

ADVANCED MATERIALS

Supporting Information

for

Advanced Materials, adma.200701389

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Supporting Information

Preparation and Surface Activity of Single Crystalline NiO(111) Nano-sheets with Hexagonal Holes, a Semiconductor Nanospanner

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Experimental Methods

Synthesis: In a typical synthesis of NiO nano-sheets, 9 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 ml absolute methanol. After the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ totally dissolved, 1 g urea and 6.7 g benzyl alcohol was added to the mixture in the ratio Ni:urea:BZ = 1:0.5:2 (molar ratio). After stirring for 1 h, the solution was transferred to an autoclave. The autoclave containing the reaction mixture was purged with 7500 torr Ar 5 times, and then a pressure of 7500 torr Ar was imposed before heating was initiated. The mixture was heated to 200 °C for 5 h, then to 265 °C and maintained at that temperature for 1.5 h, finally, the vapor inside was vented. A dry jade-green powder was collected and subsequently calcined with a ramp rate of 3 °C/min to 500 °C, then maintained at 500 °C for 6 h. The powder produced from this preparation contains solely the NiO nano-sheets possessing the (111) crystallographic planes with hexagonal holes (edge angles of 120°).

The materials were characterized by powder X-ray diffraction (XRD) using a Siemens D5000 X-ray diffractometer with nickel filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at a scanning rate of $0.1^\circ \cdot \text{min}^{-1}$ in the 2θ range of 5-80°. For the XRD pattern of NiO nano-sheets assembled on a Si wafer, the samples were prepared by dropping an ethanolic solution of NiO nano-sheets on a Si wafer and evaporating the solvent.

Transmission electron microscopic and electron diffraction characterization of the samples were carried out on a JEM-2010 operated at 200 kV. The samples were

prepared by spreading an ultrasonicated suspension in ethanol onto a grid. All TEM images in the supporting information were obtained on a Zeiss EM 900 operated at 80 kV.

In-situ DRIFTS investigation: A Thermo 4700 FTIR spectrometer with a liquid nitrogen cooled detector, a high temperature chamber and DRIFT accessory were used with the following parameters: 64 scans, 650-4000 cm^{-1} scan range, 4 cm^{-1} resolution.

In-situ DRIFTS investigation of NiO(111) nano-sheets: The sample temperature was measured through a thermocouple inserted into the sample holder directly in contact with the sample. A spectrum of the KBr was collected at room temperature under high vacuum and was used as the background. 10 mg of sample was placed into a high temperature sample holder; the chamber was evacuated and pressure remained 0.005 torr. The spectra were collected under high vacuum at room temperature. Following this scan, the temperature was raised to 100 °C, and another scan was taken. After this scan, the temperature was raised to 500 °C and maintained for 1 h, finally, the last spectra was collected.

In-situ DRIFTS investigation of methanol adsorption and surface reaction: 10 mg sample was pre-treated at 500 °C for 1 h under high vacuum to remove any water or other impurities from its surface. A spectrum of the clean sample surface was collected following this procedure at the adsorption temperature (room temperature or 70 °C) under high vacuum and was used as the background. Methanol vapour was obtained by evaporation under high vacuum. The high vacuum reactor, directly

connected to the DRIFTS chamber, allows us to work in flow conditions. Methanol was introduced into the reaction chamber at 0.005 torr while the NiO sample was maintained at the adsorption temperature (room temperature or 70 °C). For *in-situ* DRIFT spectra at room temperature, when the reaction chamber was evacuated to 1 and 0.005 Torr, respectively, the vacuum valve was closed and the spectra was collected after 2 minutes of equilibrium. For the experiments at 70 °C, after introduction of methanol and equilibrium for 3 minutes, the methanol introduction valve was closed; and the spectra were collected every several minutes.

