Graphitic carbon nanostructures via a facial microwave-induced solid-state process

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Supporting Information

Experimental:

1. Synthesis of Ni nanoparticles

Ni nanoparticles with average diameter of 40, 90, 350 and 600 nm were synthesized using a modified polyol method[1]. In a typical experiment, 5 g $NiCl_2 \cdot 6H_2O$ and 8 g polyvinylpyrrolidone (PVP) were dissolved in 150 ml ethylene glycol (EG). 2 ml aqueous solution of 1.6 g NaOH was added in the above solution under a mechanical stirring. Then the mixture was heated to 190℃ in an inert atmosphere and refluxed for about ten minutes to remove the volatile components. Subsequently, an appropriate quantity of H_2PtCl_4 aqueous solution was injected into the mixture as nucleating agents. By varying the Ni/Pt ratio, Ni particles with different sized can be obtained. For example, 40 nm Ni particles could be acquired when the molar ratio of Ni/Pt is 1000, while for 90 nm partilcles, Ni/Pt is 10000. 350 nm Ni particles were produced without adding any nucleating agents and if the amount of PVP is reduced to 6 g, 600 nm Ni particles could be obtained (also without any nucleating agents). The final products were collected by centrifugation, sonication and washed with ethanol, water, and finally dried in vacuum at 40℃.

8 nm Ni nanoparticles were fabricated by a modified W/O microemulsion method[2]. Typically, 2 mmol $NiCl_2 \cdot 6H_2O$ was dissolved in 50 g water/ CTAB/n-hexanol microemulsion (with a weight ratio of 22/33/45). Then another 50 g microemulsion solution containing 10 mmol $NaBH_4$ was added into above emulsion under violent stirring at room temperature in an inert atmosphere. After 30 minutes stirring, ethanol was added to cause phase separation. The product was centrifugated, sonicated and washed several times with ethanol, water, and dried in vacuum at 40℃.

2. Synthesis of Ni/Graphitic-shell nanocrystals and graphitic HCNSs

In a typical experiment, 0.5 g Ni nanoparticles with a certain diameter and 0.5 g PS were blended in 20 ml ethyl acetate and sonicated for half an hour to get a homogeneous solution. The solvent was evaporated in a rotary evaporator and the residual mixture of Ni/PS was weighed (W_{NiPS}) and transferred into a quartz vial. Then the sample was microwave-treated in a household microwave oven in an inert atmosphere up to 1 minute. The obtained black powder of Ni/graphitic-shell nanocrystals was weighed (W_{NiG}). Char yield was calculated by (W_{NiG} – 0.5W_{NiPS}) / 0.5 W_{NiPS}, in which the first 0.5W_{NiPS} represents the weight of Ni nanoparticles and the second one represents the weight of PS for the fact that they were equal-amount mixed. Part of this powder was washed with 1 M HCl in an ultrasonic bath for 2 hours to get graphitic HCNSs. We found the ultrasonic bath was essential for the dissolution of Ni cores.

3. **Control experiments**

In order to know whether it is possible to get similar structures through a conventional method, control experiments were carried out by heating the Ni/PS (with the size of Ni particles of 40 or 90 nm) in a tube furnace to 800°C (30℃/min) under an inert atmosphere. TEM images reveal that Ni particles agglomerated greatly and irregular carbon/metal composites (see Fig.S9) as well as a substantial amount of CNTs were produced. Char yield was less than 35%. This demonstrated the advantage of microwave-assisted approach against conventional one[3].

Characterization:

Transmission electron microscopy (TEM) measurements were carried out on a FEI Tecnai G2 Spirit transmission electron microscopy at an accelerating voltage of 120 kV, and high-resolution TEM (HRTEM) on a FEI Tecnai F30 at 300kV. The general morphology of the products was characterized by scanning electron microscopy (SEM, FEI Quanta 200FEG). Powder X-ray diffraction (XRD) were performed on a RINT D/MAX-2500 X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å). UV-Raman spectra were measured at room temperature with a Jobin Yvon T64000 triple-stage spectrograph with spectral resolution of 2 cm^{-1} and the 325 nm line from a He - Cd laser was used as excitation source. N_2 adsorption isotherms were measured using a Micromeritics ASAP 2000 analyzer at 77 K. Before the measurements, all samples were degassed at 473 K for 15 h. The microwave synthesis experiments were carried out using a Haier MA 2270EGC commercial microwave-oven at a frequency of 2.45 GHz and a power of 700 W.

