Enhanced catalytic performance of assembled ceria necklace nanowires by Ni doping

Supplementary Information

Experimental Section

Chemicals All chemicals were of analytical grade and were used as received without further purification. Deionized water was used throughout. $Ce(NO_3)_3 \cdot 6H_2O$, $NiCl_2$, ethylene glycol, nitric acid supplied by Beijing Chemical Reagent Company.

The synthesis of ceria necklace nanowires In a typical synthesis, 1.0 mL of $Ce(NO_3)_3$ solution(0.5 mol/L), 0.2 mL nitric acid(7.5 mol/L) and 30 mL glycol were added with stirring to form a uniform solution. And then, the mixed solution was sealed in an autoclave and heated at 170℃ for 15 hours. Then the products were separated from the solution by centrifugation (10000 r/min 20 minutes), washed with water and ethanol to remove ions and organic solvents possibly remnant in the products, dried at 80℃ in air and annealed at 400℃ for 4 hours.

The synthesis of nickel doped ceria necklace nanowires In a typical synthesis of Ni doped ceria necklace nanowires with Ni/Ce atom ratio of 3.8%, 1.0 mL $Ce(NO_3)_3$ solution(0.5 mol/L), 0.2 mL $NiCl_2$ solution(0.5 mol/L), 0.2 mL nitric acid(7.5 mol/L) and 30 mL glycol were added with stirring to form a uniform solution. And then, the mixed solution was sealed in an autoclave and heated at 170℃ for 15 hours. Then the products were separated from the solution by centrifugation (10000 r/min 20 minutes), washed with water and ethanol, dried at 80℃ in air and annealed at 400℃ for 4 hours.

The synthesis of Ni doped ceria necklace nanowires with Ni/Ce ratio of 2.2% followed the same procedure except that 0.1 mL of nickel chloride solution was added.

Characterization

The catalytic activity was evaluated at atmospheric pressure in continuous flow fixed-bed quartz tubular reactor with 0.2 g catalyst and reactant gas mixture of 1.0% CO, 16% O_2, balanced with nitrogen at a rate of 100 ml/min. Gases went through the quartz tubular reactor were monitored by gas chromatography. The X-ray diffraction (XRD) patterns were obtained by using the a Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å). The size and morphology of samples were obtained with a Hitachi H-7650 transmission electron microscope at 80 kV and a Tecnai G2 F20 S-Twin high-resolution transmission electron microscope at 200 kV. X-ray Photoemission Spectroscopy (XPS) experiments were carried in a PHI Quantera SXM^{TM}, calibrated internally by carbon deposit C (1s) binding energy (BE) at 284.6 eV. The nitrogen sorption isotherm was measured by volumetric method on an automatic adsorption instrument (Micromeritics, ASAP2010) at liquid nitrogen temperature (77 K). Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method from the data in a P/P_0 range between 0.05 and 0.2. H_2-TPR was performed using ChemBET Pulsar TPR/TPD by heating sample (50 mg) at 10℃/min to700℃ in H_2 flowing at 40 mL/min.

Fig. S1 TEM and HRTEM images of ceria necklace nanowires (A, D), Ni-CeO_2-2.2% (B, E) and Ni-CeO_2-3.8% (C, F)

