Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information

Controllable Green Synthesis of Supported Hollow NiO Crystals with Shape Evolution from Octahedral to Novel Truncated Octahedral

1. Experimental

1.1 Materials and methods

All the utilized materials including nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) ((99.9%, Merck) and zeolite type 5 (Acros Organics) were utilized without further purification.

1.2 Synthetic procedures

Incipient wetness impregnation method was used for (38 % by wt.) NiO-supported Materials. More in details, the required mass of the precursor $Ni(NO_3)_2.6H_2O$ was well mixed with 50 mL deionized water. ZSM-5, with the required mass, was added gradually for approximately 15 min to the aqueous solution and left overnight vigorously stirring on a flat magnetic stirrer. Following, the sample was dried with continuous stirring on a magnetic stirrer at 70 °C for 7 h. Next, the sample was placed in a covered porcelain crucible and put in a tube furnace for calcination purpose under oxygen atmosphere either at 500 °C and 900 °C (to obtain the octahedron and truncated octahedron morphologies, respectively) for 5 h. The heating rate was set to be 10 °C/min till 220 °C then 1 °C/min till the required temperature.

1.3 Characterization

X-ray Diffraction (XRD) analysis was conducted to investigate the crystallinity of the synthesized material. Bruker D8B Advance X-ray diffractometer instrument was used to record the diffractogram in the range $2\theta = 5-80°$. The surface area of the synthesized materials was obtained via N_2 physical adsorption at 77 K using a Micrometrics ASAP 2020. In addition, the specific surface area was calculated via applying Brunauer–Emmett–Teller (BET) method. Variable Pressure Field Emission Scanning Electron Microscopy (VP-FESEM) was used to study the morphology of the prepared materials utilizing ZEIZZ SUPRA SSVP. High Resolution Transmission Electron Microscope (HRTEM) and

Transmission Electron Microscope (TEM) were conducted utilizing Zeiss Libra 200FE at 200 kV. The diffraction patterns of the synthesized material were obtained utilizing the selected area electron diffraction (SAED) mode. The surface chemistry of the synthesized catalysis powder was determined by X-ray photoelectron spectroscopy (XPS). The spectra were obtained on a K-Alpha instrument utilizing a monochromatic Al Kα source. The binding energy scale was preliminarily calibrated utilizing the position of the peaks for the Au 4f$_{7/2}$ (83.96 eV) and Cu 2$p_{3/2}$ (932.62 eV) core levels of pure metallic gold and copper. The charge compensation was performed with carbon adventitious C 1s (C-C, C-H) at 284.8 eV. Narrow spectral regions of Ni2p was recorded.

2. Supporting Figures and Tables

The demonstrated XRD patterns of supported NiO catalysts Figure 1 indicates clearly that both of metal oxide modified catalyst and support have sharp peaks which assigned to the presence of a crystalline NiO phase (JCPDS 47-1049). The NiO catalyst has five main peaks at 37.2°, 43.2°, 62.8°, 75.4°, and 79.4° assigned to (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2) planes and referring to face-centered cubic (FCC) NiO as illustrated from the patterns of fresh catalysts. The metallic oxide phase in the fresh catalysts confirms that 5 h calcination at 500 °C is sufficient to decompose $Ni(NO_3)_2.6H_2O$ to obtain the NiO species.