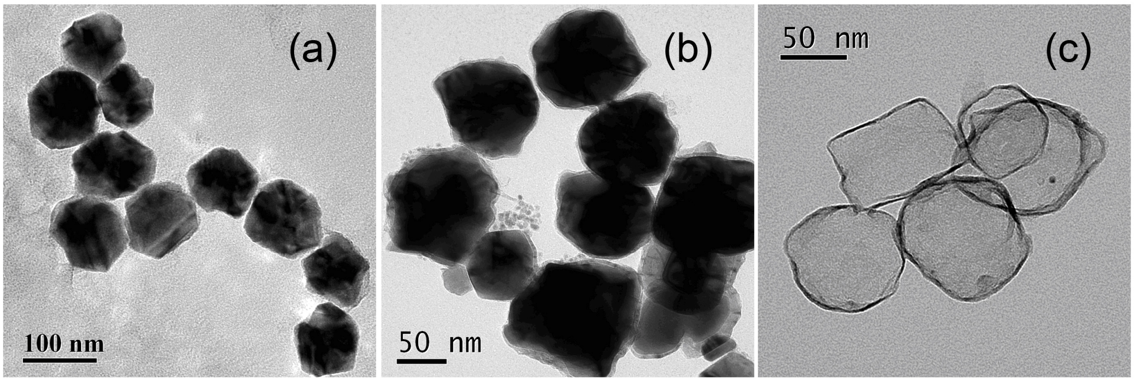


Fig. S1 TEM image of as synthesized 90 nm Ni particles (a), Ni/graphitic-shell nanocrystals (b), and graphitic HCNSs (c)

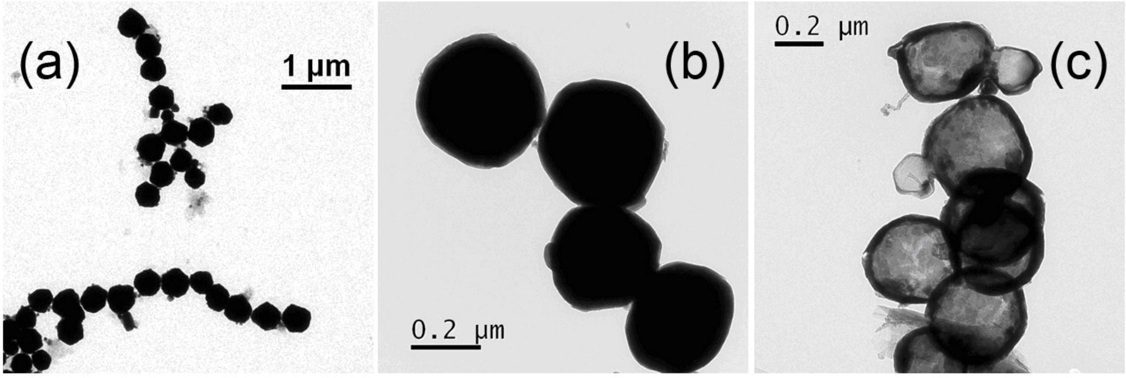


Fig. S2 TEM image of as synthesized 350 nm Ni particles (a), Ni/graphitic-shell crystals (b), and graphitic HCNSs (c)