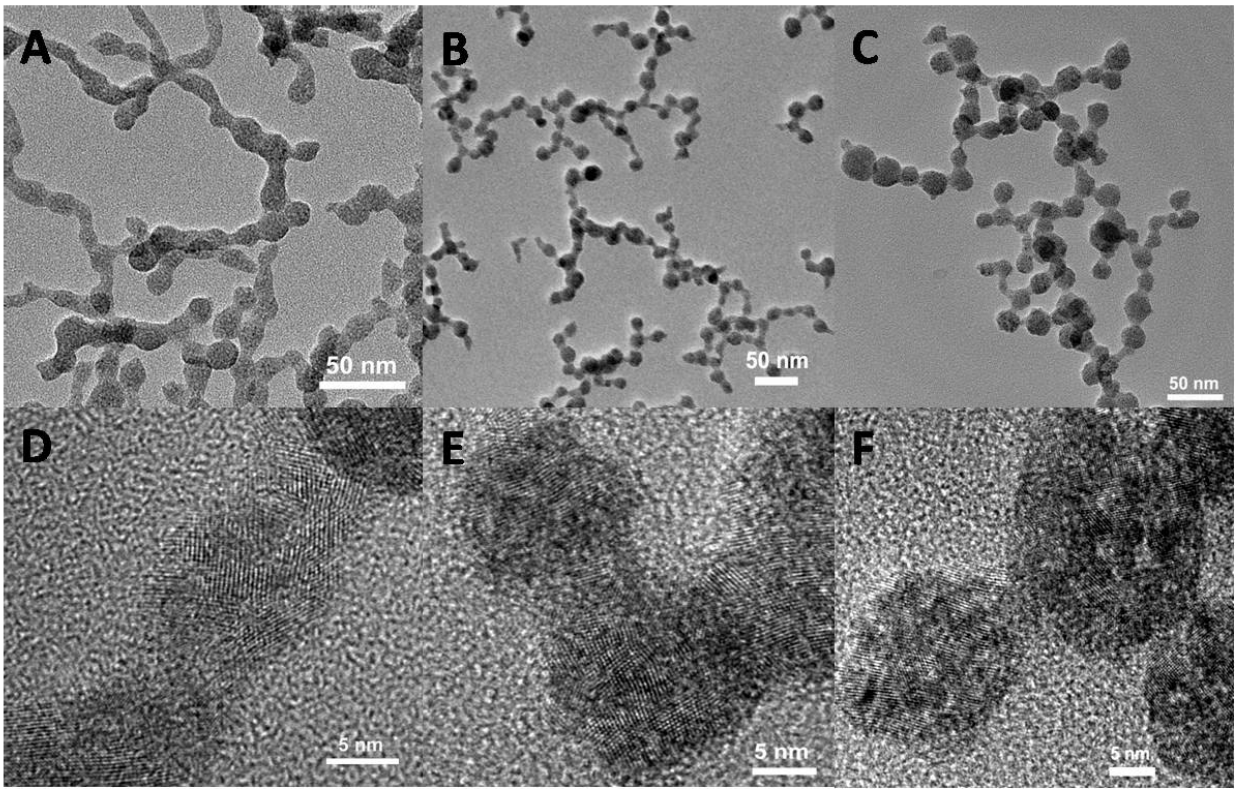

Fig. S2 XRD patterns of ceria necklace nanowires (black), Ni-CeO_2-2.2% (red) and Ni-CeO_2-3.8% (blue)