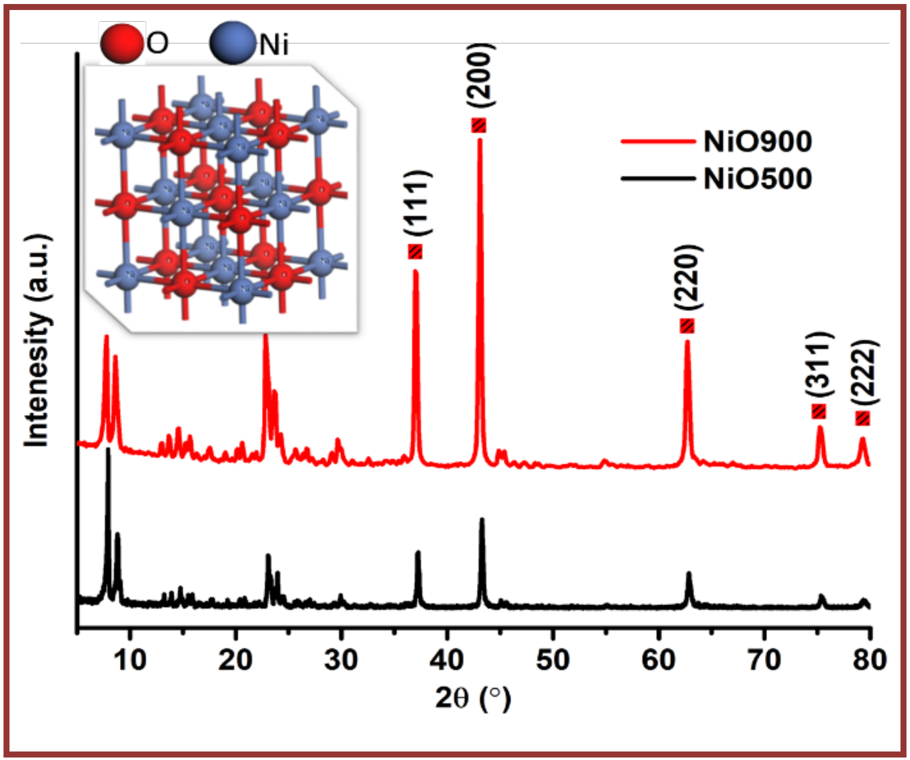

Fig. S1. XRD diffractogram of the synthesized material.
(inset) The crystal structure of FCC NiO crystal

Significantly, ZSM-5, as a support, and NiO500 as well as NiO900 exhibit a plateau and higher relative pressures which corresponding to type I isotherm indicating the characteristics of microporous material with limited mesoporosity (Figure 2). By comparing the calculated mesoporosity volume with the obtained one, it can be seen that the mesoporosity was not influenced significantly in NiO500 and NiO900.

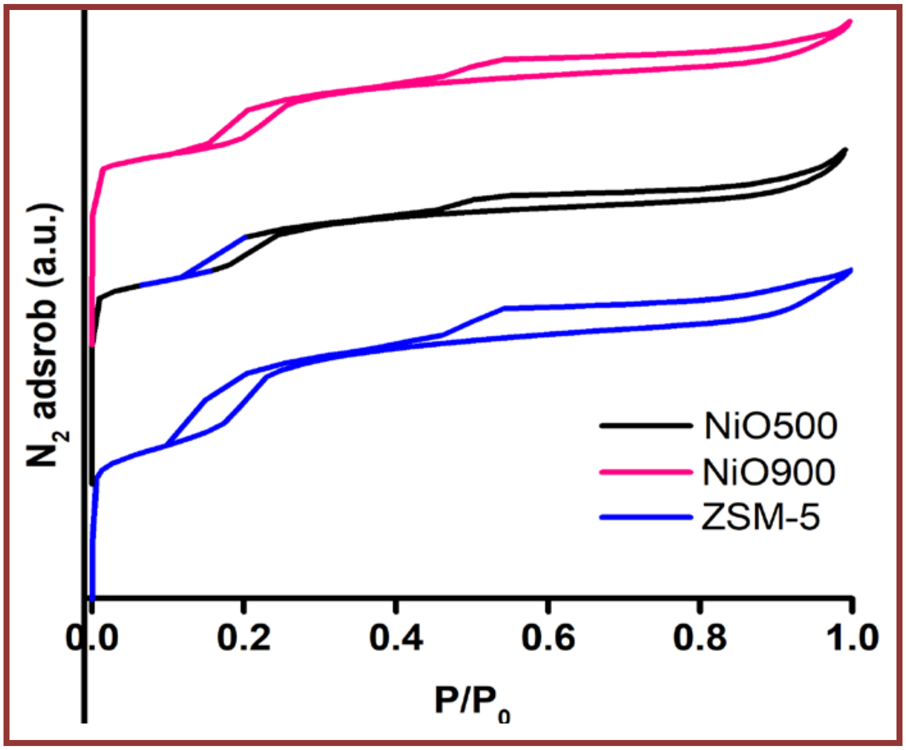

Fig. S2. Adsorption isotherms of N_2. (inset) Mesopore size distributions of ZSM-5, NiO500 and NiO900

