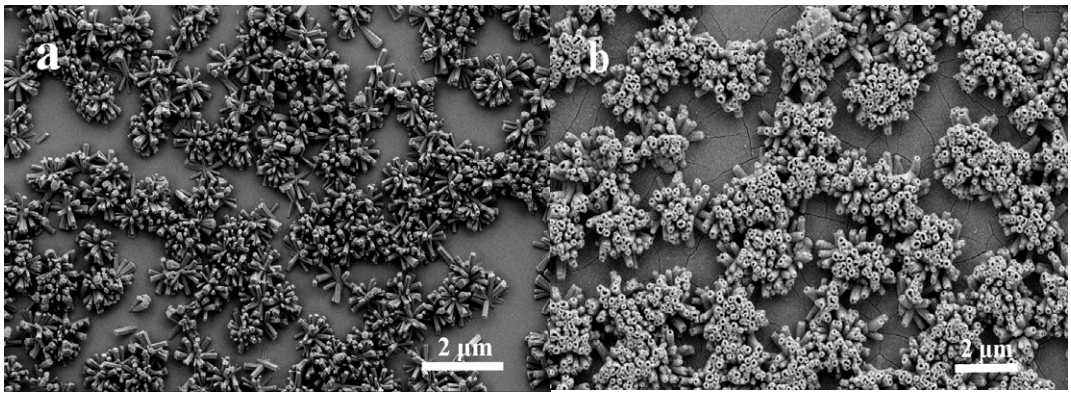
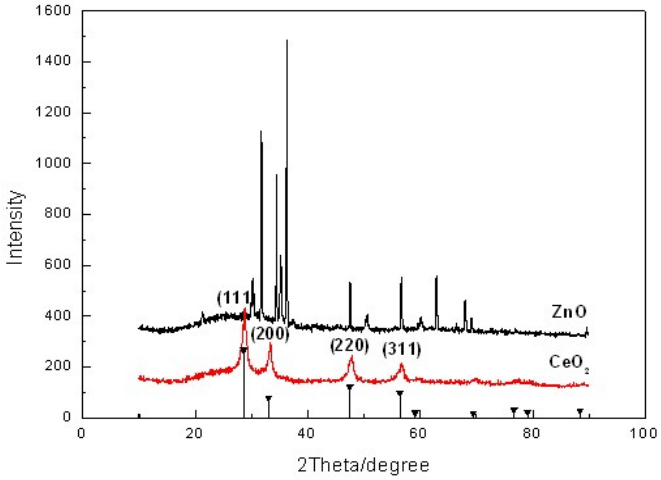
Supporting information

Hydrothermal Synthesis and Automotive Exhaust Catalytic Performance of CeO_2 Nanotube Arrays

