Ethanol-Directed Morphological Evolution of hierarchical CeO_2 Architectures as Advanced Electrochemical Capacitors

Adnan Younis*, Dewei Chu* and Sean Li

School of Materials Science and Engineering, University of New South Wales, Sydney, 2052, NSW, Australia

*Corresponding Author: Tel.: +61 (0)2 9385 5386; Fax: +61 (0)2 9385 6565

E-mail address: a.younis@unsw.edu.au, d.chu@unsw.edu.au

Supporting Information

S1. X-Ray diffraction:

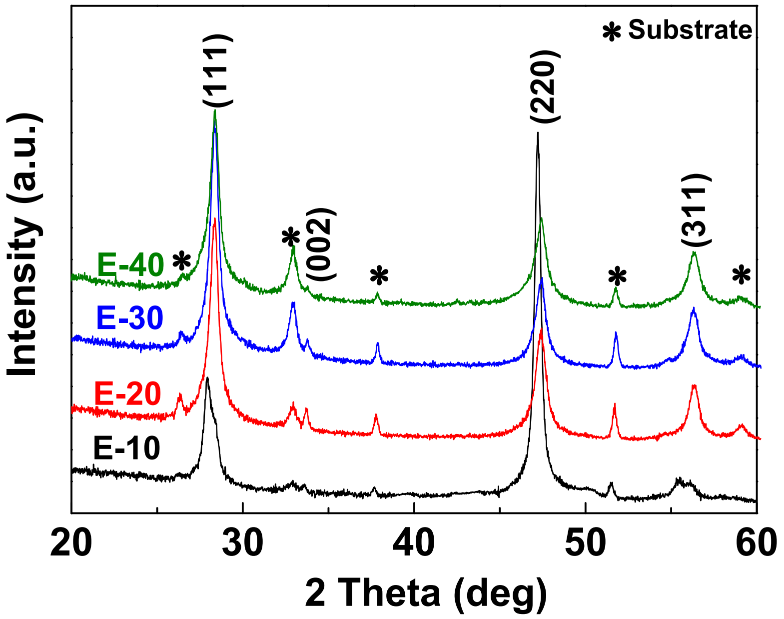

Figure S1: X-ray diffraction patterns of all samples (E-10, E-20, E-30 and E-40).

S2. Growth mechanism:

The details of CeO_2 nanowires formation process by the aid of potential-time curve and controlled experiments with different deposition times were studied. The potential-time curve of CeO_2 nanowires deposited with the current density of 0.5 mA.cm^{-2} at 70 °C is shown in figure S2. The potential first decreased rapidly in the initial stage of deposition and reached the minimum at 20 min, which indicate a fast nucleation process and growth on FTO substrate[1]. Subsequently, the potential increased gradually between 20 and 60 minutes and then remained relatively stable. This variation in potential versus time can be attributed to the growth of nanowires, because the resistance increases with the growth of product. The growth rate of these nanowires was quick at the beginning and became slow with increasing deposition time.

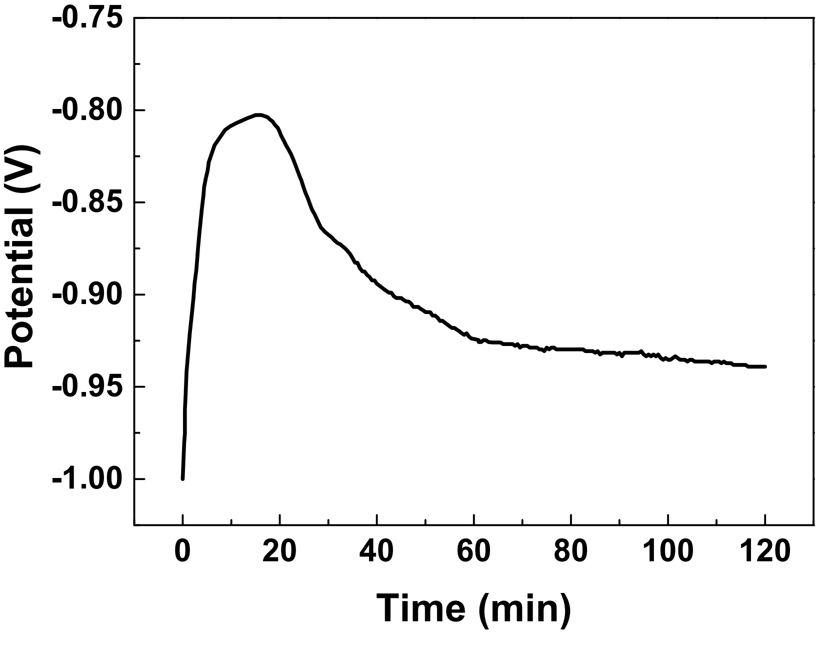

Figure S2: Potential-time curve of the as-synthesized CeO_2 nanowires in the presence of 10 ml of ethanol at 70 °C with a current density of 0.5 mA·cm^{-2}.

