Supplementary Data

Surface Diffusion Driven Nanoshell Formation by Controlled Sintering of Mesoporous Nanoparticle Aggregates

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Experimental Section

Synthesis: Porous aggregates of ceria were obtained by solvothermal synthesis in a mixed solvent of ethylene glycol and water at 225ºC using $Ce(NO_3)_3.6H_2O$ as the starting material.[1] The ceria aggregates obtained were annealed at 250ºC, 500ºC, 700ºC and 900ºC in air to investigate the transformation of the porous aggregate to hollow structures. Nanoporous aggregates of platinum were synthesized by hydrothermal method at 200ºC using $H_2PtCl_6.6H_2O$ as the starting material.[2] The Pt aggregates were annealed at various temperatures i.e. 200ºC, 300ºC, 400ºC and 500ºC in air in a muffle furnace. Porous aggregates of SnO_2 were prepared by a solvothermal synthesis using $K_2SnO_3.3H_2O$ as the precursor in water: ethanol mixed solvent at 150°C. [3] TiO_2 in anatase phase in spherical aggregates was formed by hydrolysis of TiF_4. [4]The SnO_2 nanoclusters were annealed at 600°C, 800°C and 900°C and TiO_2 sample was annealed at 600°C and 800°C.

Characterization: The as synthesized nanoporous aggregate samples as well as the samples obtained by annealing the aggregates at different temperatures were characterized by various techniques. The crystallographic information of the samples were investigated by X-ray powder diffractometer, Bruker D8Advance equipped with a Cu Kα radiation source (λ = 1.5418 Å). Transmission Electron Microscopy (TEM) and HRTEM were performed on a Tecnai F30/Tecnai T20 at a voltage of 200 kV. Scanning transmission electron microscope (STEM) imaging and compositional line profiling were done in Tecnai F30 equipped with STEM-EDS analysis system at a voltage of 300 kV. Spot size 6 with the spatial resolution of few nm was used for obtaining compositional line profile

across the hollow nanostructures. TEM samples were prepared by evaporating a drop of a colloidal dispersion of the sample in acetone/alcohol on 300 mesh formvar/carbon-coated Cu grid. Specific surface area of the samples were obtained in Quantachrome Autosorb by BET method using nitrogen adsorption-desorption isotherms at 77K.

Molecular Dynamics Simulation Details: The initial system is created as follows. First, the center positions of 300 nanoparticles are generated using a Monte Carlo algorithm to mimic the reaction limited aggregation process. Then, randomly oriented nanoparticles (hexagonal 2D lattice) with a radius of 2.5 nm are placed at the above centers. The system is then subjected to thermal relaxation at a temperature around 10% of the bulk melting point. Subsequently, 44000 additional atoms with very high kinetic energy are distributed outside the cluster and then are quenched down to the same low temperature to form the polycrystalline outer shell. During the formation process of this outer shell, atoms belong to the original nanoparticle aggregates are not allowed to move. Thus created outer shell is reasonable since the coalescence between peripheral nanoparticles is easier due to their greater degrees of freedom comparing to the constrained interior nanoparticles. Finally, the whole system (about 100000 atoms) is ready for high temperature thermal annealing to study the coalescence of nanoparticles and the evolution of trapped voids.

The system is then subjected to a canonical ensemble at a temperature of about 40% of the bulk melting point for about 0.1 microseconds. This temperature is chosen to maximize the mobility of atoms without melting during the accessible simulation time frame.

The simulation shows dramatic differences in stability between voids inside a grain and those at the grain boundaries. Grain sliding can effectively remove inter-granular voids. However, eliminating intra-granular voids requires successive atomic diffusion which is much more time consuming.