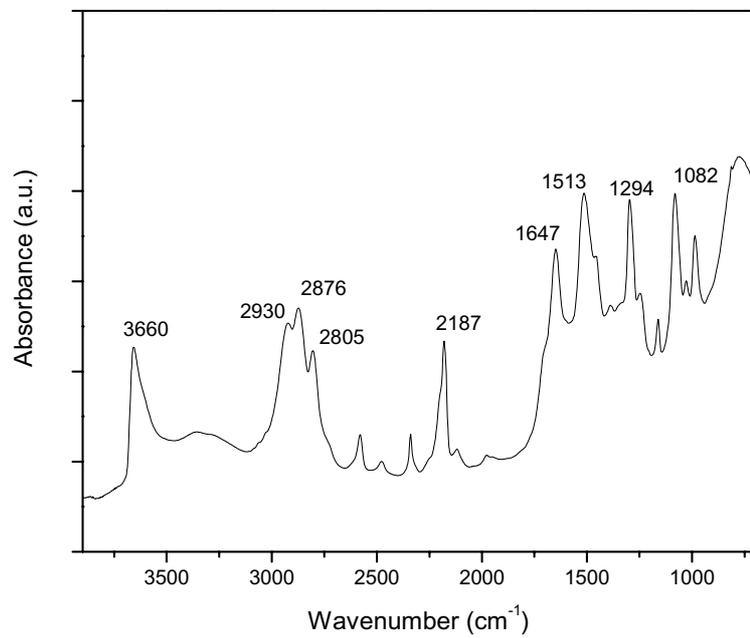


Figure S1. DRIFTS of the as-synthesized material at room temperature.

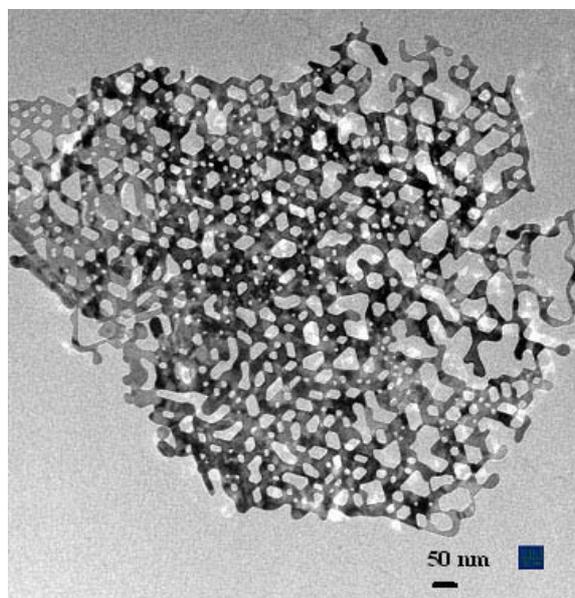


Figure S2. A typical TEM image of isolated NiO nano-sheets with holes prepared with the 1: 0.5 ratio of nickel nitrate to urea calcined at 500 °C with a temperature ramp of 3 °C/min. The diameter of the isolated nano-sheet is about 1 μm . There are numerous hexagonal holes in the nano-sheet and the edge angles are 120°.

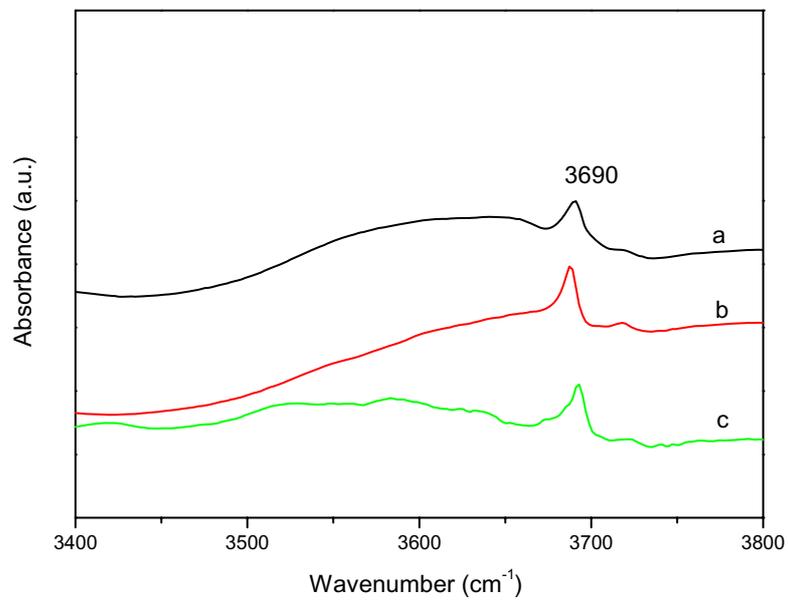


Figure S3. DRIFTS of NiO nano-sheets treated under high vacuum at (a) room temperature, (b) 100 °C, (c) 500 °C.