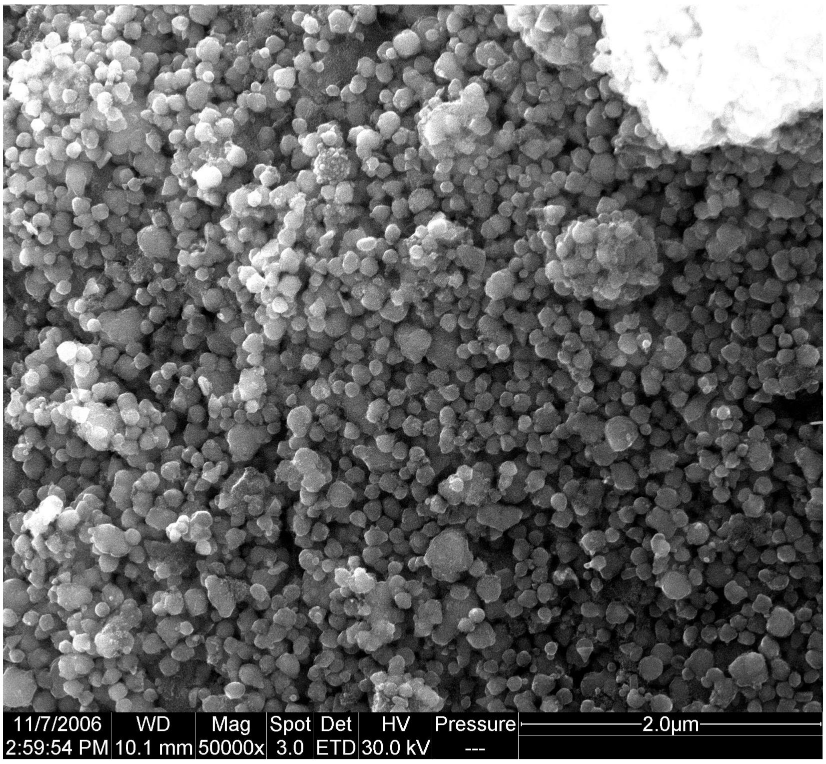


Fig. S3 SEM image of 90 nm Ni/graphitic-shell nanocrystals.