XPS characterizations were conducted on ZSM-5 supported NiO catalyst to detect the successful formation of the pure NiO. The BE of the main Ni2p$_{3/2}$ peak of NZ0.0-500 and NZ0.0-900 were 854.9 and 855.6 eV, respectively, which is higher than BE of the bulk NiO (854.7 eV [1]).

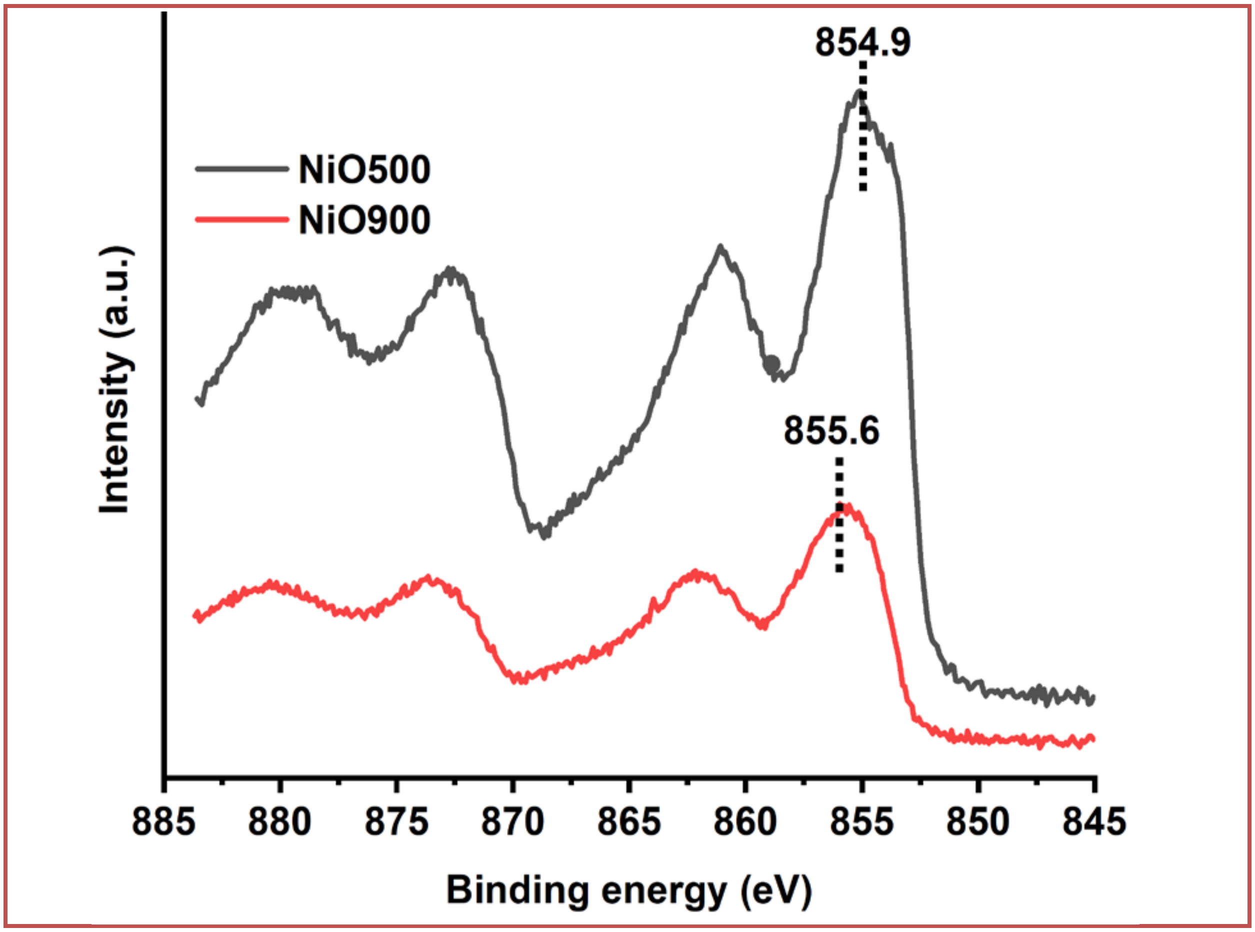

Fig. S3. XPS spectra of the Ni 2p region

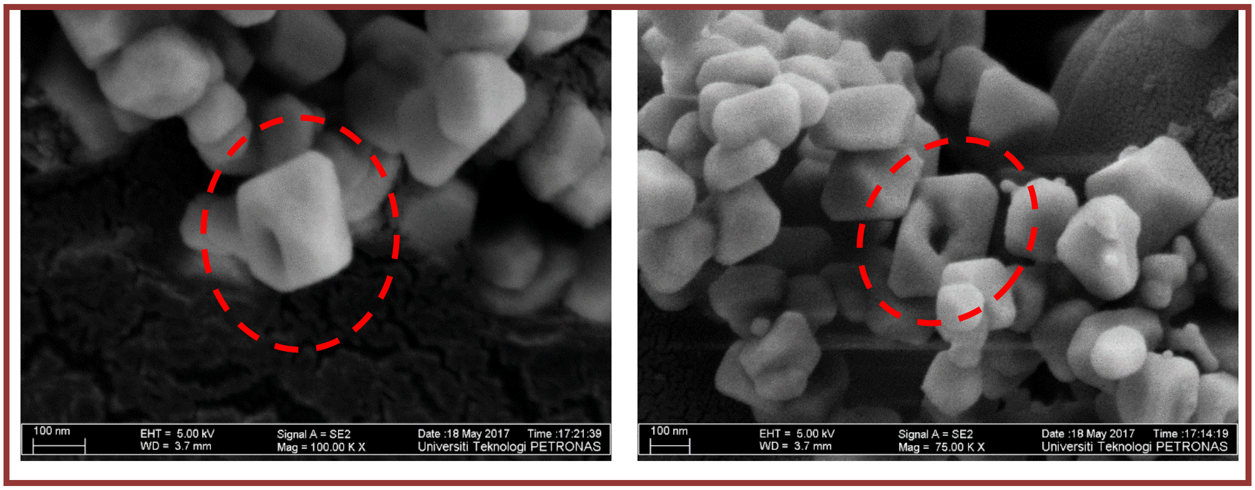

Fig. S4. FESEM images demonstrate the hollow into the core of some truncated octahedral NiO700 particles