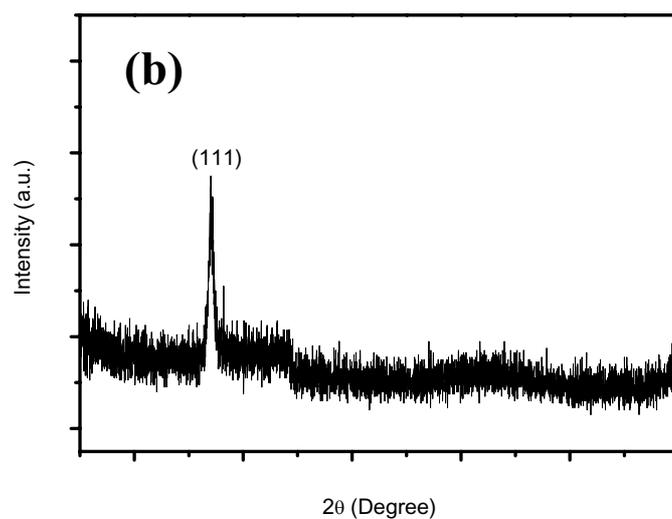
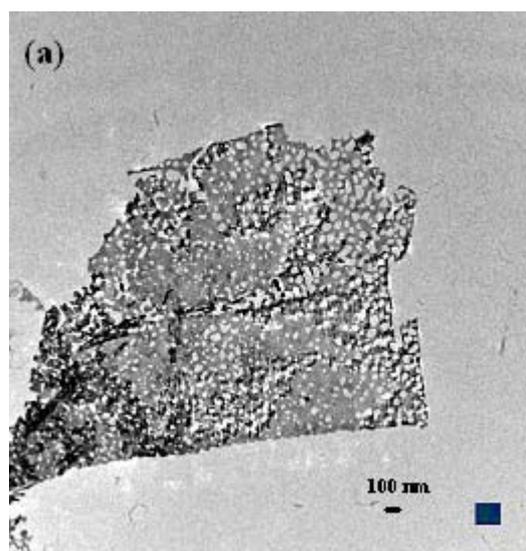


Figure S4. A typical TEM image (a) and XRD pattern (b) of isolated NiO nano-sheets with holes prepared in the absence of urea calcined at 500 °C with a temperature ramp of 3 °C/min. The diameter of the isolated nano-sheet is about 3 μm . There are numerous hexagonal holes in the nano-sheet and the edge angles are 120°. The NiO nano-sheets assembled on the Si wafer are perfect single crystalline sheets and the (111) planes form the main surfaces of the nano-sheets.

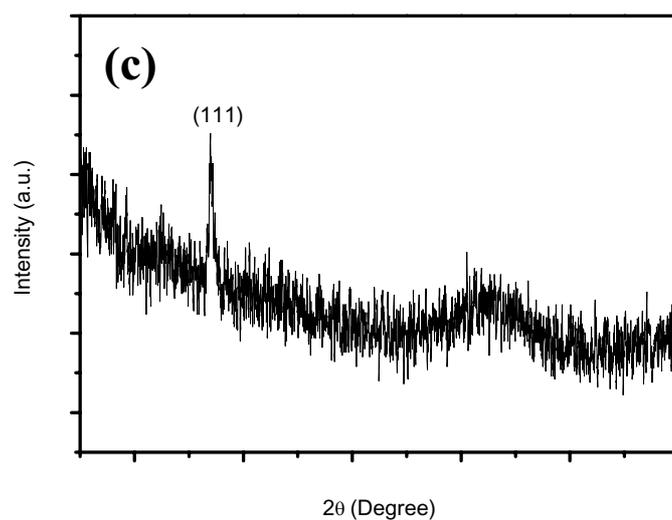
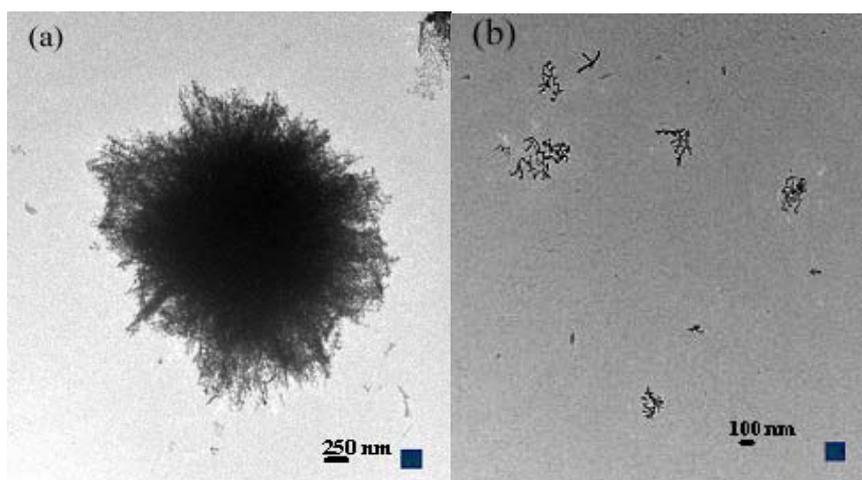