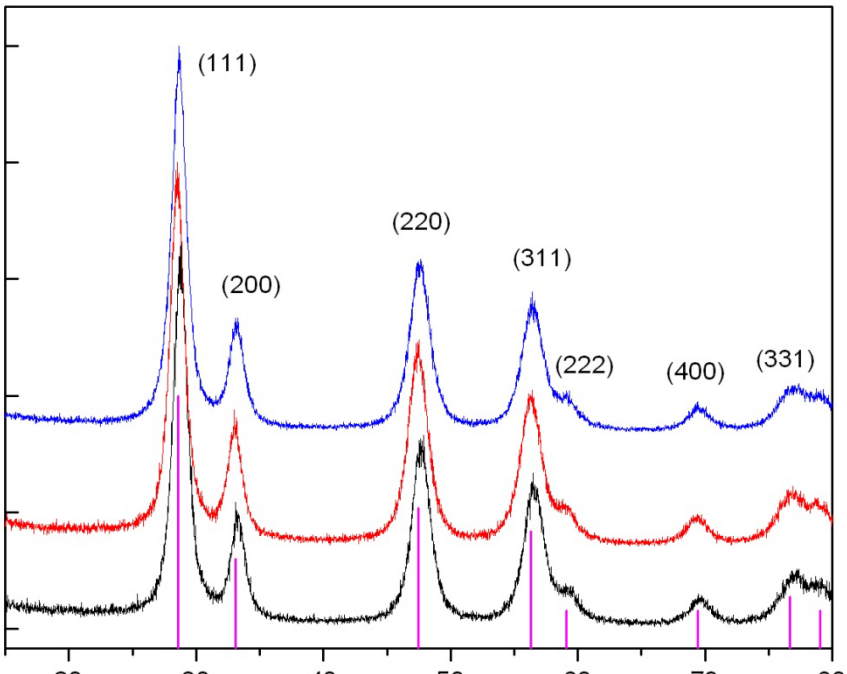

Fig. S3 TEM images of ceria necklace nanowires at different reaction time (A: 1 h, B: 2 h, C: 4h, D: 8h, E: 16h, F: 3days

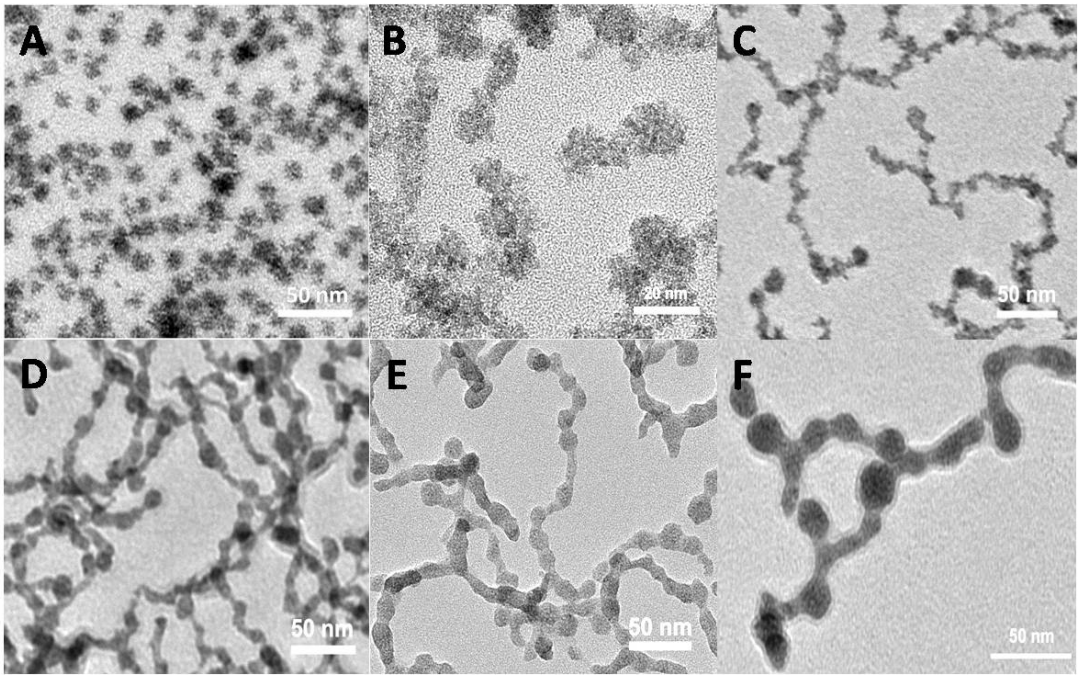

Fig. S4 HRTEM images of ceria necklace nanowires during the early stage of the reaction (2 hour)