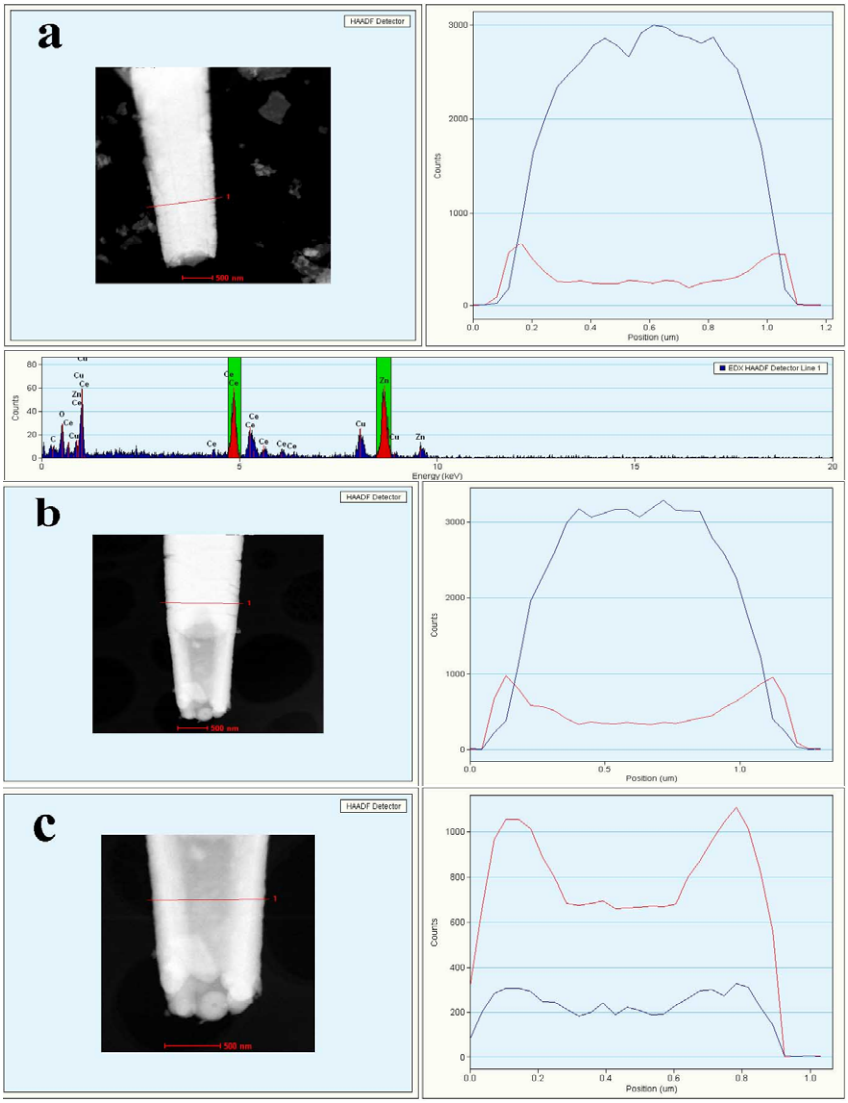
Ying-jie Feng, Li-li Liu, and Xi-dong Wang



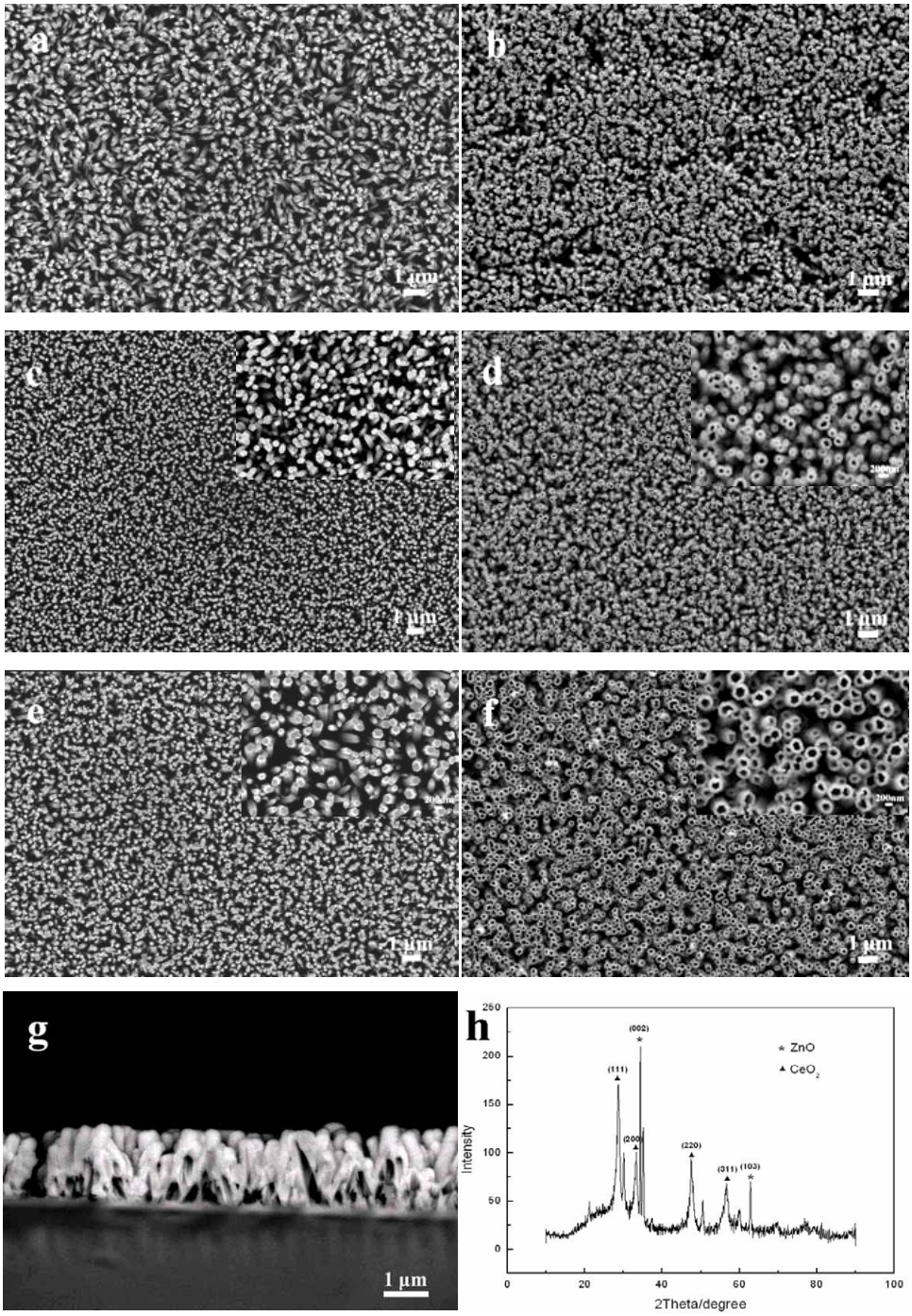
SI-1 SEM images of (a) clusters of ZnO nanorods and (b) CeO_2 nanotubes.



