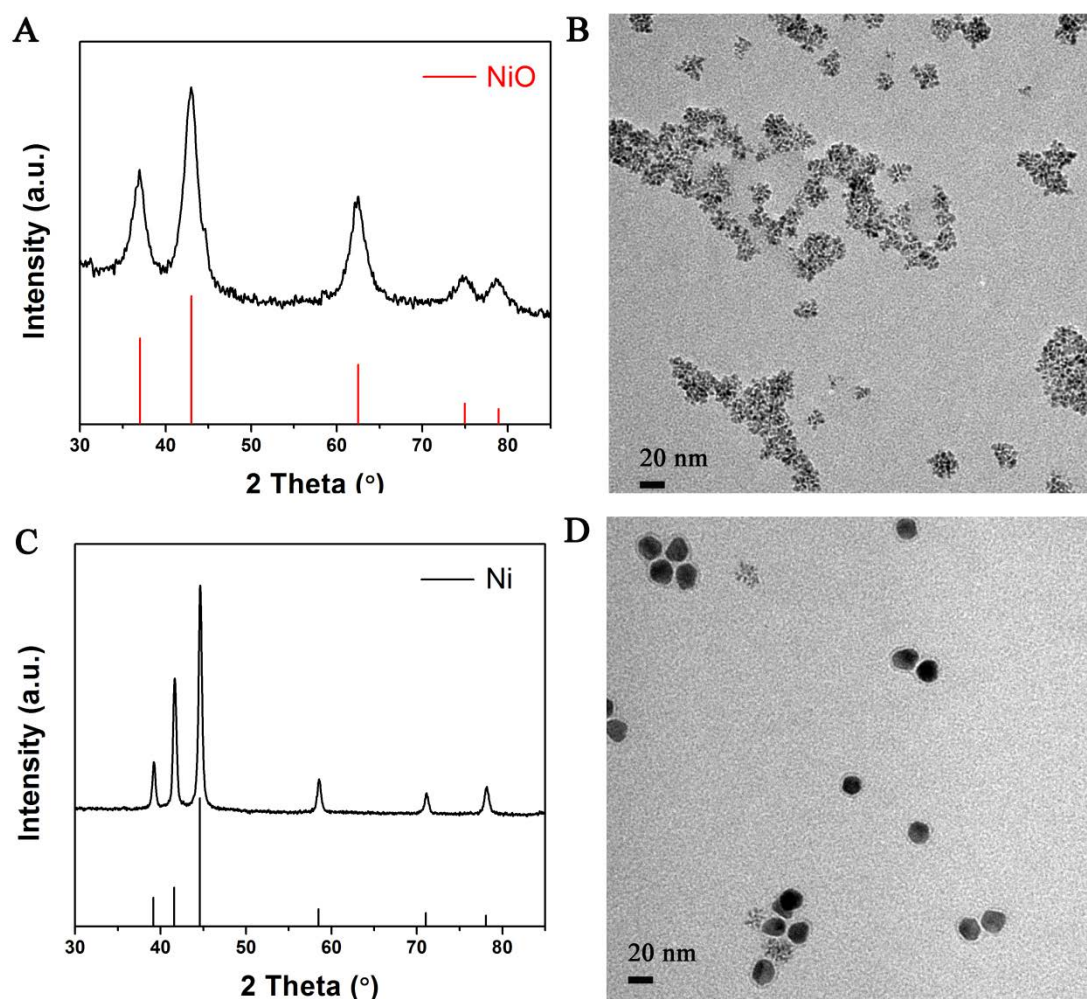


Figure S12. Synthesis of NiO nanocrystals by the aminolysis approach. Typically $\text{Ni}(\text{St})_2$ (0.5 mmol) and oleylamine (2 mmol) were used as the reagents. The reaction temperature was 240 °C. The reaction time was 2 h. (A) XRD profile and (B) a typical TEM image of the products from the LiSt (0.2 mmol) assisted aminolysis reactions. (C) XRD profile and (D) a typical TEM image of the products from the aminolysis reactions without the introduction of LiSt.