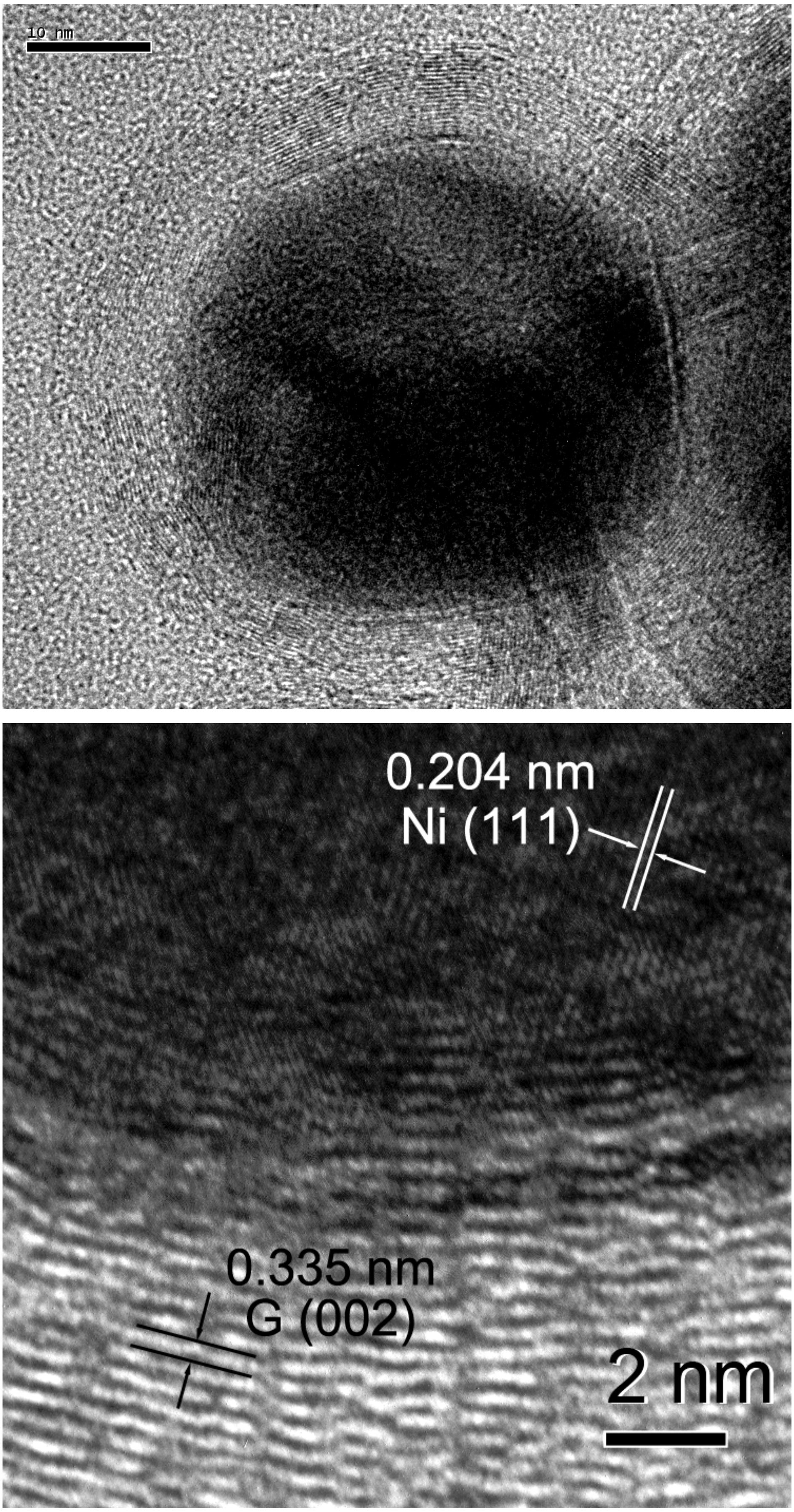


Fig. S4 HRTEM image of the 40 nm Ni/graphitic-shell nanocrystals;