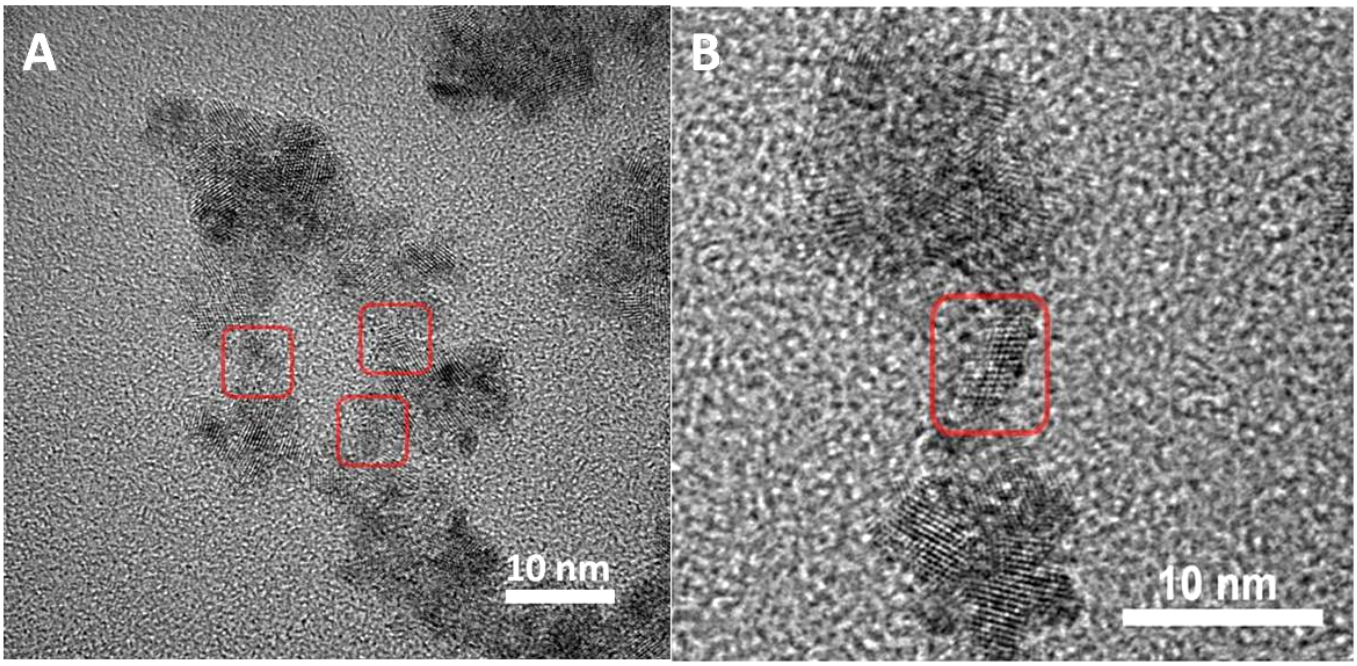

Fig. S5 TEM and HRTEM images of ceria prepared under different conditions (A, B 0.02 mL nitric acid added; C 0.6 mL nitric acid added)