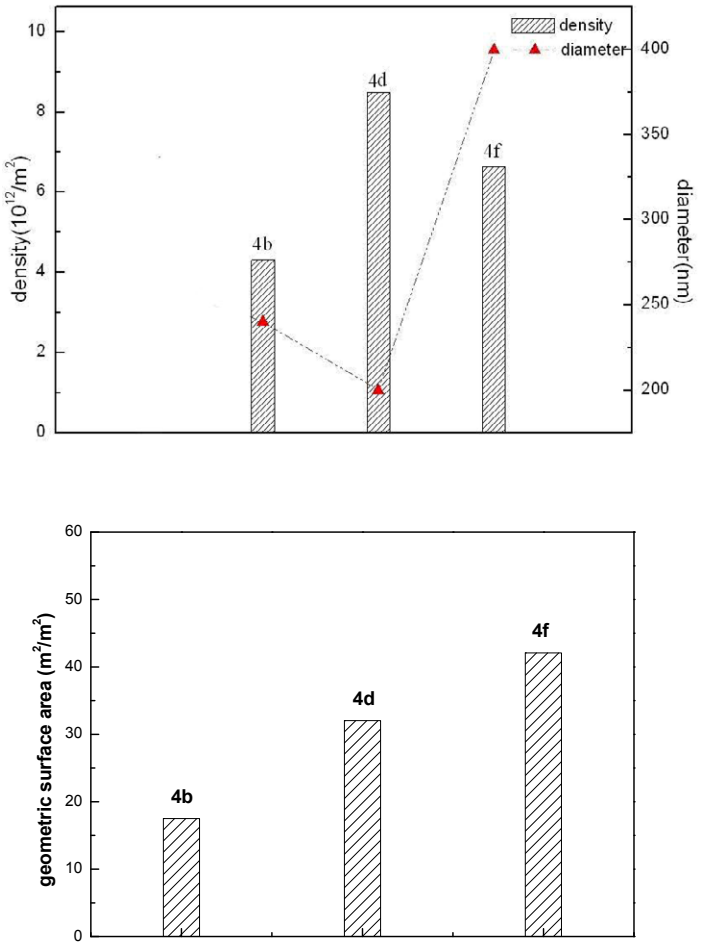
SI-2 XRD patterns of the clusters of ZnO nanorods and CeO_2 nanotubes.