These arguments were further validated by carrying out ex-situ SEM studies on the CeO_2 nanowires samples deposited for different times. A layer of CeO_2 nanoparticles was first occurred after 10 min electrodeposition, as shown in figure S3a. These particles have roughly uniform diameter distribution about 150-180 nm. CeO_2 nanowires with a 150-180 nm diameter sprouted from the layer of CeO_2 nanoparticles when the electrodeposition time prolonged to 20 minutes as shown in figure S3b. Vertical CeO_2 nanowires with diameter of 200 nm could be observed in figure S3c when the reaction prolonged to 40 minutes. Further lengthening the electrodeposition to 60 minutes, high density nanowires were formed as illustrated in figure S3d. Finally, for the deposition time of 80 minutes, CeO_2 nanowires with diameters in the range of 200-230 nm and lengths up to 7 μm were formed as shown in figure S3e and S3f. The average diameter and length of these nanowires is about 200 nm and 6.1 μm, respectively. It is noted that the diameter of the nanowires remained almost same as that of the initial particles during the growth process, implying the particles are crucial for the final diameter size of the nanowires. Moreover, the length of the nanorods increased quickly from 20 to 80 minutes, resulting in the fast increase of resistance. Subsequently, the resistance increased slowly with the length of the nanowires. These results are in well agreement with the variation of the potential time curve and the preferential growth direction is the same during deposition.

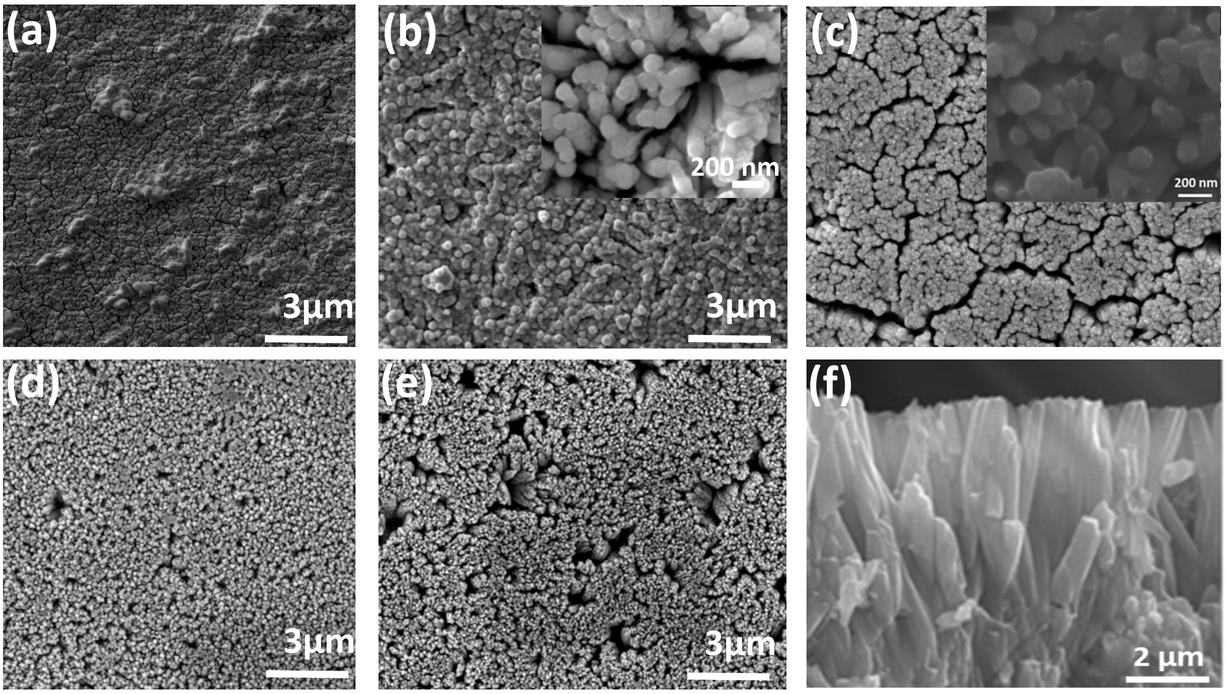

Figure S3: SEM images of the as-synthesized CeO_2 nanowires samples with 10 ml ethanol after electrodeposition at 70 °C for: (a) 10 min, (b) 20 min, (c) 40 min, (d) 60 min, and (e, f) 80 min.