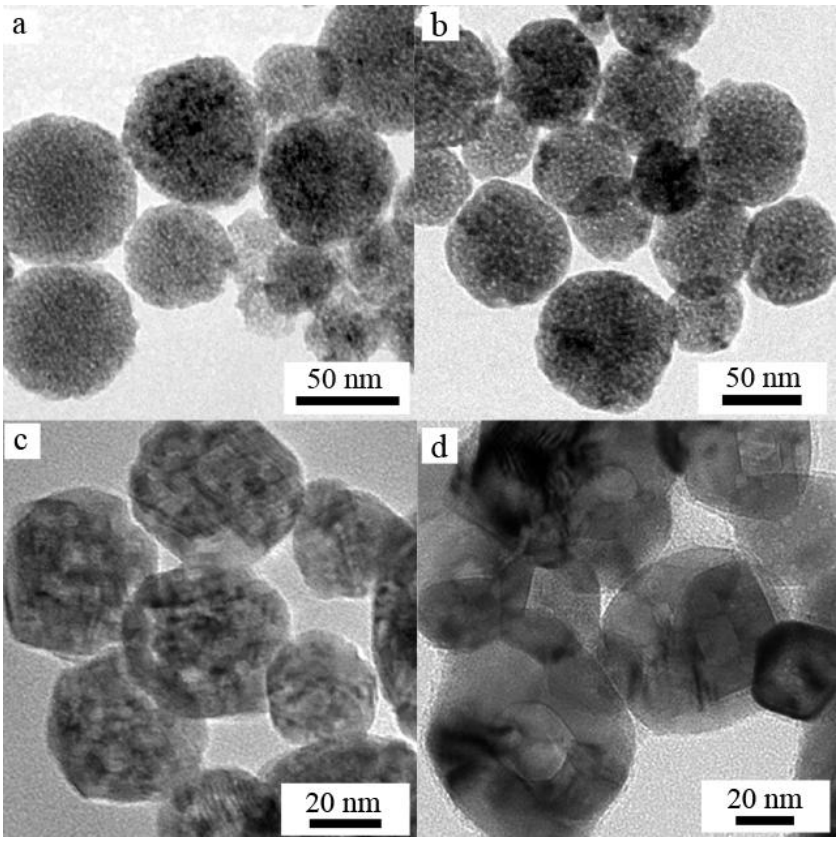

Figure S1 (a) shows the TEM bright field image of as synthesized ceria nanoclusters. (b), (c) and (d) are the images of CeO_2 nanoclusters annealed at 500ºC, 700ºC and 900ºC respectively, showing the gradual formation of hollow structures as a function of annealing temperature.

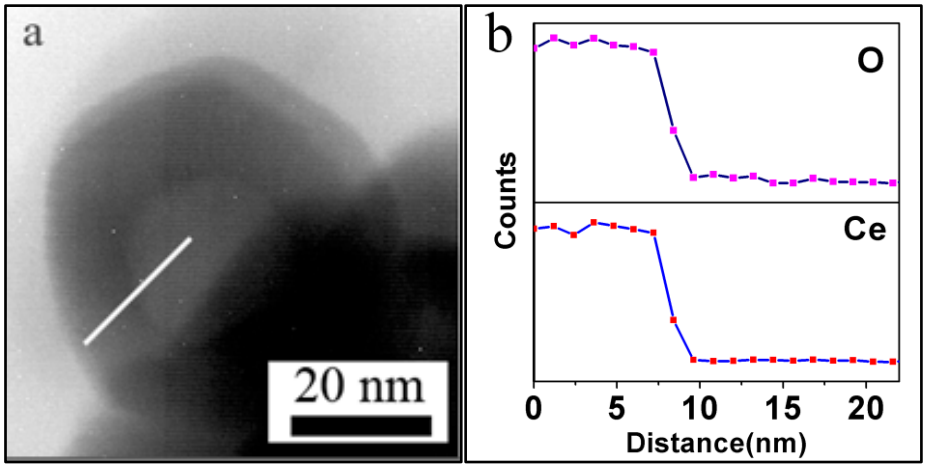

Figure S2. (a) is the STEM Bright Field image of a hollow CeO_2 cluster and (b) is the STEM-EDX line profile of Ce and O along the line indicated in (a). This clearly shows the hollow nature of the particle

