Electronic supplementary information (ESI)

Introducing Nanocrystalline CeO_2 as heterogeneous Environmental Friendly catalyst for the Aerobic Oxidation of *Para*-xylene to Terephthalic Acid in Water

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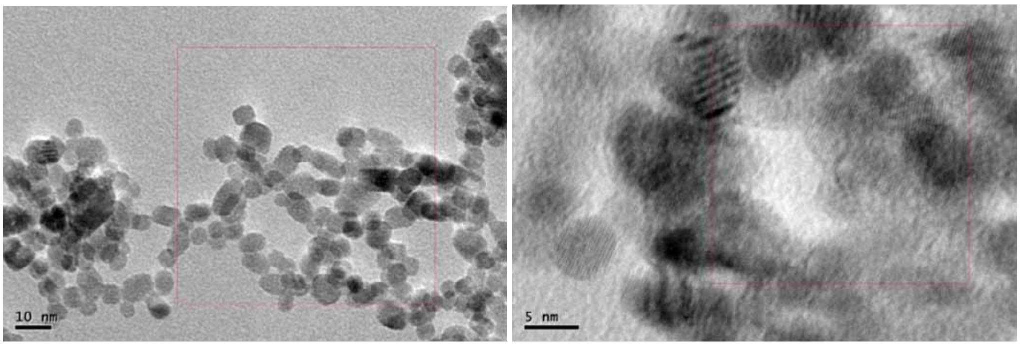

Figure S1. TEM and HRTEM images of an as-synthesized CeO_2 sample in different locations showing {111} and {100} factes.

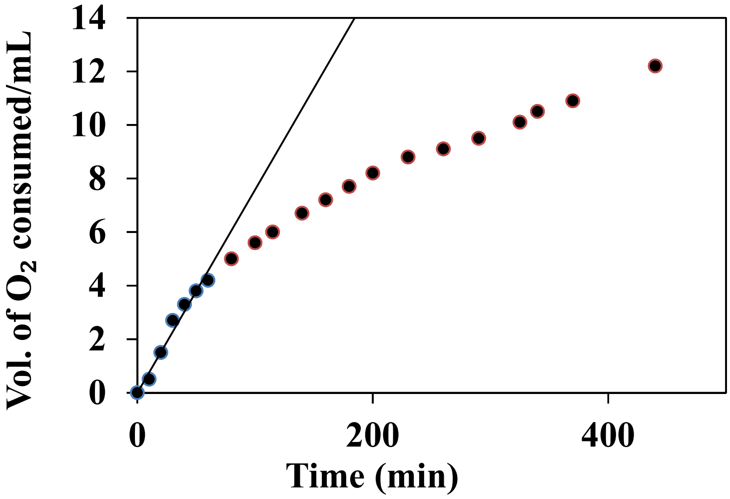

Figure S2. The volume of O_2 consumed is displayed as a function of time for the oxidation of *para*-xylene under the following reaction conditions: *para*-xylene =100 mM, CeO_2 =10 mg, DI water =6mL and temp = 70 ˚C.

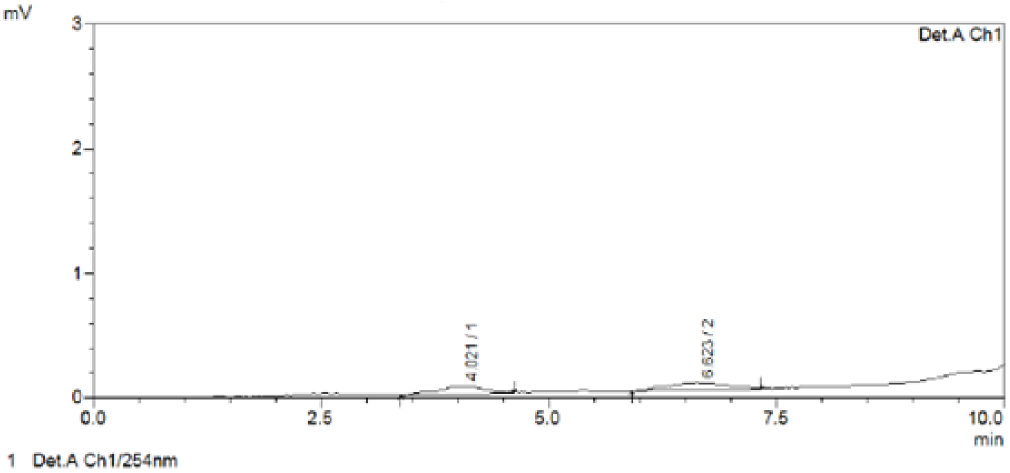

Figure S3. HPLC chromatogram of the product solution obtained for 100 mM *para*-xylene oxidation with 10 mg commercially purchased CeO_2 catalyst at 85 ºC for 8 hr.