On the basis of the above E-T curve analysis and SEM observations, the possible formation process can be defined as a seed-assisted electrochemical growth mechanism. The whole evolution process can be divided into three steps (i) nucleation, (ii) formation of Ceria seed layer on the substrate and (iii) further growth of nanowires on the seed layer.

Firstly, CeO_2 nuclei are formed via electrochemical reactions, and the process can be described as follows: OH^- ions generated by electro-reduction of NO^{3-} ions on the surface of Cathode (FTO). Then the OH^- ions react with Ce^{3+} and dissolved O_2 to form CeO_2.

As the concentration of CeO_2 has reached super saturation, CeO_2 nuclei form. Then the nuclei grow into a layer of CeO_2 particles as a seed layer for the further growth of nanowires. By increasing deposition time, the nanowires gradually occur on the surface of CeO_2 seed layer and finally form CeO_2 nanowires. In our case, these nanowires have a low crystallinity and a quasi-polycrystalline nature. However, it is still evident from HRTEM and SAED patterns (figure 1d of the revised manuscript), that these nanowires grew along [110] direction. For the face-centred cubic CeO_2 crystal, the normal growth rate "R" of the three lowest crystallographic planes is $R_{(110)} > R_{(100)} > R_{(111)}$ because of the surface energy for the three planes is $\Upsilon\{111\} < \Upsilon\{100\} < \Upsilon\{110\}$[2]. Therefore 1D CeO_2 nanostructures nanowires[3] or nanorods are frequently acquired as they grow along [110] direction.

S3. Calculation of capacitance, specific capacitance, energy density and power density.

The electrochemical parameters such as discharge capacitance, specific capacitance, energy and power density presented in this work are calculated from the galvanostatic charge-discharge curves using the relations as given in the literature:

$$C = \frac{I \, X \, \Delta t}{\Delta V} \tag{1}$$

$$C_s = \frac{C}{m} \tag{2}$$

$$E = \frac{C_s X (\Delta V)^2}{2}$$

(3)

$$P = \frac{E}{t} = \frac{I X \Delta V}{2}$$

(4)

Where: I is constant discharge current, m is the active mass of working electrode, ΔV is the voltage range, and Δt_D, Δt_C are discharging and charging time respectively.

Sample ID	SA(m^2 g^{-1})	TPV (cm^3)
E-10	11.524	0.0142
E-20	15.892	0.0974
E-30	27.124	0.2531
E-40	21.794	0.1681

S4. Brunauer–Emmett–Teller (BET) surface area and pore size distribution

Table 1: The BET surface areas and pore structures of all samples[a]

[a]SA: BET surface area; TPV total pore volume

S5. Cyclic Retention Test.