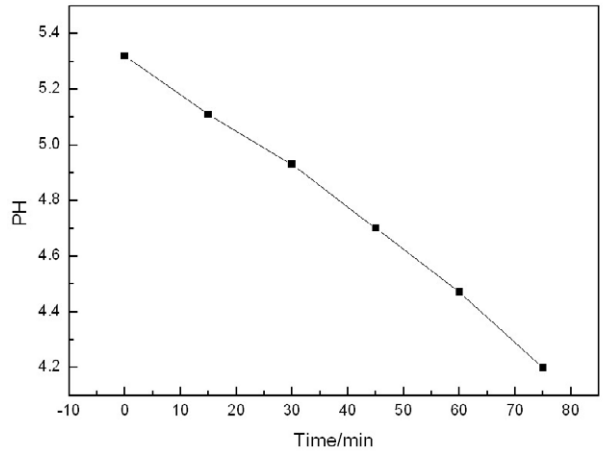
SI-3 EDS spectra of (a) CeO_2 nanotube obtained at 30min; linear scanning EDS of (b) undissolved part and (c) dissolved part of CeO_2 nanotube obtained at 60min.



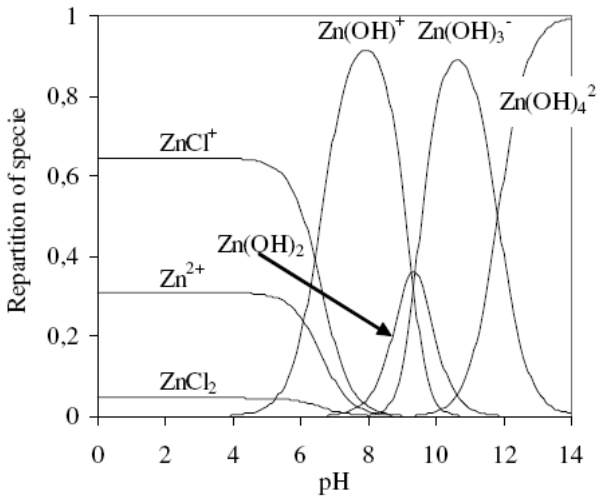
SI-4 (a) SEM image of ZnO nanorods array obtained on the substrate with pretreatment that zinc nitrate (0.05 mol L^{-1}) and methenamine aqueous (0.05 mol.L^{-1}) solutions were respectively dripped on the ITO glass for a natural mixture of 5 min and then the substrate was spun for 30 s at the rate of 3000 $r.m^{-1}$; (b) CeO_2 nanotubes array obtained by the template of (a); (c) SEM image of ZnO nanorods array obtained on the substrate with pretreatment that zinc nitrate (0.05 mol L^{-1}) and methenamine aqueous (0.05 mol L^{-1}) solutions for a natural mixture of 10 min; (d) CeO_2 nanotubes array obtained by the template of (c); (e) SEM image of ZnO nanorods array obtained on the substrate with pretreatment that zinc nitrate (0.1 mol L^{-1}) and methenamine aqueous (0.1 mol L^{-1}) solutions for a natural mixture of 10 min; (f) CeO_2 nanotubes array achieved by the template of (e); (g) side face SEM image of CeO_2 nanotube arrays; (h) XRD result of the CeO_2 nanotubes.



SI-5 Statistical analysis of density, diameters and geometric surface area of CeO_2 nanotube arrays shown in SI-4.



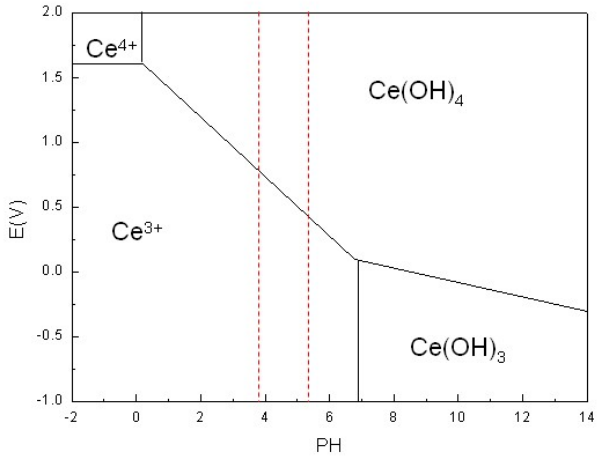
SI-6 Profile of precursor solution's pH variations for dynamic experiments