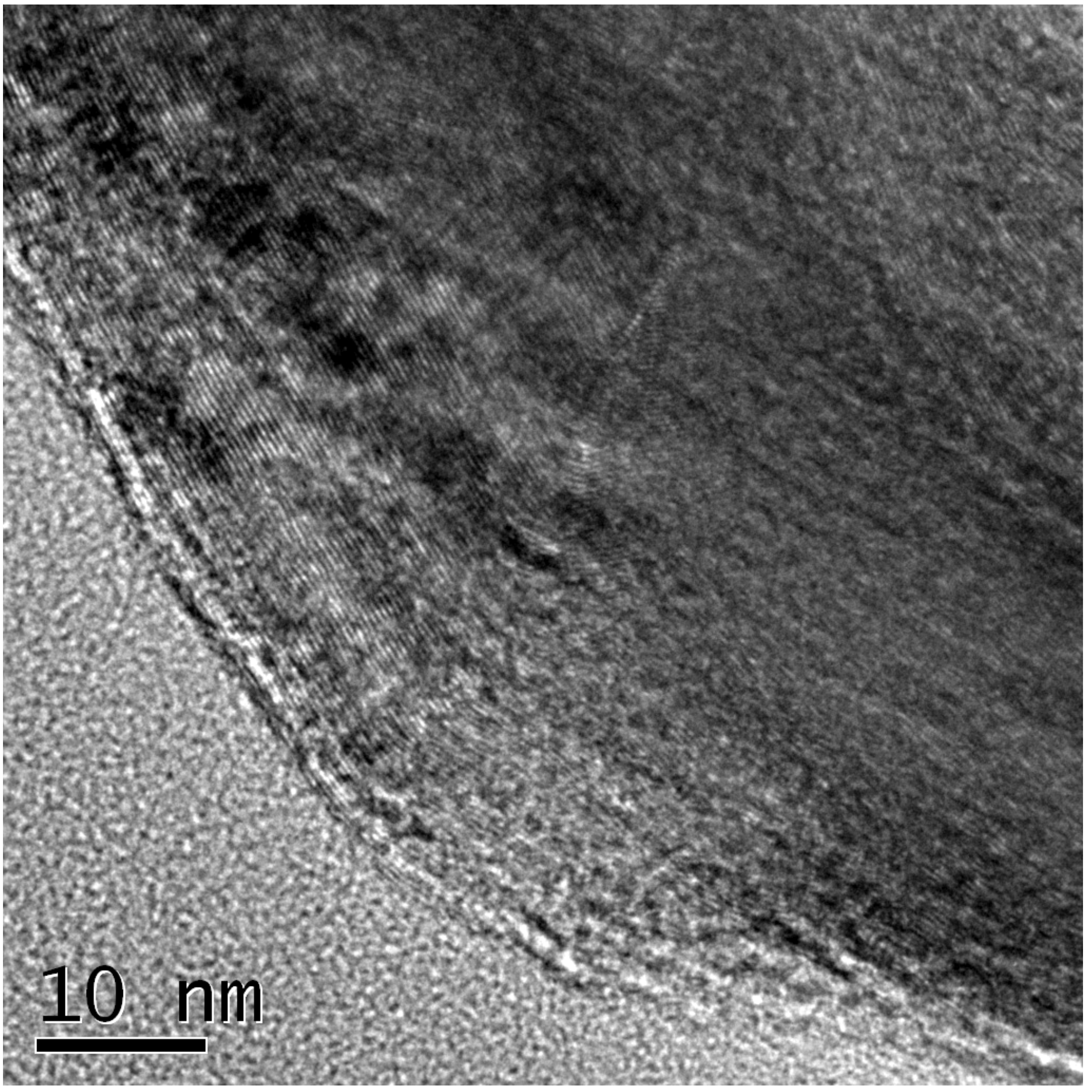


Fig. S5 HRTEM image of the shell of 600 nm Ni/graphitic-shell crystals;