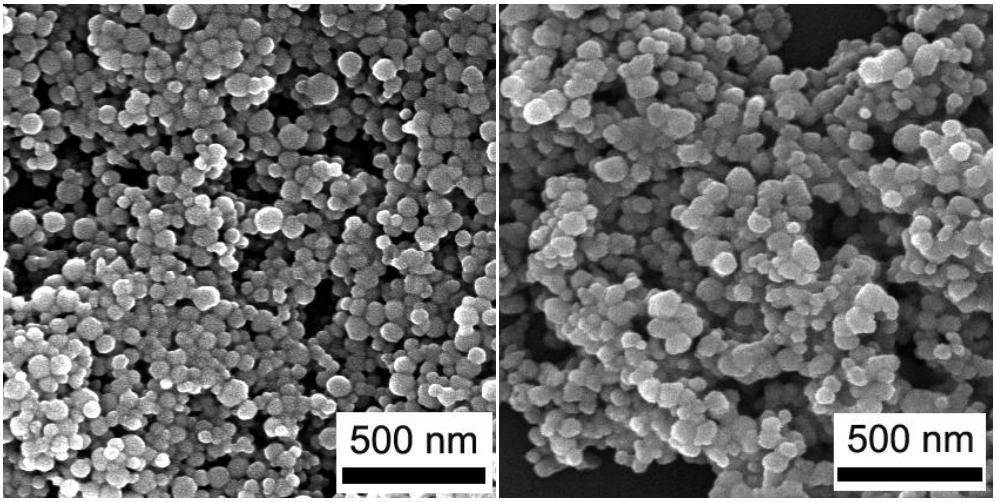

Figure S3. SEM images of CeO_2 aggregates annealed at 700°C (left) and hollow CeO_2 obtained by annealing the aggregates at 900°C (right).

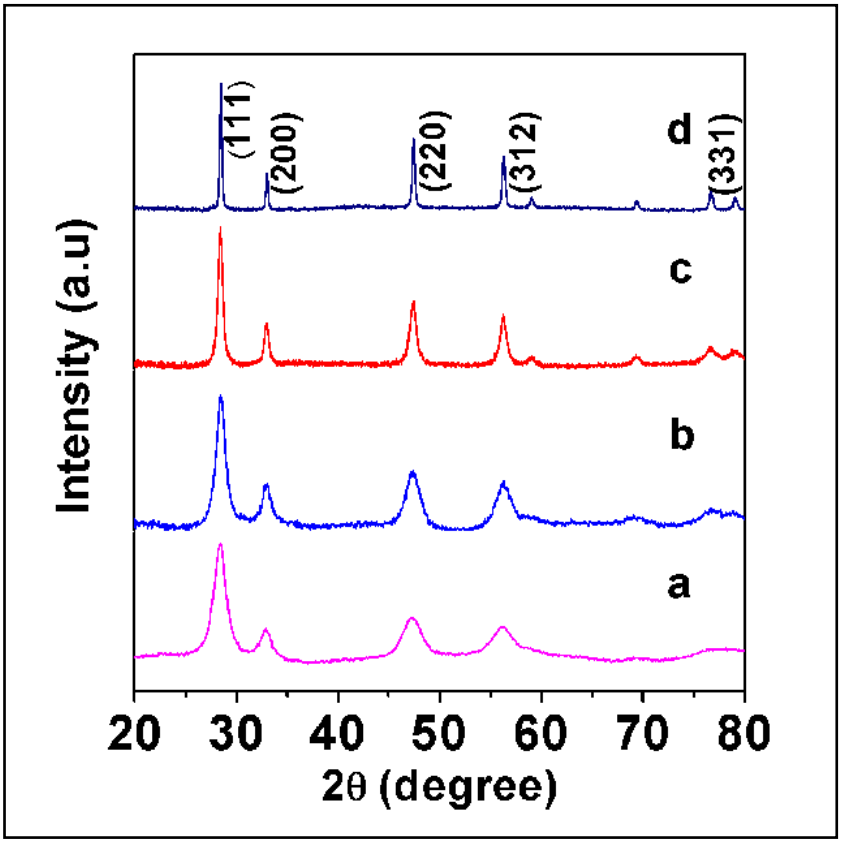

Figure S4 shows the powder x-ray diffraction patterns of the CeO_2 nanoclusters. (a) is the as synthesized CeO_2 whereas (b), (c) and (d) are the patterns obtained from samples annealed at 500°C, 700°C and 900°C respectively