Figure S5. TEM image of aggregated NiO nano-sheets (a), dispersed NiO nano-sheets with holes prepared with the 1: 1 ratio of nickel nitrate to urea calcined at 500 °C with a temperature ramp of 3 °C/min (b) and their XRD pattern of the corresponding NiO nano-sheets (c). The diameters of the dispersed nano-sheets are about 300 nm. However, there are still some hexagonal holes in these nano-sheets and the edge angles are 120°. The NiO nano-sheets assembled on the Si wafer are perfect single crystalline sheets and the (111) planes form the main surfaces of the nano-sheets.

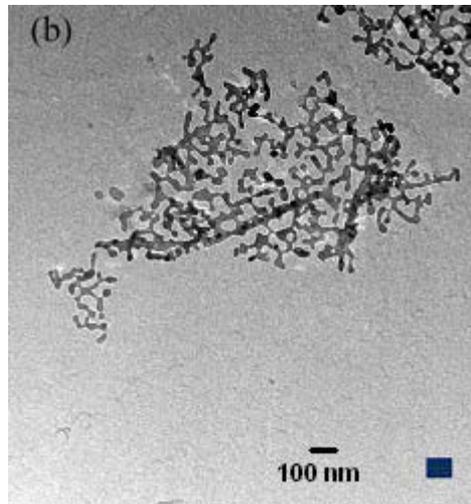
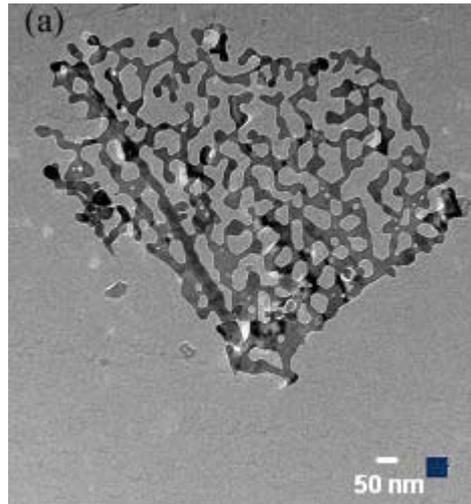


Figure S6. TEM images of NiO nano-sheets prepared in the absence of urea and calcined at 500 °C in oxygen with a temperature ramp rate of 3 °C/min.

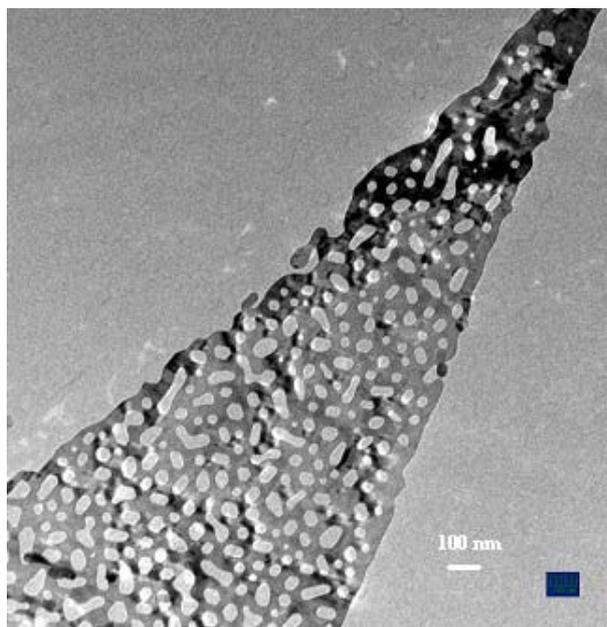


Figure S7. TEM images of NiO nano-sheets prepared in the absence of urea and calcined at 500 °C in nitrogen with a temperature ramp rate of 3 °C/min.