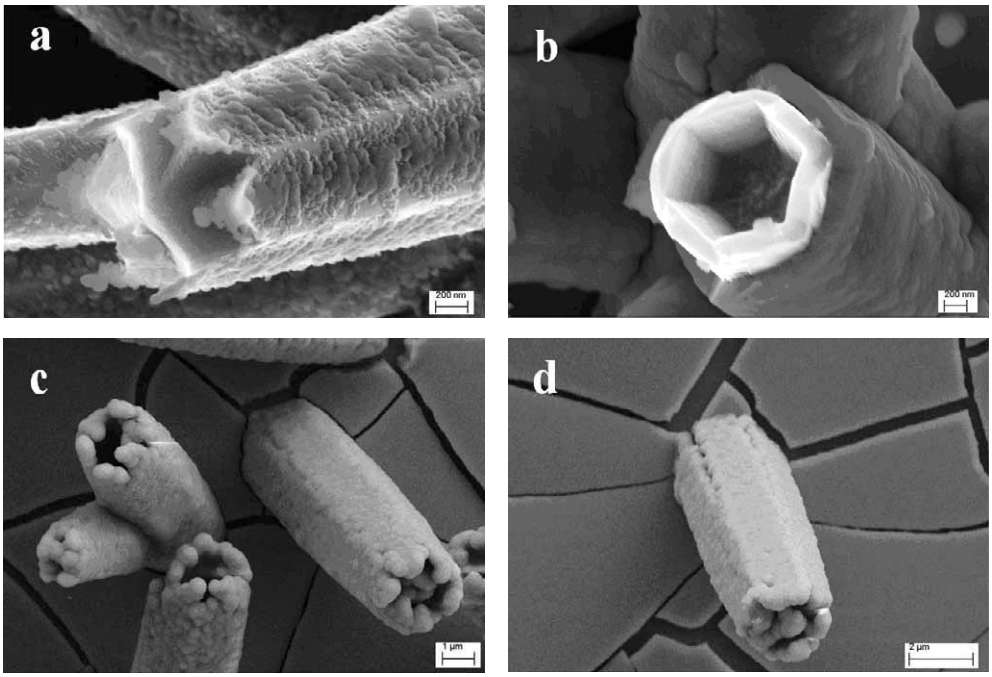
SI-7 Profile of zinc species in solution.

As amphoteric oxide, stable maintenance of ZnO requires nearly neutral solution. According to the measurement of the dynamic experiments shown in SI-6, the original PH value for 0.1M cerium nitrate solution is 5.31. With the growth time increasing, the PH value decreased at a nearly constant rate. Therefore, during the hydrothermal process, the ZnO nanorods will be dissolved and the solubility of ZnO should get faster.