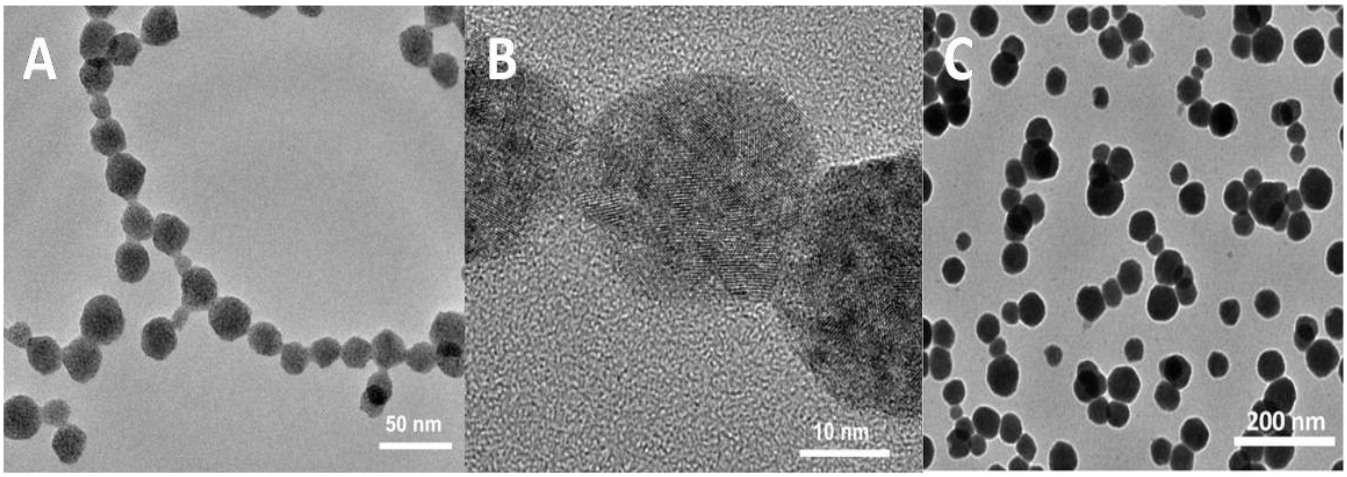

Fig. S6 Catalytic performance of ceria necklace nanowires (black), nickel doped ceria (2.2% blue, 3.8% red) and nickel oxide (green)

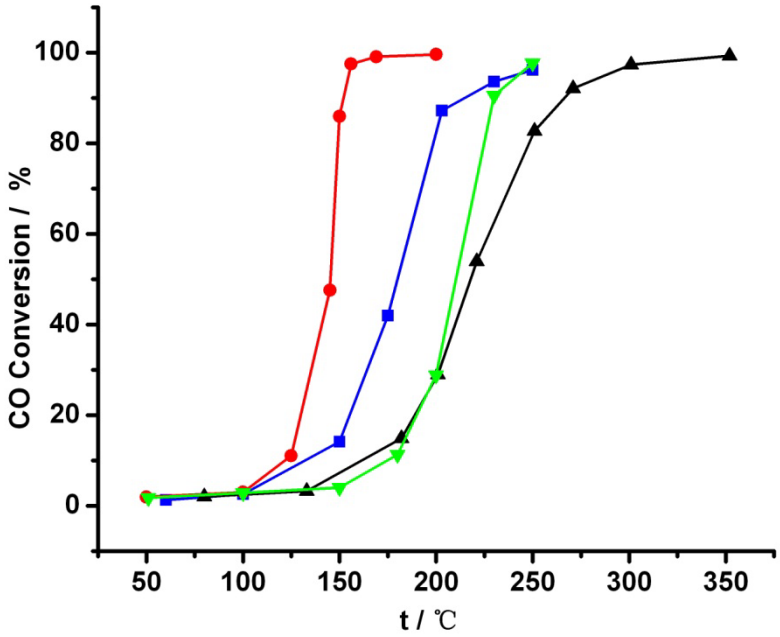

Fig. S7 Diffuse reflectance spectrum of ceria and nickel doped ceria necklace nanowires

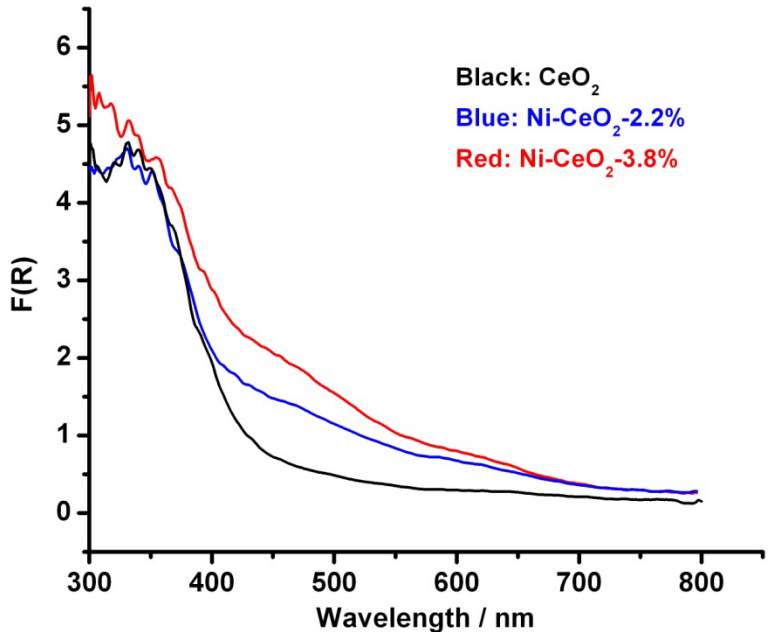

Fig. S8 XPS full spectrum of ceria necklace nanowires (black), nickel doped ceria (2.2% blue, 3.8% red)