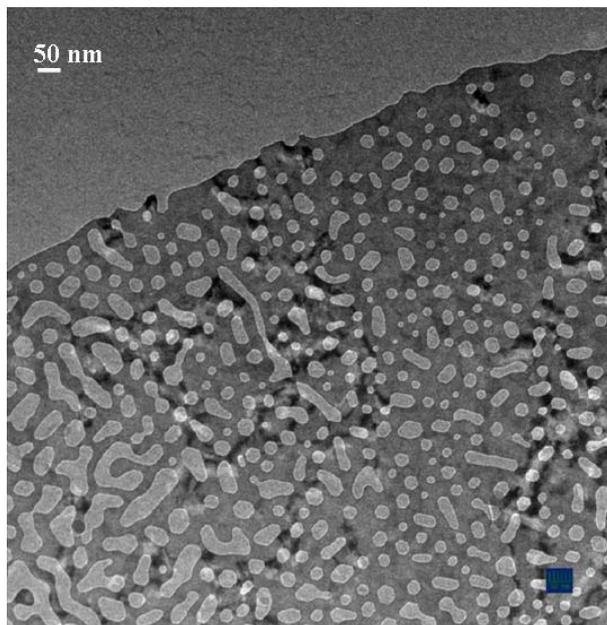


Figure S8. TEM image of NiO nano-sheets prepared in the absence of urea and calcined at 500 °C in air with a temperature ramp rate of 50 °C/min.

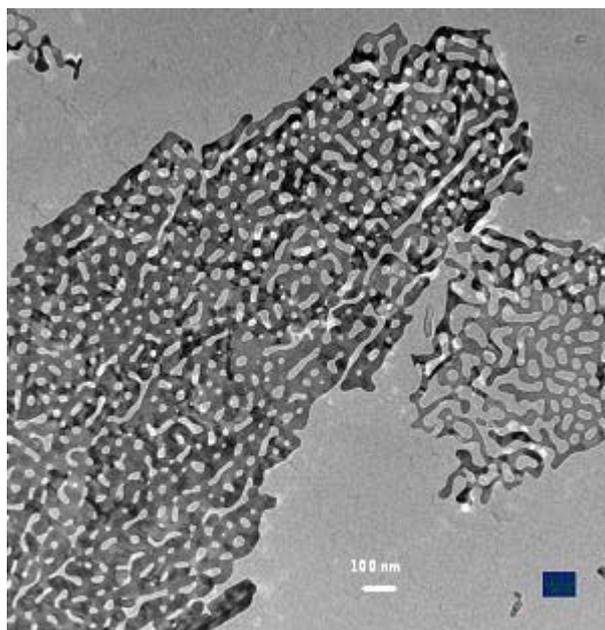


Figure S9. TEM image of NiO nano-sheets prepared in the absence of urea and calcined at 500 °C in air with a temperature ramp rate of 0.5 °C/min.

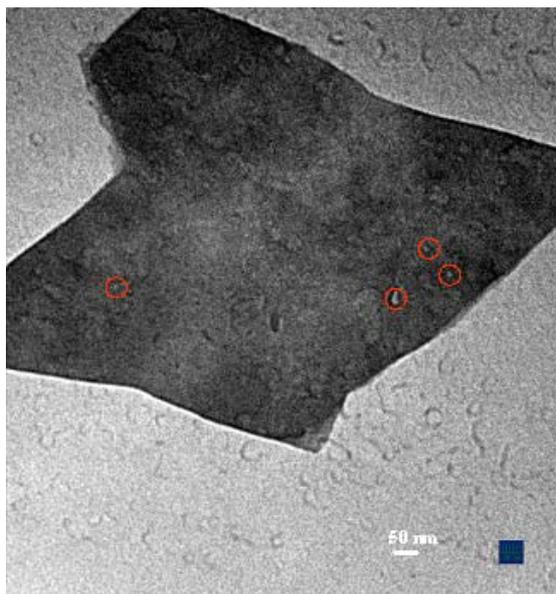


Figure S10. TEM image of NiO nano-sheets prepared in the absence of urea and calcined at 250 °C in air with a temperature ramp rate of 0.5 °C/min. There are several holes marked by red circles on the nano-sheets.