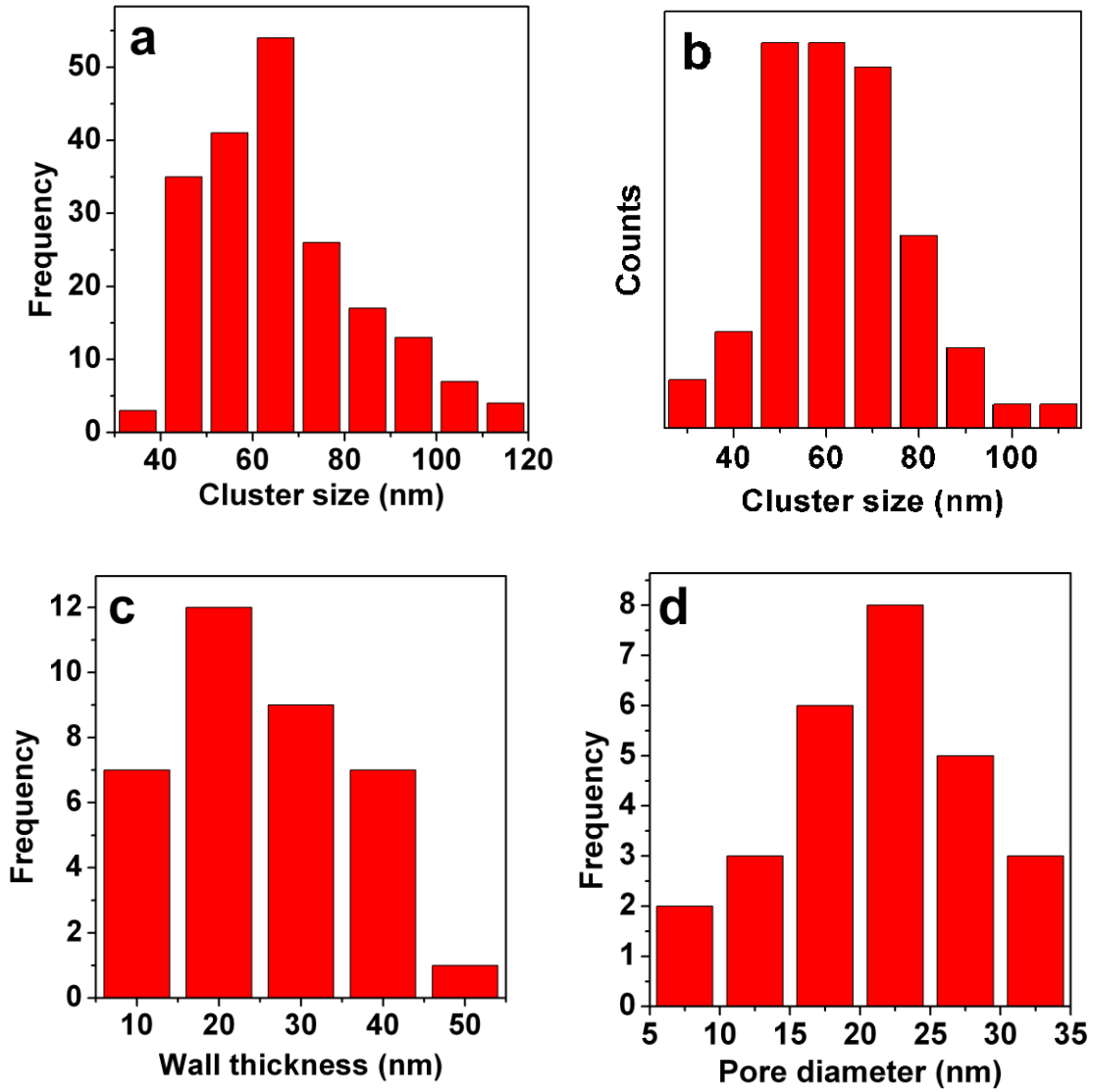

Figure S5. Histogram showing the cluster size distribution of (a) Nanoporous CeO_2 aggregates (b) Annealed at 900^{o}C (c) wall thickness distribution and (d) pore diameter distribution of hollow CeO_2 particles.