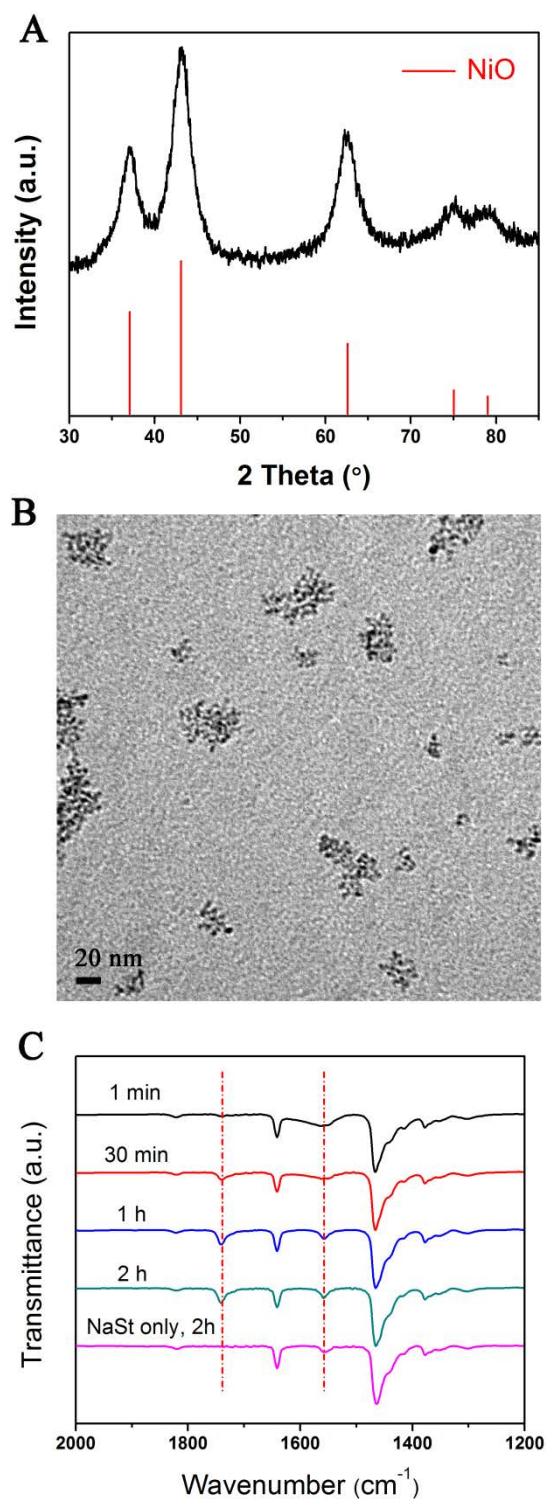


Figure S13. NaSt assisted synthesis of NiO nanocrystals. (A) XRD pattern and (B) a typical TEM image of the products. (C) Temporal evolution of FTIR spectra. The spectrum of the mixture of NaSt (0.2 mmol), ODA (3 mmol) and ODE (5 mL) heated at 235 °C for 2 h was also plotted.

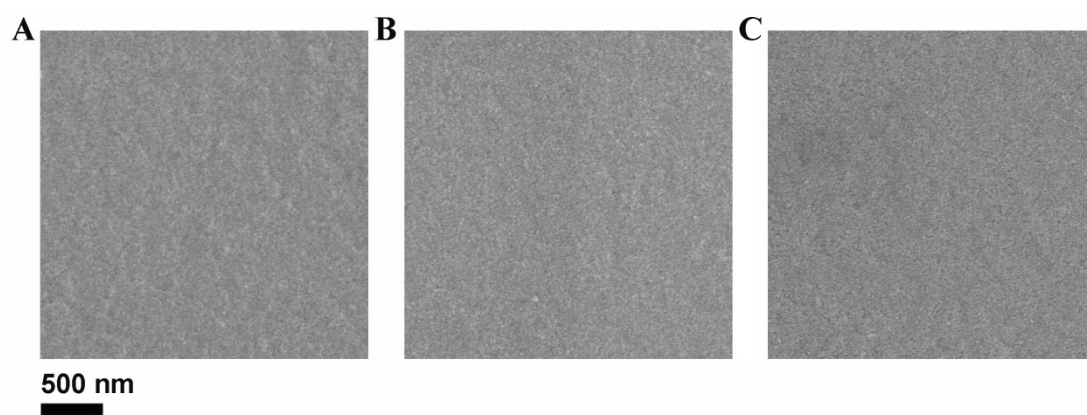


Figure S14. Typical SEM images of NiO nanocrystal films. (A) as-deposited films, (B) annealed films and (C) UV-ozone treated films.