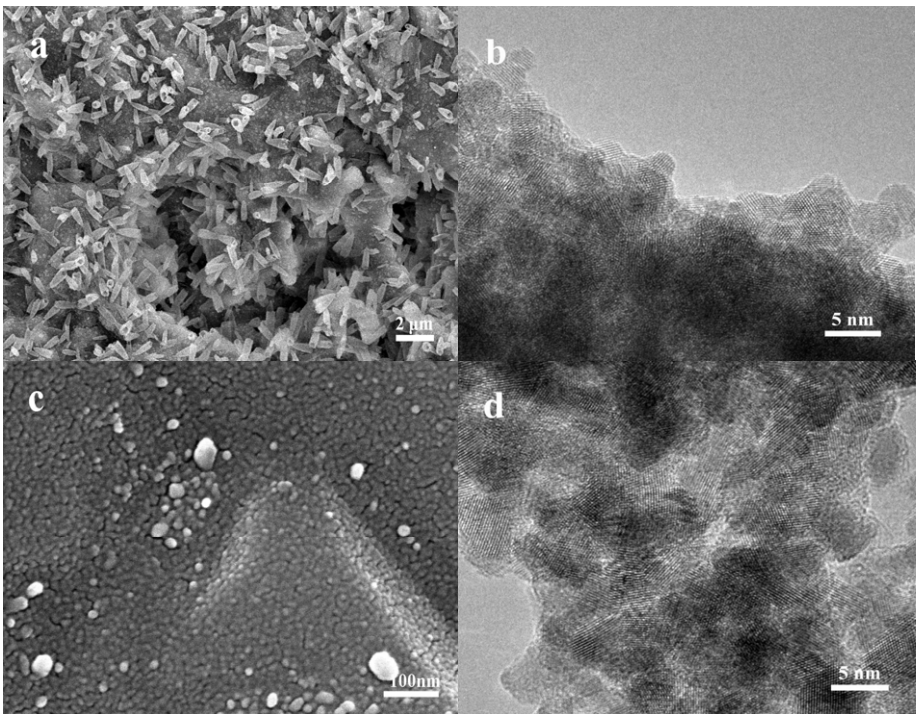
According to previous literature, when hydrothermally treated in low -OH concentrations (C-OH < 1 mol L^{-1}) at a low temperature of 100℃, there might exist inadequately high chemical potential for driving the anisotropic growth of the $Ce(OH)_3$ nuclei and the instantaneous oxidization conversion from $Ce(OH)_3$ to CeO_2 will happen instead.



SI-8 Diagram of PH-E(v) for cerium species.



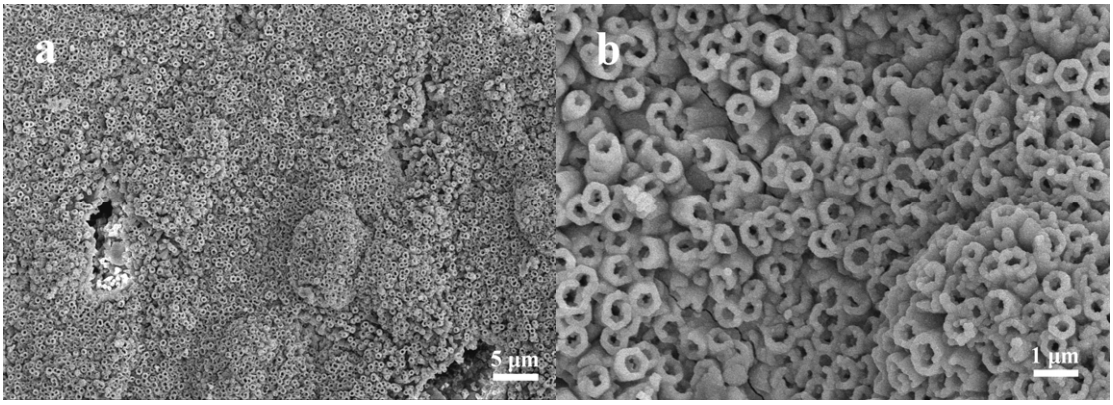
SI-9 SEM images of CeO_2 tubes obtained with different cerium nitrate concentrations: (a) 0.08M, (b) 0.09M, (c) 0.12M, (d) 0.14M.