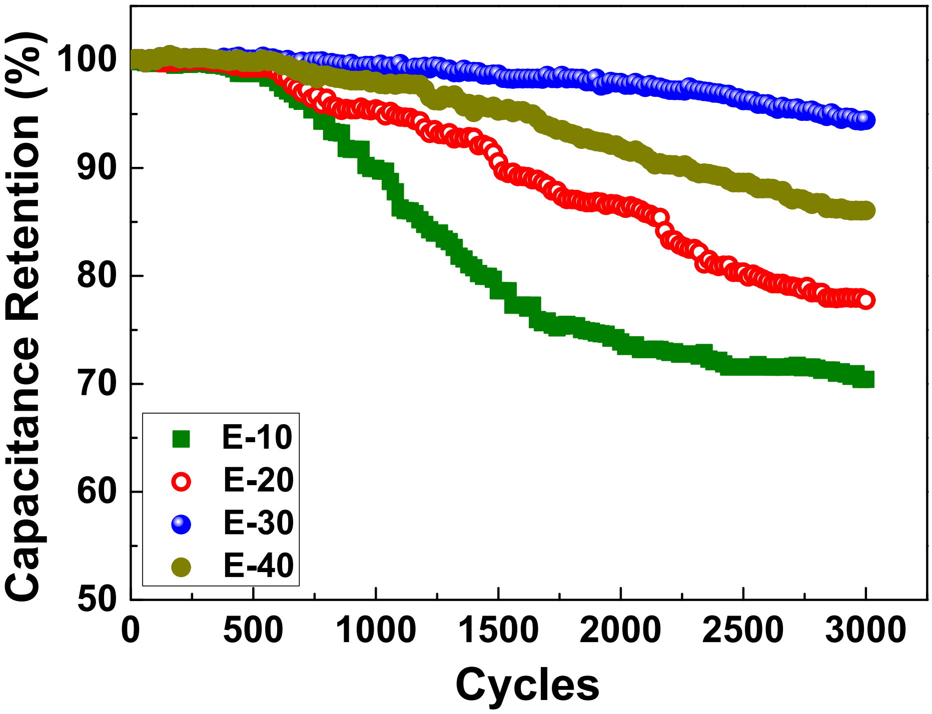

Figure S4: Cycle performance of E-10, E-20, E-30 and E-40 (in an increment per twenty cycles) with a voltage of 1 V at a current density of 10 A g^{-1} for 3000 cycles.

S6. Morphology Stability

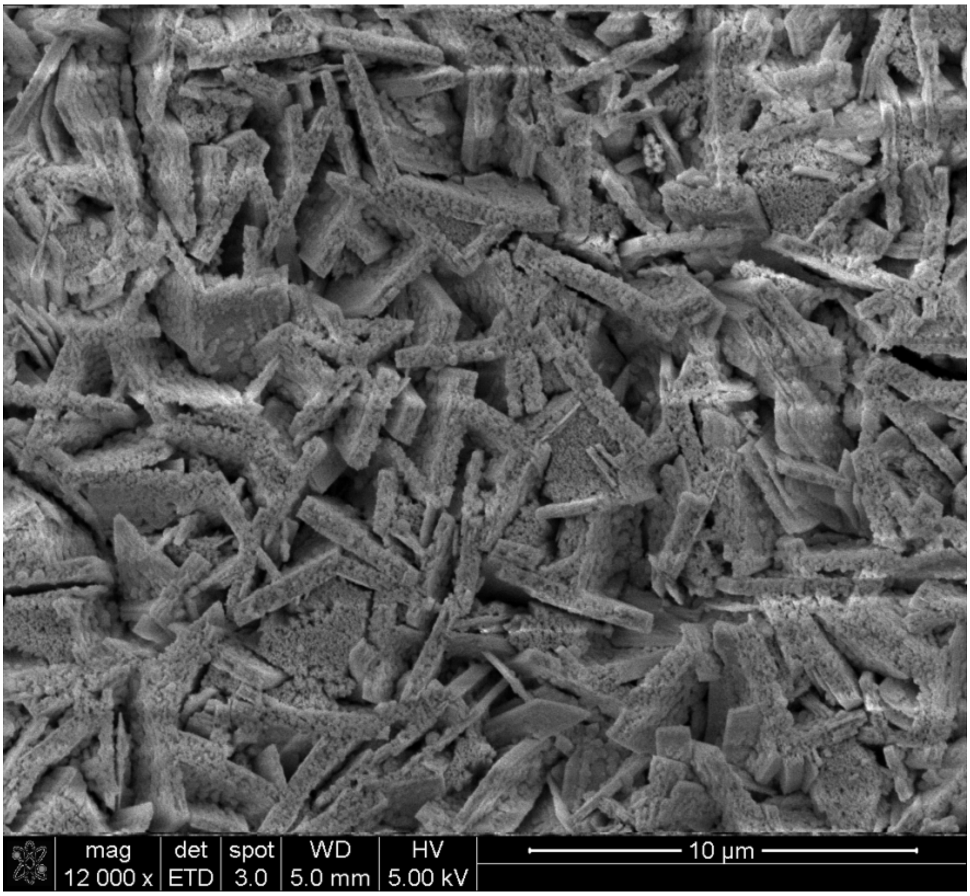

Figure S5: Surface Morphology of CeO_x nano-micro biscuits (E-30) after cyclic retention test.