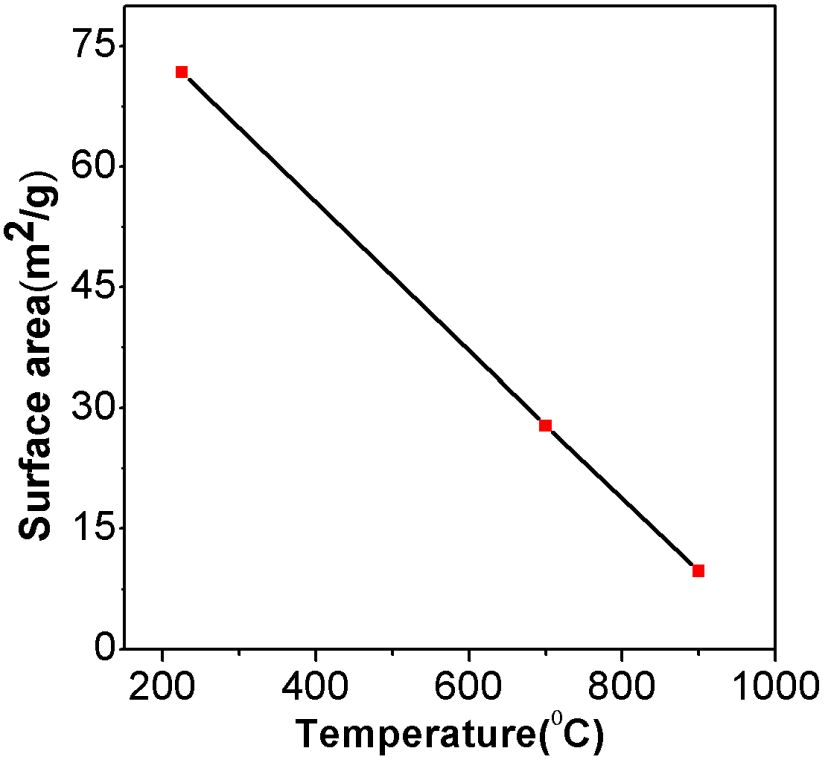

Figure S6. BET surface area versus annealing temperature for the CeO_2 sample showing the decreases in surface area on annealing at high temperatures

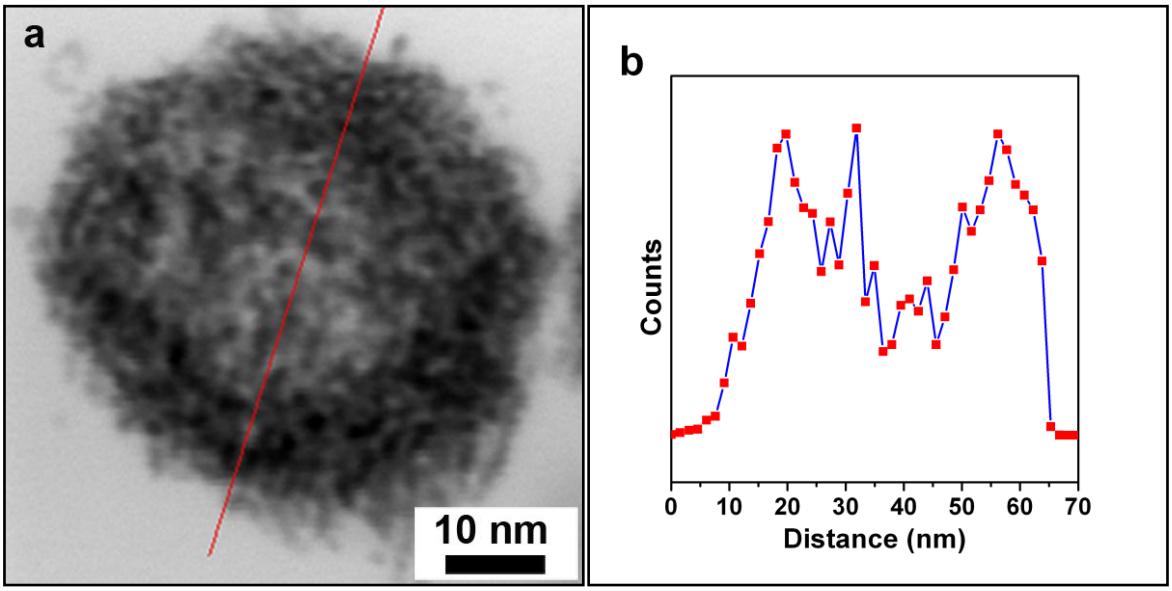

Figure S7. (a) is the STEM Bright Field image of a hollow Pt cluster and (b) is the STEM-EDX line profile of Pt corresponding to the line indicated in (a).