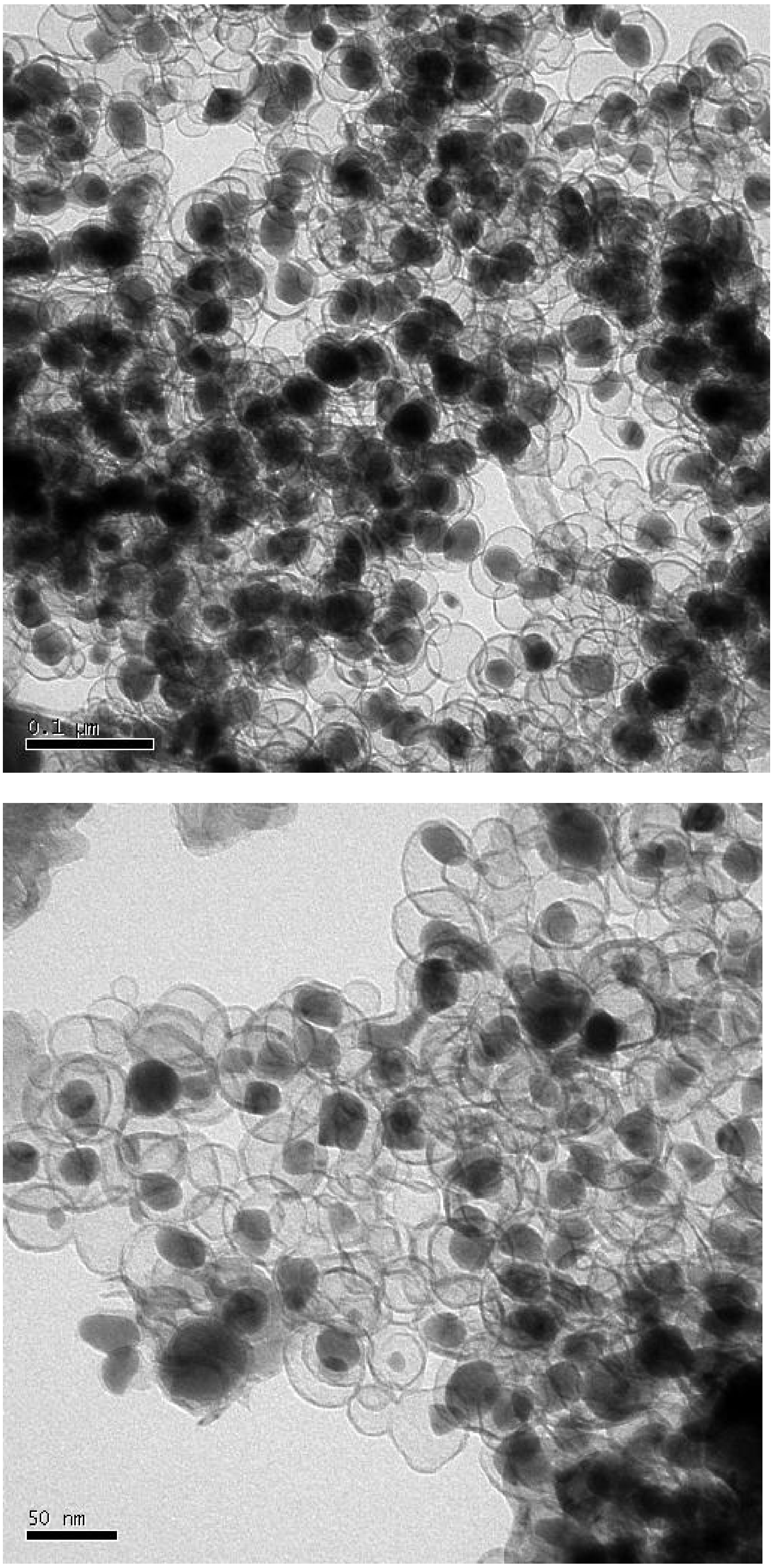
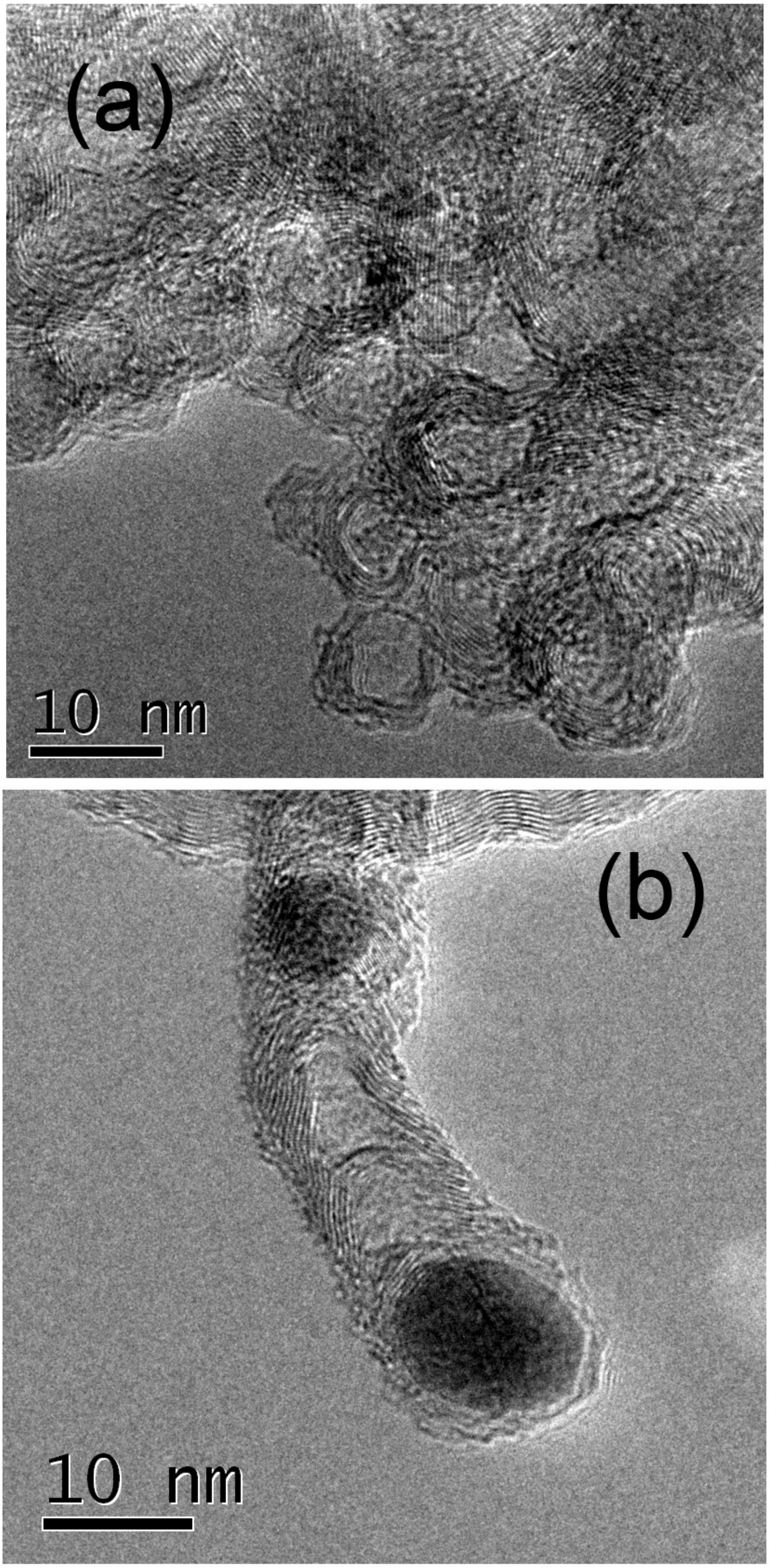