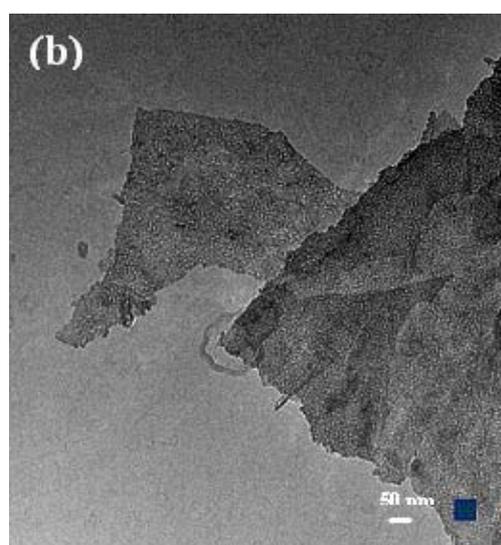
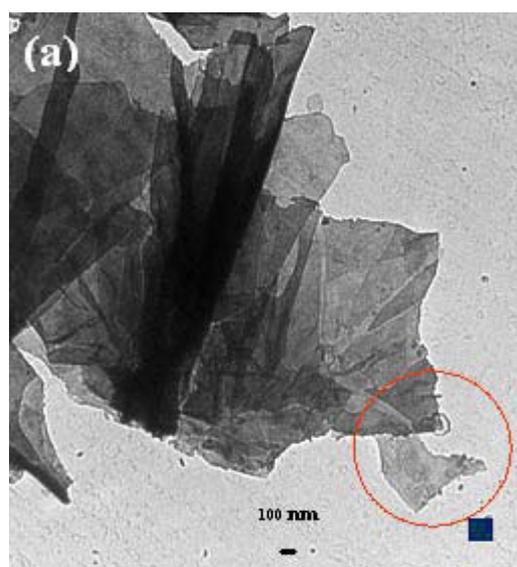


Figure S11. Low magnification TEM image of NiO nano-sheets (a) and high magnification TEM image of the marked area (b) prepared in the absence of urea and calcined at 350 °C in air with a temperature ramp rate of 0.5 °C/min.

Table S1. Summary of the effects of preparation and calcination conditions on the resulting NiO nano-sheets.

Run	Preparation and calcinations conditions				Typical sizes of nano-sheets (μm)	Typical sizes of holes (nm)
	Molar ratio (Nickel nitrate/urea)	Calcination gas circumstances	Temperature ramp ($^{\circ}\text{C}/\text{min}$)	Calcination temperature ($^{\circ}\text{C}$)		
1	1 : 1	air	3	500	ca. 0.3	20-100
2	1 : 0.5	air	3	500	ca. 1	20-100
3	Urea-free	air	3	500	ca. 3	20-100
4	Urea-free	oxygen	3	500	ca. 1	20-100
5	Urea-free	nitrogen	3	500	ca. 3	20-100
6	Urea-free	air	50	500	ca. 3	20-100
7	Urea-free	air	0.5	500	ca. 3	20-100
8	Urea-free	air	0.5	350	ca. 3	<10
9	Urea-free	air	0.5	250	ca. 3	<5

The effects of preparation and calcination conditions on the resulting NiO nano-sheets are summarized in Table S1. Entries 1-3 show that the sizes of NiO nanosheets can be controlled from 0.3 to 3 μm by varying the amount of urea. No distinct difference is observed for the NiO nano-sheets calcined in nitrogen (entry 5). The calcination in oxygen results in nano-sheets that are about 1 μm and have the appearance of interconnected NiO nano-bars because of the formation of partly overlapped holes (entry 4). The heating rates were also investigated and TEM images of NiO nano-sheets calcined at 500 $^{\circ}\text{C}$ in air with a rapid ramp rate of 50 $^{\circ}\text{C}/\text{min}$ and a slow ramp rate 0.5 $^{\circ}\text{C}/\text{min}$ are shown in Figure S8 and S9, there is no distinct difference for these samples (entry 6 and 7). The holes are produced during the calcinations, and higher calcination temperatures lead to the formation of larger holes (entries 7-9).

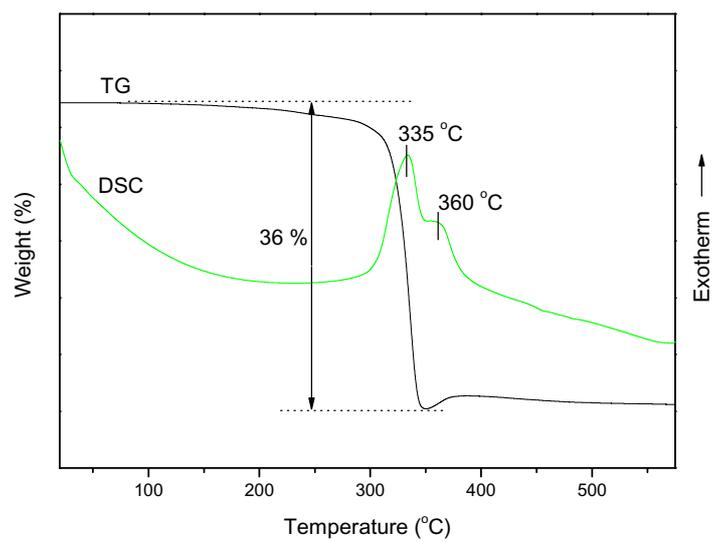


Figure S12. TG-DSC analysis of the as-synthesized organic-inorganic crystals before calcination.