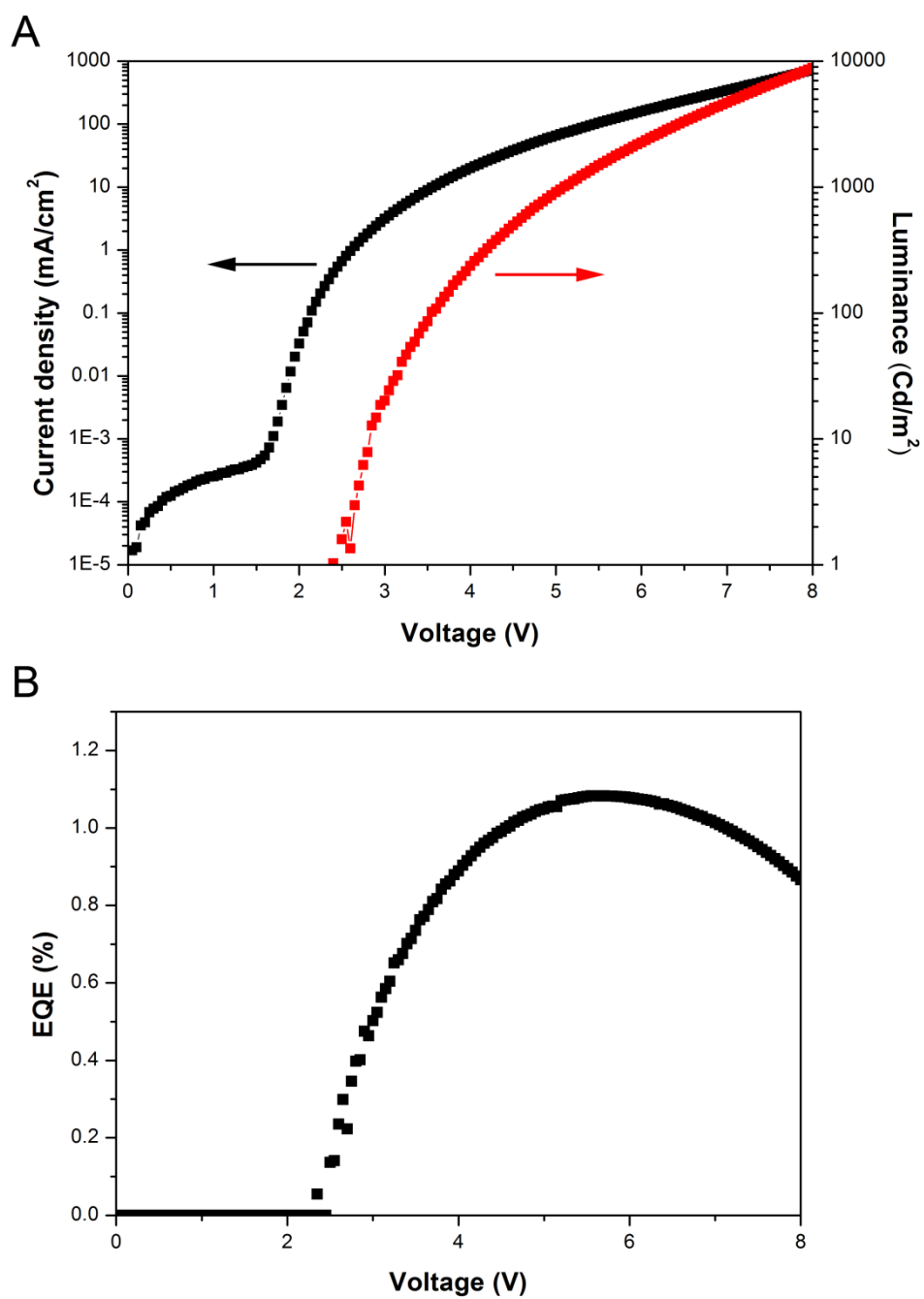


Figure S15. Flexible PLED device based on NiO nanocrystal HTLs. (A) Curves of current density and luminance versus applied bias. (B) EQE curve as a function of the applied bias.