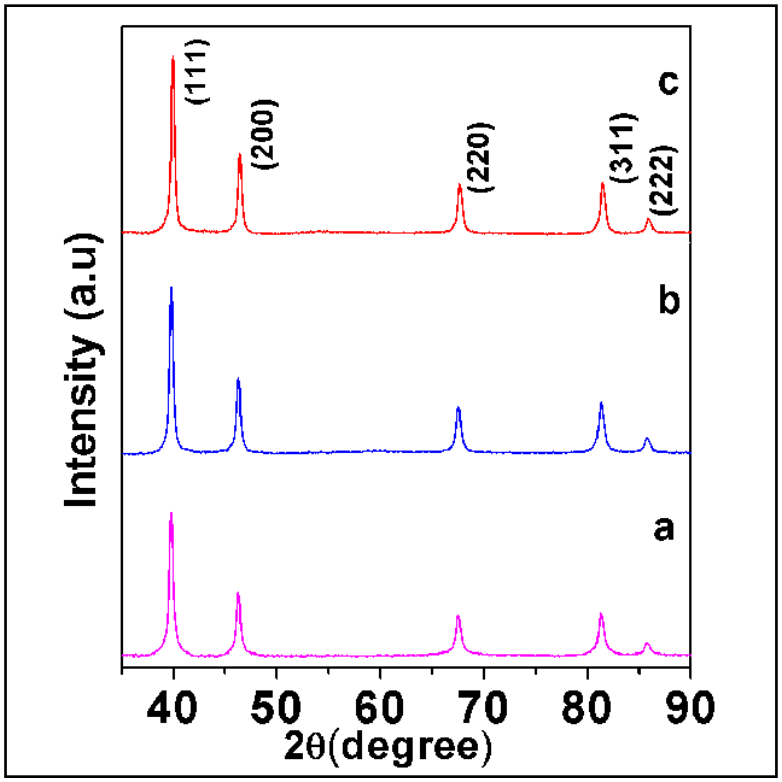

Figure S8. X-ray diffraction patterns of Pt nanoclusters (a) as-synthesized Pt nanoclusters, (b) and (c) are the patterns obtained from samples annealed at 300°C and 400°C respectively.

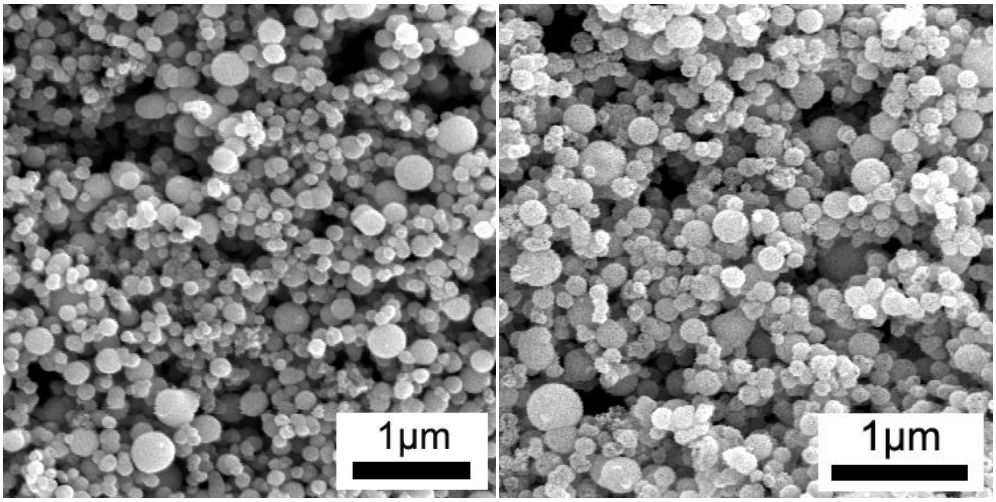

Figure S9. SEM images of nanoporous aggregates of SnO_2 annealed at 600°C(left) and the hollow spheres of SnO_2 obtained by annealing the aggregates at 800°C(right)