Fig. S6 TEM image of the product of Ni/graphitic-shell nanocrystals (40 nm) after acid etching under sonication for 0.5 h. If the treatment time is sufficient long (2 h), HCNSs were obtained (see Fig.1f).


(a)
10 nm
(b)
10 nm

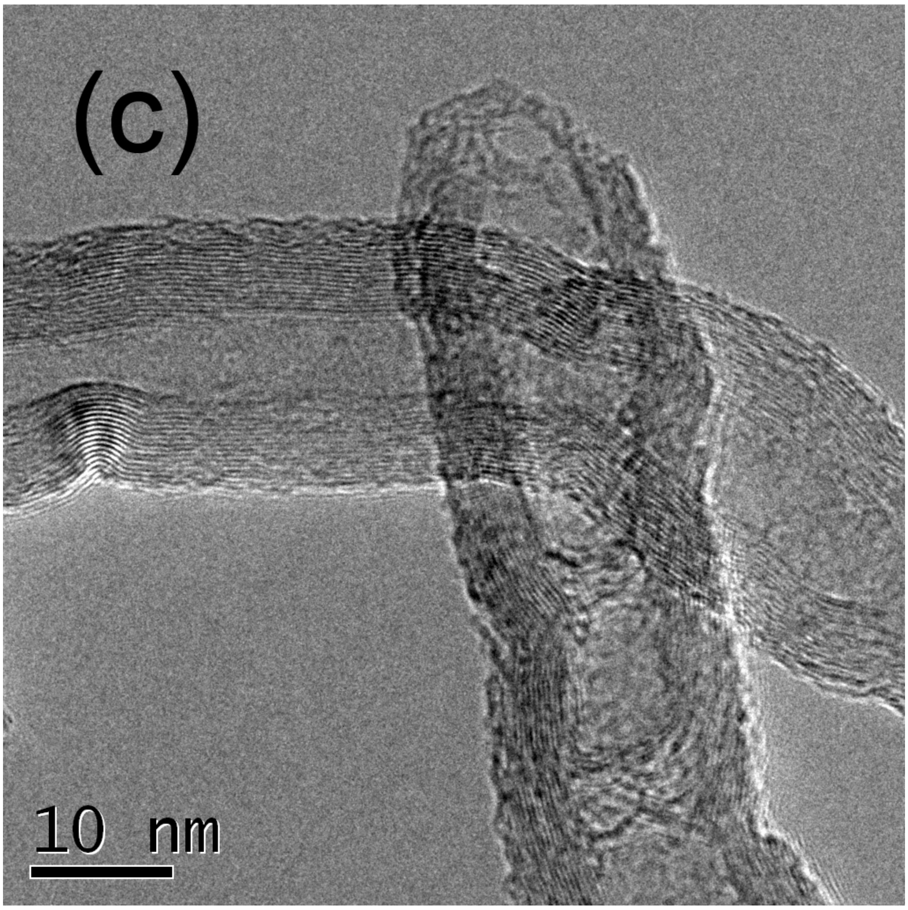


Fig. S7 HRTEM image of the product of microwave and then acid-treated 8 nm sample. (a) HCNSs; (b, c) carbon nanotubes. It is clear that both the HCNSs and MWNTs have graphitic structure while tubular and herringbone-like MWNTs have been observed.

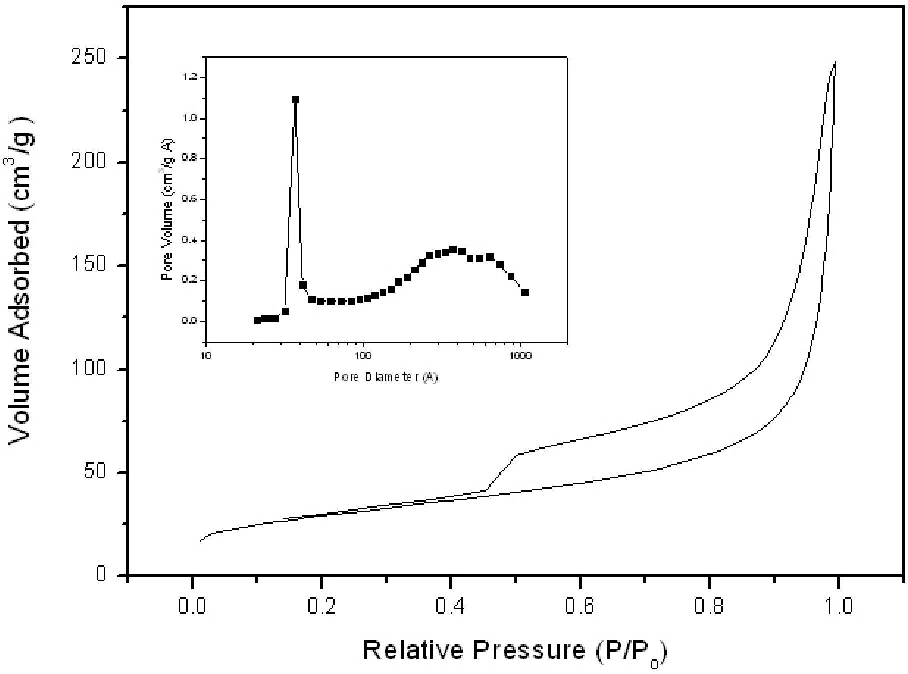


Fig. S8 N_2 adsorption isotherm and pore size distribution (inset, from desorption) plot of HCNSs (40 nm).