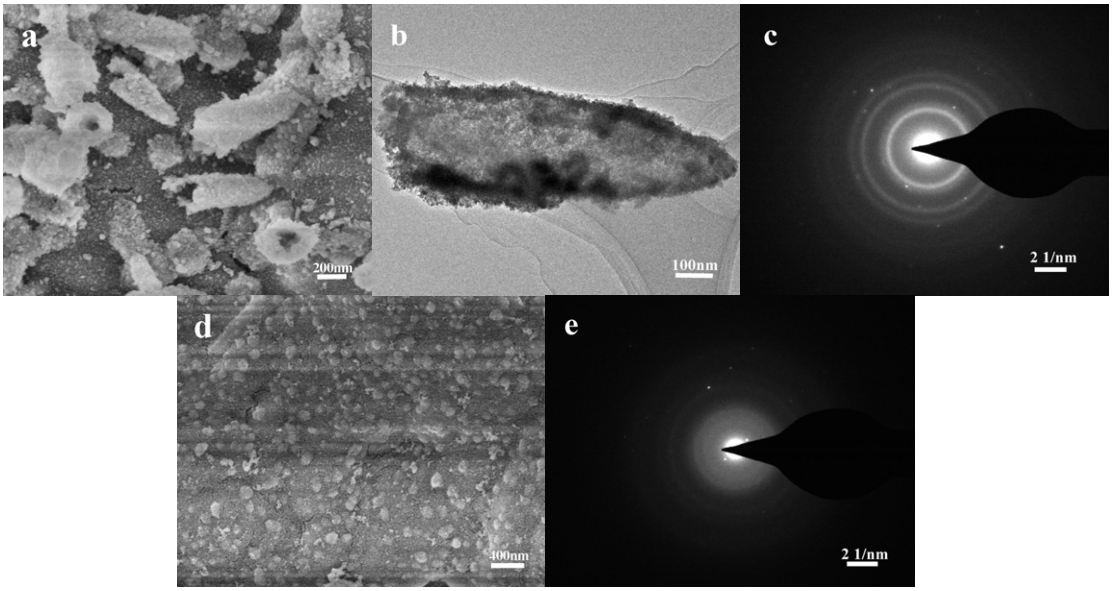
SI-10 (a) SEM image and (b) HRTEM image of pd/ceria tubes/cordierite, (c) SEM image and HRTEM image of pd/ceria particles/cordierite

From SI-10, it could be observed that the ceria nanoparticles were well dispersed on cordierite and the particle size ranges between 5 to 10nm. Based on our investigations, it is known that the ceria tube is actually composed of numerous ceria crystalline grains. After the TWC catalytic test with the temperature range from 100℃ to 500℃, the ceria nanoparticles will be sintered into larger ones. Obviously, compared with the rough surface of ceria tubes, it is reasonable to believe that the specific surface area of ceria tube is higher than the ceria particle film with the same ceria loading.

Additionally, the specific surface area of the ceria tubes/cordierite could be controlled by adjusting the density of ceria tube arrays on the cordierite. In our later work, the density of ceria tubes prepared on the cordierite could be increased greatly as shown in SI-11 and the catalytic performance should be improved further.



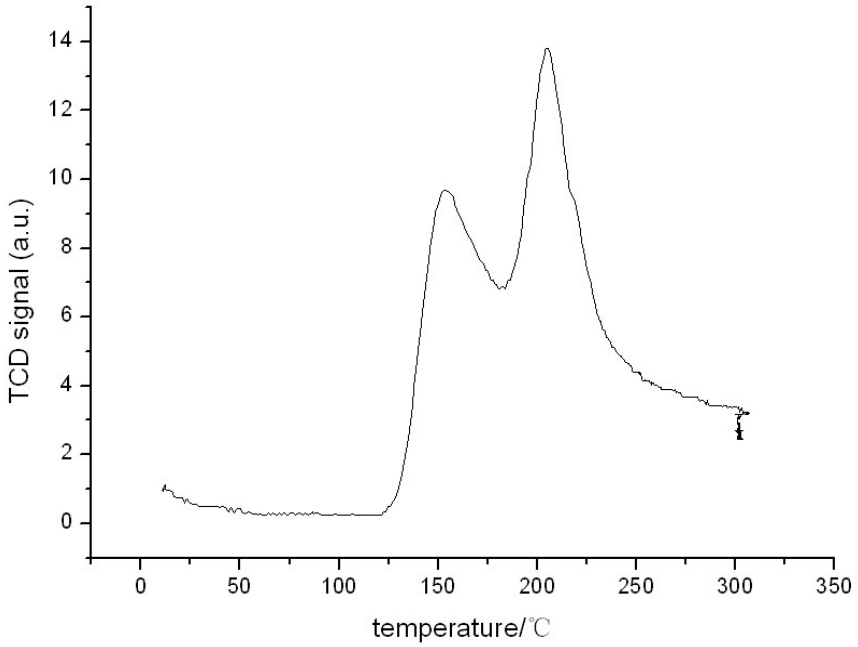
SI-11 (a) (b) SEM images of cordierite supported ceria tubes prepared by pre-coating ZnO seed layers.