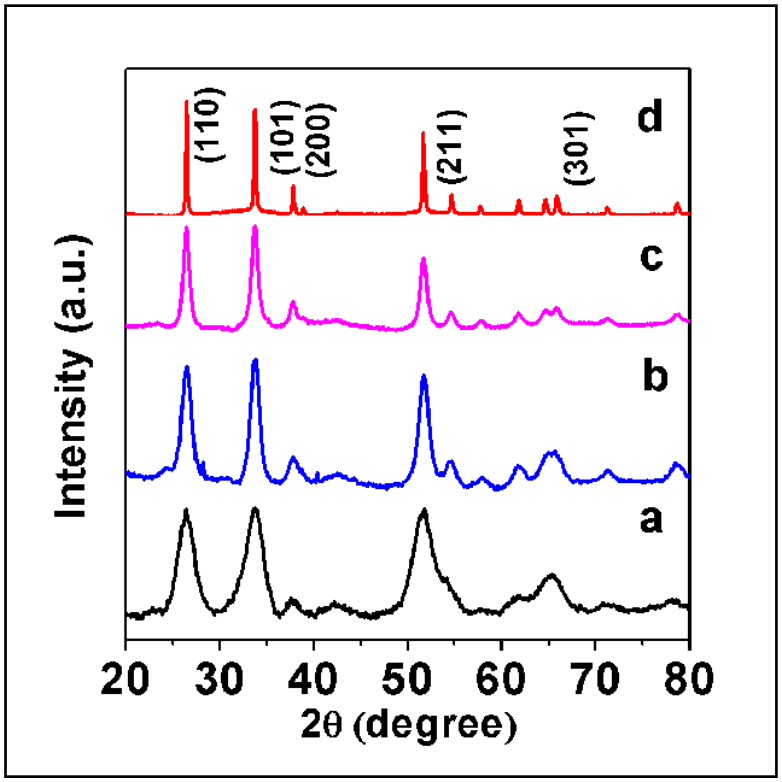

Figure S10. X-ray diffraction patterns of SnO_2. (a) is the as synthesized SnO_2 whereas (b), (c) and (d) are the patterns obtained from samples annealed at 600°C, 800°C and 900°C respectively

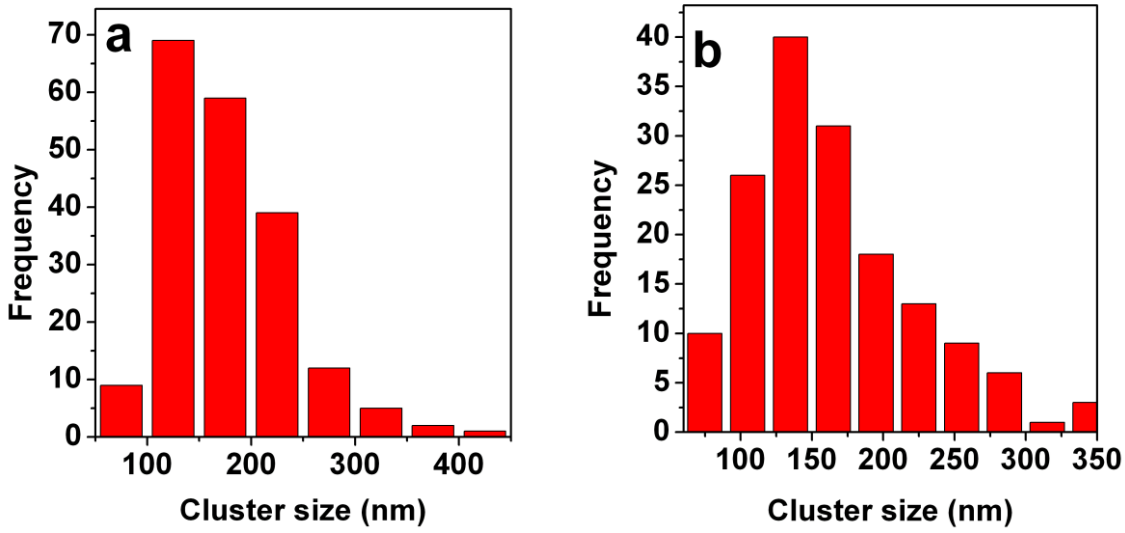

Figure S11 (a) and (b) are the histograms showing the cluster size distribution corresponding to the as prepared SnO_2 aggregates and the sample annealed at 800°C respectively indicating that the average size of the clusters do not change appreciably on annealing