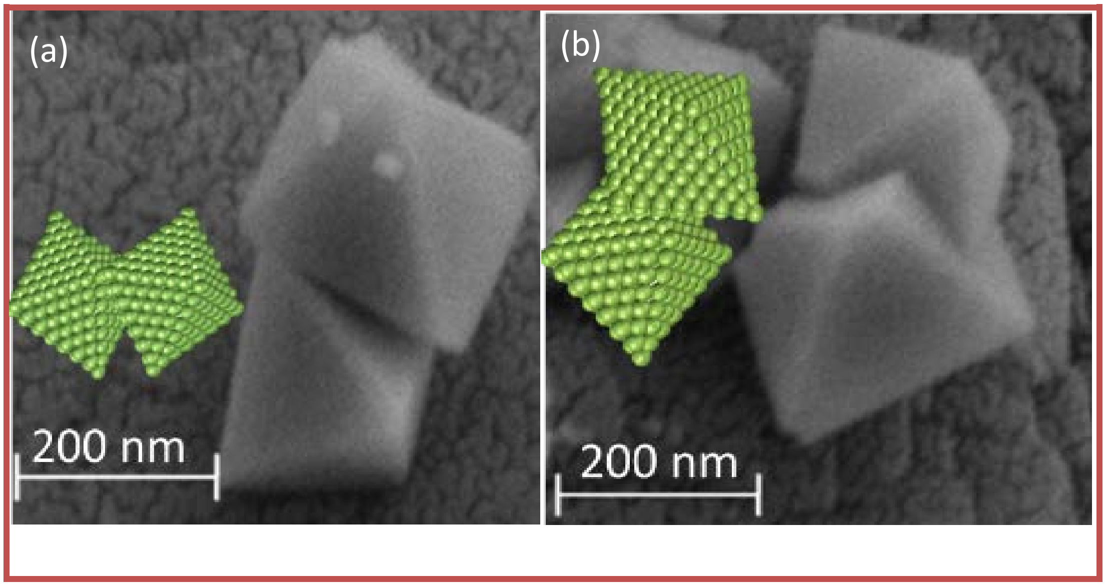

Fig. S5. FESEM images of attachment form of octahedral particles: (a) sharing the same edge and (b) imperfectly oriented connection. (Inset) shows a schematic diagram of the connected particles

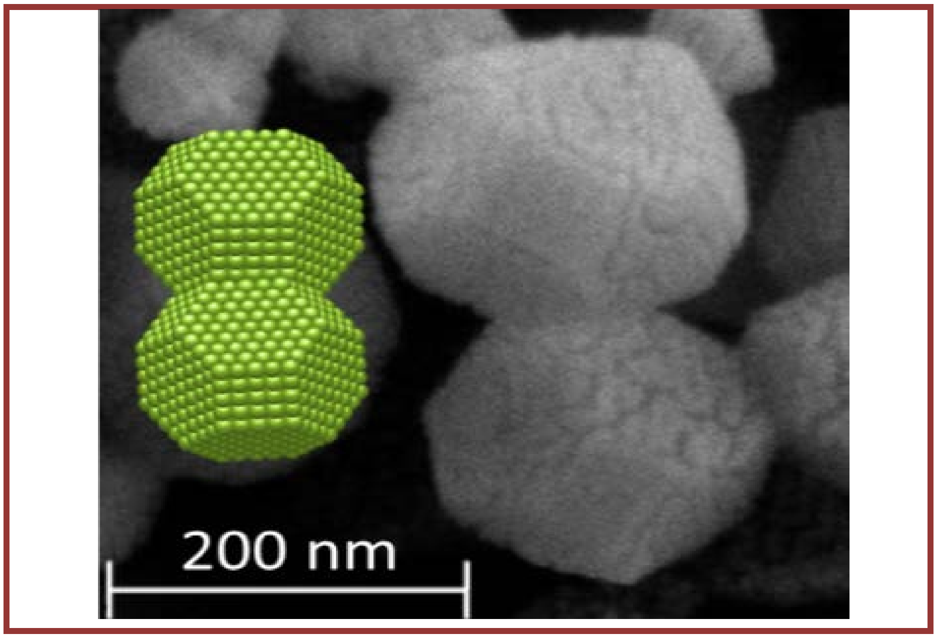

Fig. S6. FESEM image of attachment form of truncated octahedral particles sharing the same (100) edge. (Inset) demonstrates a schematic diagram of the connected particles

Table 1. Physicochemical properties of the synthesized catalyst

Sample	Surface area [a] (m^2/g)	Pore size [b] (Å)	Pore volume [b] (cm^3/g)	Micropore volume [c] (cm^3/g)
ZSM-5	368.1	43.9	0.215	0.049
62 % ZSM-5	*228.2	-	*0.13	*0.030
NiO500	239.0	32.7	0.14	0.042
NiO900	233.5	33.0	0.10	0.031

[a] Obtained using BET method.

[b] Obtained using BJH method.

[c] Obtained using v-t plot analysis.

* The obtained value via multiplying 0.62 by the value in the same column of 100% ZSM-5.

Reference:

1. C. P. Li, A. Proctor and D. M. Hercules, *Applied spectroscopy*, 1984, **38**, 880-886.