S7. <u>XPS Studies.</u>

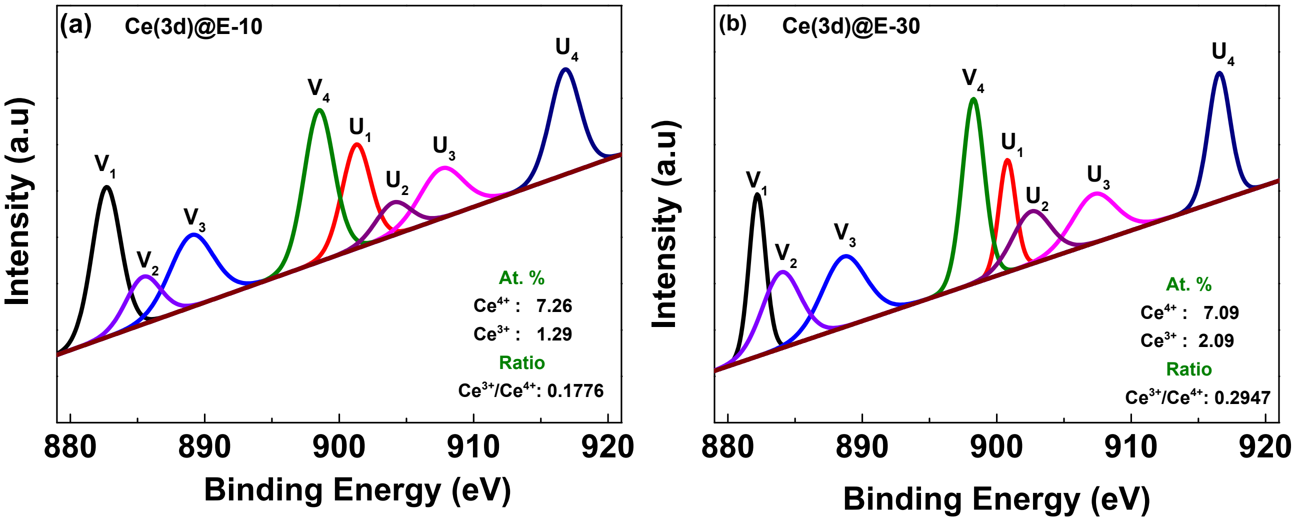

Figure S6: XPS spectra of the Ce 3d regions of (a) E-10 and (b) E-30 samples.

S8. Impedance measurements.