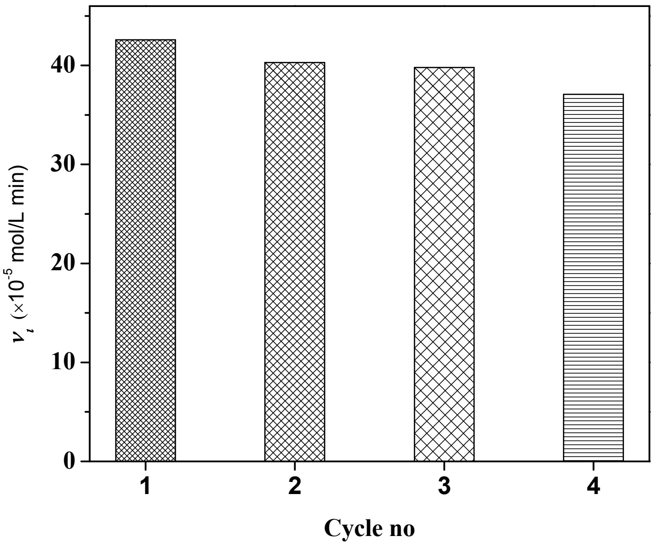

Figure S4. Initial rates for aerobic oxidation of 100 mM *para*-xylene with the recovered CeO_2 NCs catalyst. The reaction were carried out at 85 ºC and 1 bar O_2 pressure.

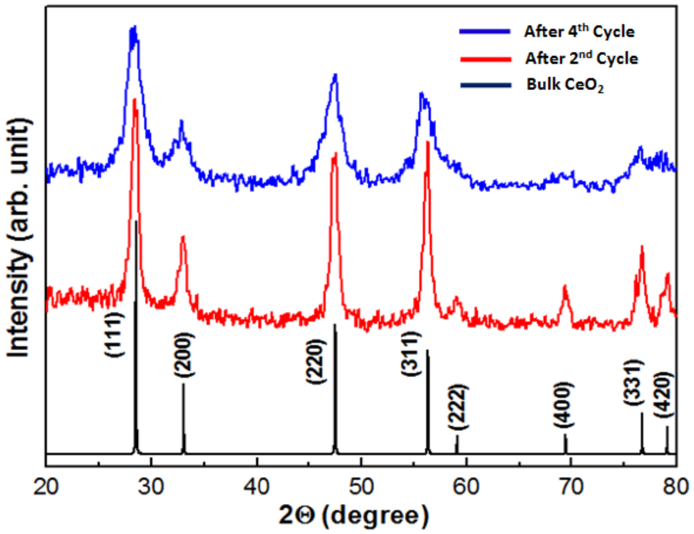

Figure S5. Powder XRD pattern of the recovered ceria catalyst after second (2nd) and Fourth (4th) recycle.