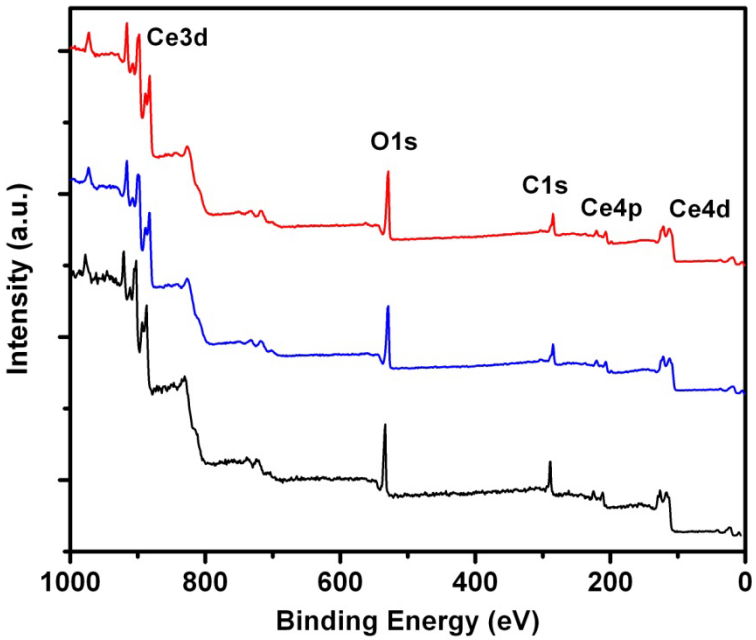

Fig. S9 EDS profiles of nickel doped ceria (up: Ni/Ce 3.8 at. %, down: 2.2 at. %)