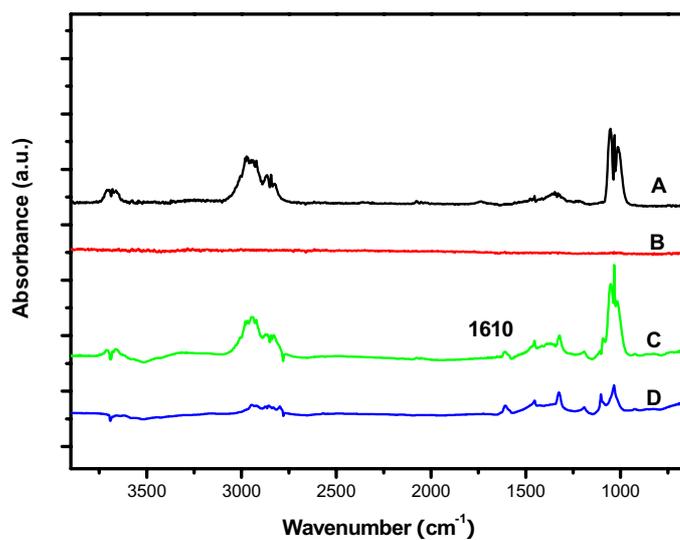


Figure S13. DRIFTS of methanol vapor at (A) 1 torr, (B) 0.005 torr in equilibrium with CP-NiO, and (C) 1 torr, (D) 0.005 torr in equilibrium with NiO nano-sheets at room temperature in the range of 3900 - 700 cm⁻¹.

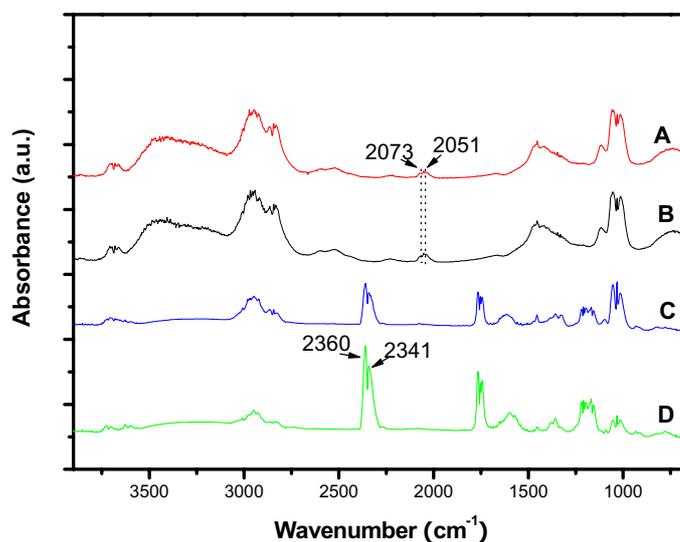
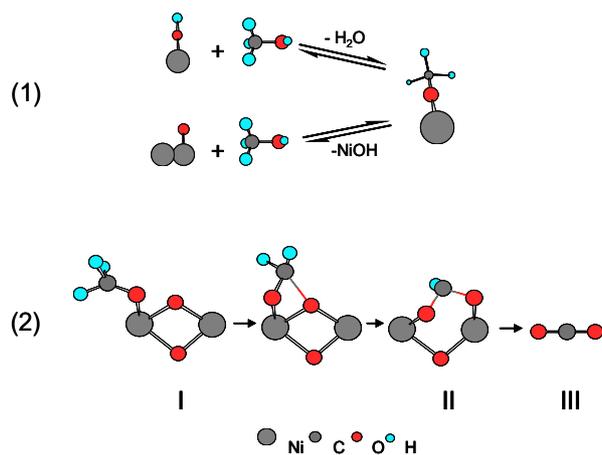


Figure S14. DRIFTS of methanol adsorption and reaction at 70 °C on CP-NiO at (A) 5 min, (B) 15 min, and on NiO nano-sheets at (C) 5 min, (D) 15 min in the range of 3900 – 700 cm⁻¹.