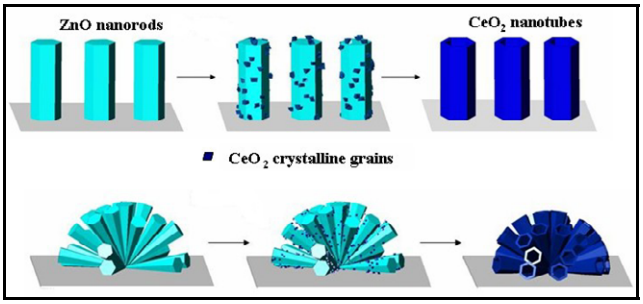
SI-12 (a) SEM image, (b) TEM image and (c) diffraction patterns of pd/ceria tubes/cordierite, (d) SEM image and (e) diffraction patterns of pd/ceria particles/cordierite

The impregnation method we employed to load previous metal Pd is a common method in the previous literatures. As the literatures reported, the Pd metallic particle size was about 3 nm.[1] For the ceria particles supported Pd (in SI-12(d)), it could be observed that, the Pd particles have been sintered into large ones after the catalytic performance test. For the Pd/ceria tubular/cordierite sample, although much effort has been made to confirm the Pd dispersion and particle size on ceria tubular, the ceria tubular with Pd is very difficult to be scraped off because of the cordierite's rough surface. However, from the TEM diffraction patterns composed of circles and some spots in SI-12(c), it is reasonable to believe that besides the multi-crystallized ceria tube, some metal particles should exist in the ceria tube.

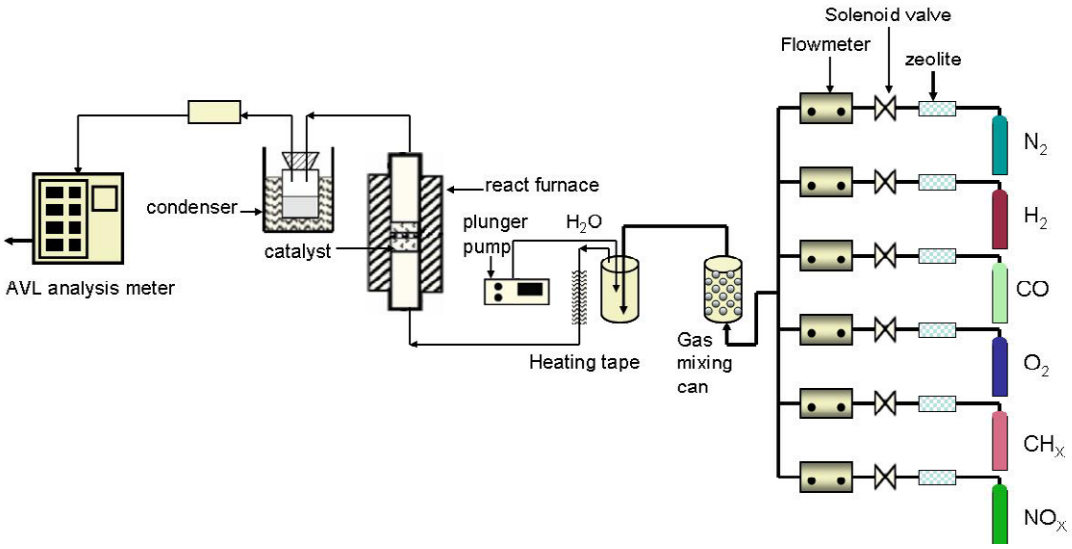
[1] Jhon F. Sánchez M, Orlando J. González Bello, Mario Montes, Gabriela M. Tonetto, Daniel E. Damiani, *Catalysis Communications* **2009**,*10*,1446



SI-13 TPR profiles of the catalyst samples



SI-14 Schematic illustration of the growth mechanism for CeO_2 nanotube arrays



SI-15 Experimental set-up for evaluation of three-way catalysis performance