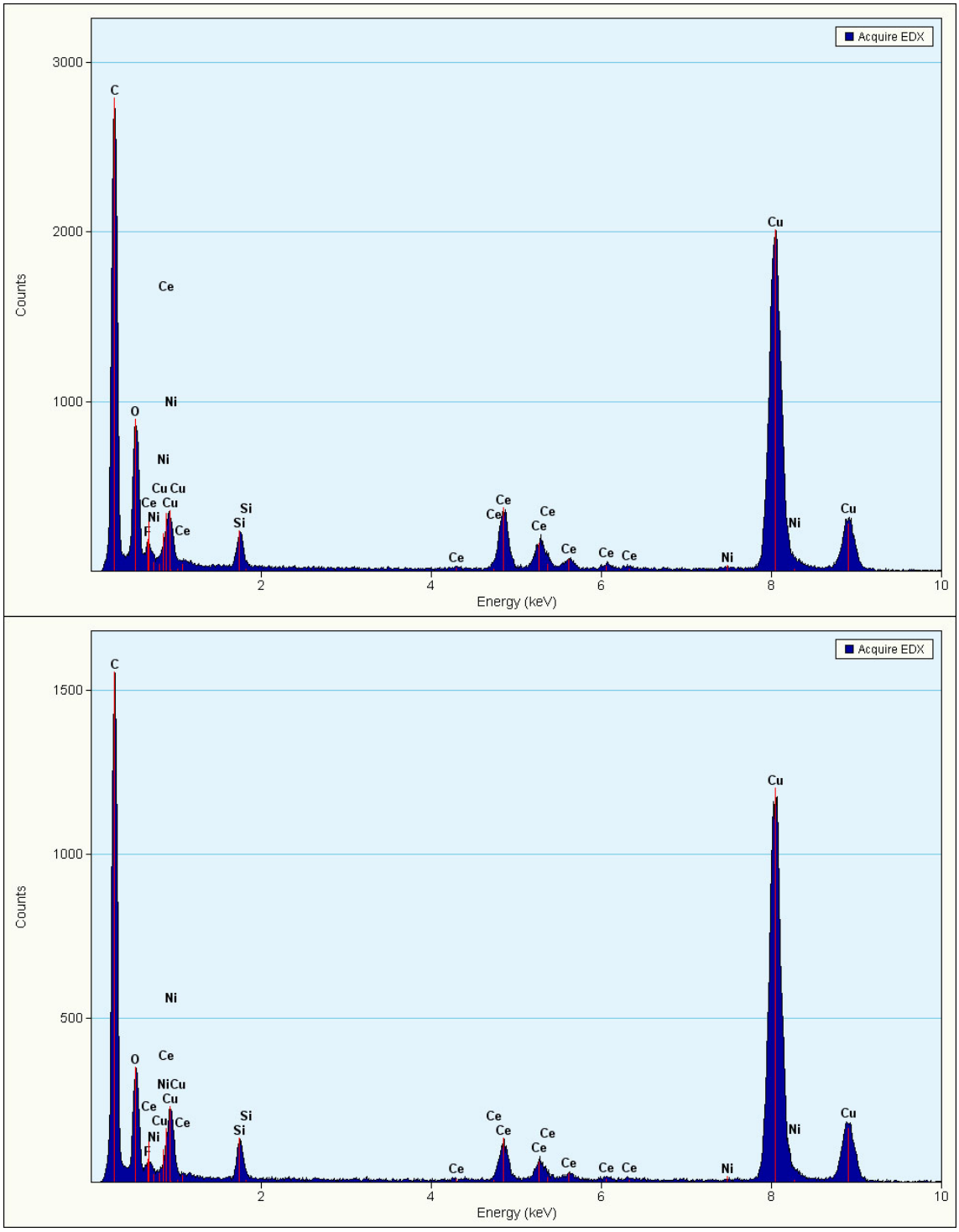

Table S1 Calculated Ni/Ce atom ratio of nickel doped ceria necklace nanowires by EDS profiles

Sample	Ni/Ce atom ratio (%)
Ni-CeO_2-2.2%	4.9
Ni-CeO_2-3.8%	2.9

Fig. S10 N_2 adsorption-desorption curves of nickel doped ceria necklace nanowires (left: Ni/Ce 2.2 at. %, right: Ni/Ce 3.8 at. %)

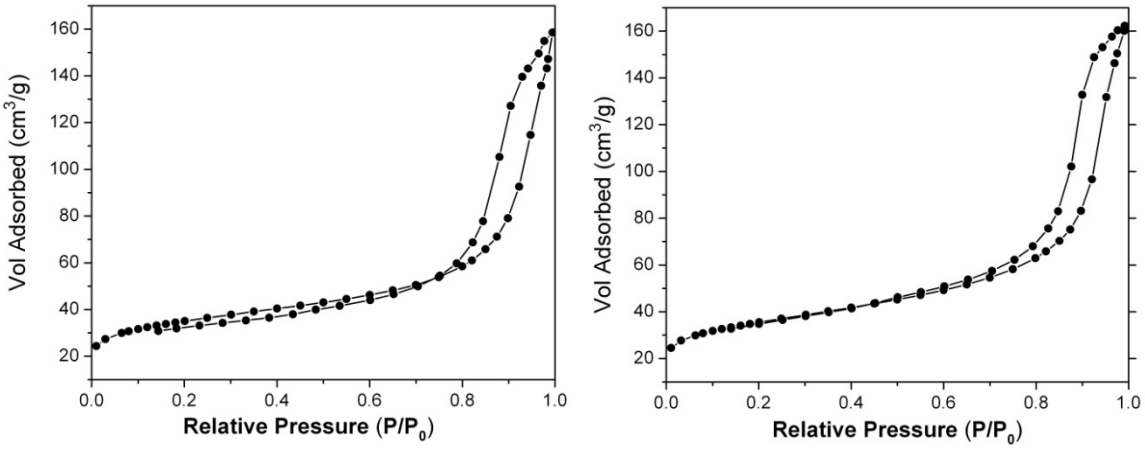

Table S2 BET surface area of ceria and nickel doped ceria necklace nanowires

Sample	BET Surface Area (m^2/g)
CeO_2	148.734
Ni-CeO_2-2.2%	124.192
Ni-CeO_2-3.8%	122.370