DRIFT spectra of NiO(111) nano-sheets exposed to methanol vapor pressures of 1 and 0.005 torr at room temperature were collected. The presence of gas-phase and weakly adsorbed methanol in the DRIFT spectra obtained after exposure of the NiO(111) nano-sheets to methanol at room temperature, is suggested by the characteristic absorptions in the spectral region of C-O stretching (Figure S13C, 1050, 1034, and 1015 cm^{-1}) and is confirmed by the broad and intense O-H bands (between 3500 and 3200 cm^{-1}) and C-H bands (between 2700 and 3200 cm^{-1}) stretching contributions. The negative peak at 3690 cm^{-1} suggests that surface hydroxyl groups react with methanol by forming a hydrogen bond or forming water by methanol dissociative chemisorption. It is noteworthy that an intense peak at 1606 associated with a pair of bands at 1452 and 1320 is observed, which is assigned to the OCO asymmetric and symmetric stretching modes of an intermediate formate species adsorbed on the NiO(111) nano-sheets surface. These results indicate that methanol can be oxidized on the surface of NiO(111) nano-sheets at room temperature. Both undissociated and dissociated methanol have been observed when NiO(111) nano-sheets are exposed to methanol at 70 °C (Figure S14). A large amount of CO_2 formed upon exposure to methanol at 70 °C (peaks at 2360 and 2341 cm^{-1}) and increased with time. A weak, pair of peaks at 1764 and 1743 cm^{-1} , can be attributed to the C=O asymmetric stretching of formic acid.^{1,2} The bands of CO_2 at 2360 and 2341 cm^{-1} increases and the bands of C-H stretching between 2800 and 3100 cm^{-1} decrease in intensity with the time, indicating that the methanol decomposition continues with time. This suggests that NiO(111) nano-sheets are active for methanol decomposition. In comparison with the room temperature spectra, the region of O-H stretching has no distinct change; indicating that methanol interacts primarily with surface oxygen anions and oxygen defects at 70 °C. This implies that the main active sites for methanol decomposition are oxygen defects and oxygen anions. The detailed methanol adsorption and decomposition mechanism is shown in Scheme S1. Methanol reacts with the hydroxyl groups and oxygen defects on the surface of NiO(111) nano-sheets to form methoxyl groups(I), then, the methoxy groups interact with the surface oxygen anions to lose hydrogen and mutate to formate species(II), finally, formate species decomposition and dehydrogenation produce CO_2 (III). This result is relevant for applications in fuel cells and other alternative energy technologies. Methanol is also an excellent fuel in its own right and it can also be blended with gasoline, although it has half the volumetric energy density relative to gasoline or diesel.³ It is also used in the direct methanol fuel cell (DMFC). Performance of the liquid feed methanol fuel cells is already attractive for some applications and is approaching the levels required for electric vehicle propulsion.³ In these electrochemical cells, methanol is directly oxidized with air to carbon dioxide and water to produce electricity, without the need to first generate hydrogen.^{4,5} This greatly simplifies the fuel cell technology and makes it available to a broad range of applications. The conventional Cu/ZnO-based methanol synthesis catalysts performed poorly in the methanol decomposition as the catalysts suffered from rapid deactivation.⁶ The activity and stability of the catalysts have been two major challenges associated with methanol decomposition. The NiO(111) nano-sheets in the present manuscript can decompose methanol at low temperature and their preparation is simple and has scale-up potential. The large-scale application of NiO(111) nano-sheets catalysts without transition metals for low temperature methanol decomposition may be feasible.



Scheme S1. The mechanism of methanol oxidation and decomposition on the surface of NiO nano-sheets.

Reference

- [1] Millikan, R.C.; Pitzer, K.S. *J. Am. Chem. Soc.* **1958**, *80*, 3515..
- [2] Kustov, L. M.; Ostgard, D.; Sachtler W. M. H. *Catal. Lett.* **1991**, *9*, 121.
- [3] Olah, G.A. *Angew. Chem. Int. Ed.* **2005**, *44*, 2636; *Angew. Chem.* **2005**, *117*, 2692.
- [4] Surumpudi, S. S.; Narayanan, R.; Vamos, E.; Frank, H.; Halpert, G.; Laconti, A.; Kosek, J.; Prakash, G.K.S.; Olah, G.A. *J. Power Sources* **1994**, *47*, 217.
- [5] Prakash, G. K. S. M.; Smart, C.; Wang, Q.J.; Atti, A.; Pleyner, V.; Yang, B.; McGrath, K.; Olah, G. A.; Narayanan, S. R.; Chun, W.; Valdez, T.; Surumpudi, S. *J. Fluorine Chem.* **2004**, *125*, 1217.
- [6] Cheng, W. *Acc. Chem. Res.* **1999**, *32*, 685