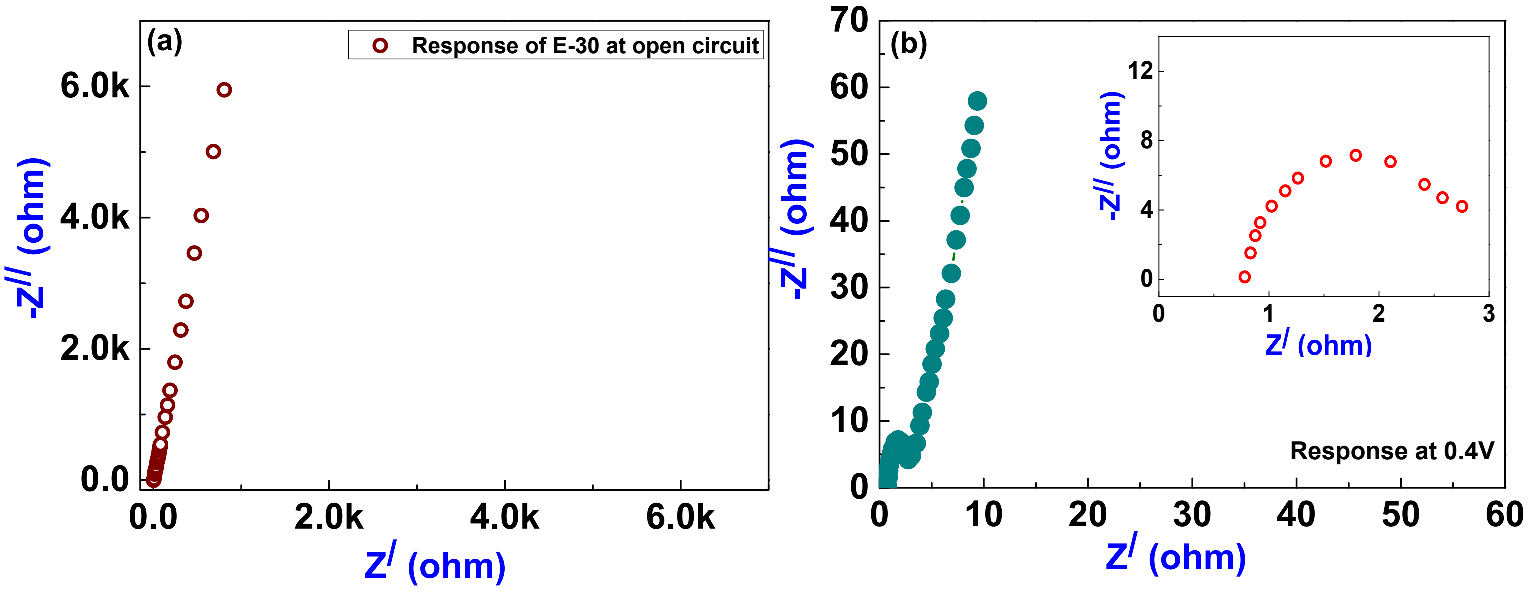

Figure S7: Nyquist representation of impedance spectra for E-30 at two different potentials, before any potassiation at (a) open-circuit and (b) after potassiation to 0.4 V.

S9. Surface Morphology of Carbon foam.

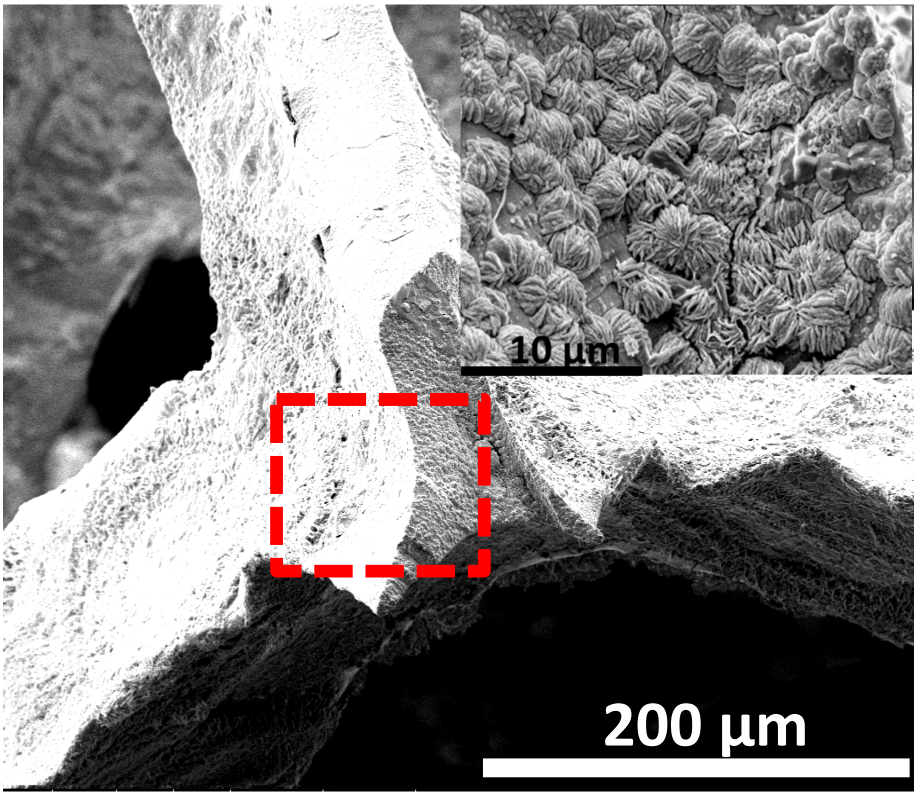

Figure S8: Surface morphology of Carbon foam at low magnification and in the inset the morphology at high magnification.

References:

1. Tsakova, V., D. Borissov, and S. Ivanov, *Role of polymer synthesis conditions for the copper electrodeposition in polyaniline.* Electrochemistry Communications, 2001. **3**(6): p. 312-316.
2. Wang, Z.L. and X. Feng, *Polyhedral Shapes of CeO2 Nanoparticles.* The Journal of Physical Chemistry B, 2003. **107**(49): p. 13563-13566.
3. Zuwei, Z., et al., *Synthesis of Ba-doped CeO 2 nanowires and their application as humidity sensors.* Nanotechnology, 2007. **18**(46): p. 465504.