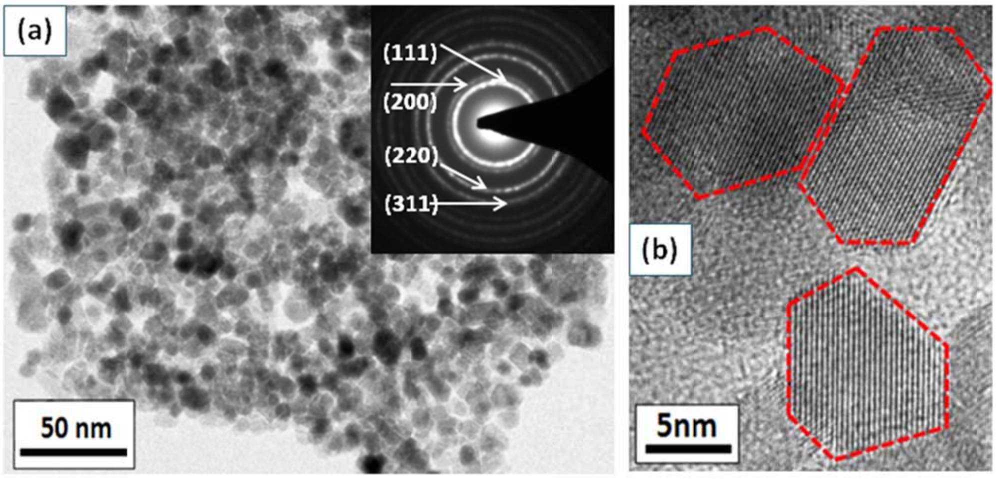

Figure S6: (a) Low magnification TEM image (inset: SAED pattern) and (b) HRTEM image of few hexagonal morphologies of recovered 13-15 nm CeO_2 nanoparticle catalyst after fourth recycled test.

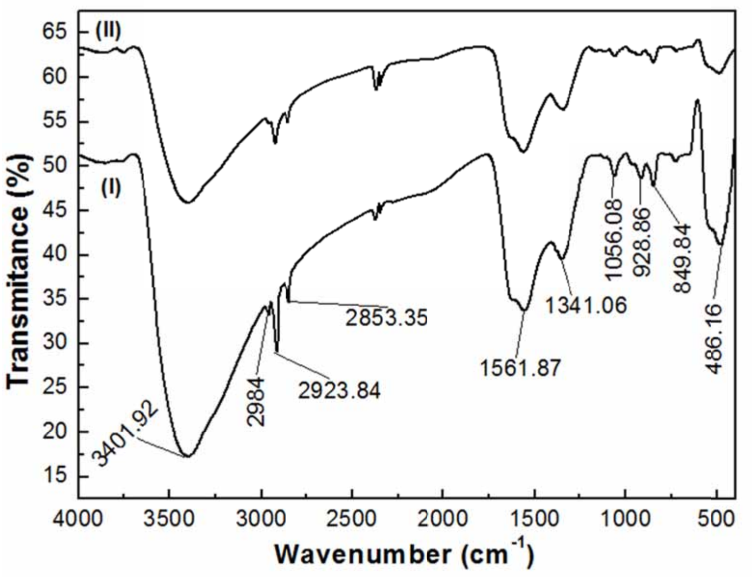

Figure S7: FT-IR spectra of (I) as-synthesized fresh catalyst and (II) recovered catalyst after 3rd catalytic reaction cycle.

The FTIR spectra of CTAB surfactant assisted fresh CeO_2 and recovered CeO_2 catalyst after 3rd cycle in the range 4000-400cm^{-1} are shown in Figure X. The sharp absorptions in the region 2800-3020 cm^{-1} are attributed to CTAB surfactant. The band in the region 2853.35 cm^{-1} is assigned for symmetric stretching and in the region 2923.84 is assigned for asymmetric stretching of C-CH_2 and C-CH_3 vibrations while absorption at 2984 cm^{-1} can be attributed to N–CH_3 symmetric stretching vibrations for the solid surfactant CTAB, which were detected in both fresh and recovered catalyst. This indicates the presence of CTAB with the as synthesized catalyst even after washing with water and ethanol and drying for overnight at 40°c. The similar absorption peaks in the FTIR spectrum of recovered catalyst again indicate that CTAB was not removed even after 3rd catalytic cycle. The broad absorption in 3401.92 cm^{-1} range is assigned to the stretching vibration of hydroxyl groups of adsorbed water on the surface of the samples. The literature also reports that the sharp bands in the region of 1400–1600 cm^{-1} are attributed to the deformation of –CH_2– and –CH_3 of the incorporated surfactants and bending vibration of absorbed molecular water. In addition to the bands in the 850–1600 cm^{-1} regions, the band due to the stretching frequency of Ce–O can be seen in the 486.16 cm^{-1} region, which confirms the formation of CeO_2.[1-3]

References:

1. C. S. Riccardi, R. C. Lima, M. L. dos Santos, P. R. Bueno, J. A. Varela and E. Longo, *Solid State Ionics*, 2009, **180,** 288–291.
2. H. Li, G. Wang, F. Zhang, Y. Cai, Y. Wang and I. Djerdj, *RSC Advances*, 2012, **2**, 12413–12423.
3. J. Lv, Y. Shen, L. Peng, X. Guo and W. Ding, *Chem. Commun*., 2010, **46**, 5909–5911.