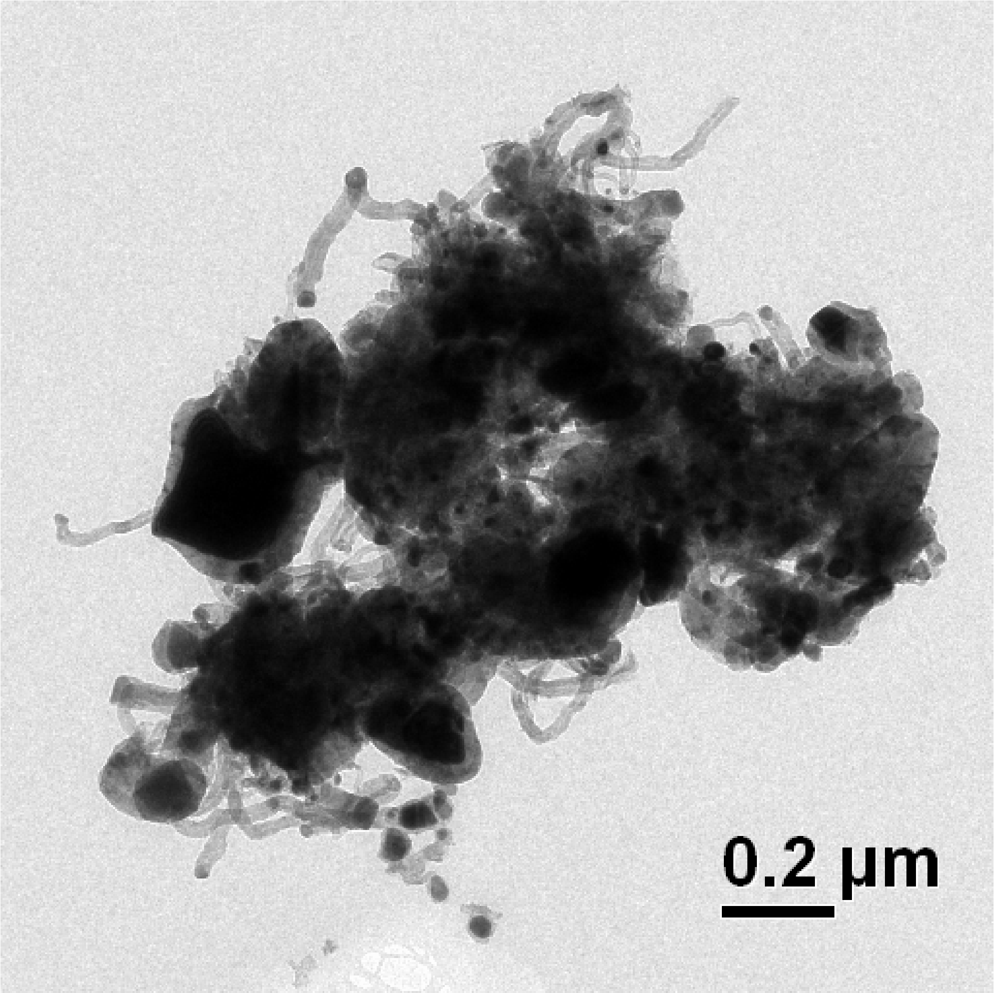


Fig. S9 TEM image of the product of control experiment: 40 nm Ni/PS heated in furnace under inert atmosphere at 800°C. Aggregation of Ni particles happened and irregular carbon/metal composites as well as a substantial amount of CNTs were produced.

(1) Hegde, M. S.; Larcher, D.; Dupont, L.; Beaudoin, B.; TekaiaElhsissen, K.; Tarascon, J. M. *Solid State Ionics* **1996**, *93*, 33-50.
(2) Chen, D. H.; Wu, S. H. *Chemistry of Materials* **2000**, *12*, 1354-1360.
(3) Landry, C. C.; Barron, A. R. *Science* **1993**, *260*, 1653-1655.