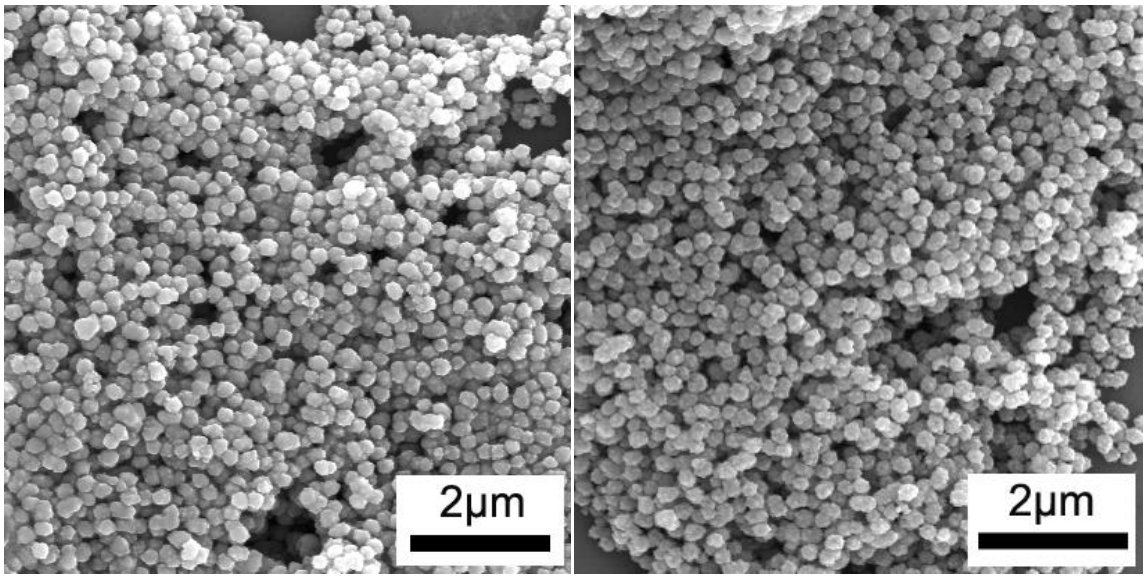

Figure S12. SEM images of as synthesized TiO_2 aggregates(left) and hollow TiO_2 sphere obtained by annealing the aggregates at 600°C(right)

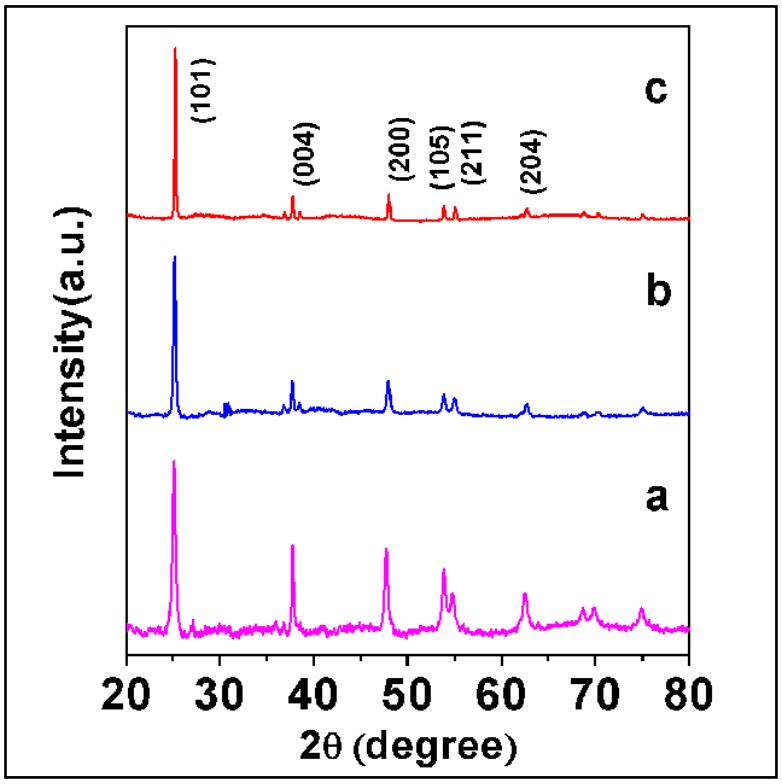

Figure S13. X-ray diffraction patterns of TiO_2. (a) is the as synthesized TiO_2 whereas (b)and (c) are the patterns obtained from samples annealed at 600°C and 800°C respectively

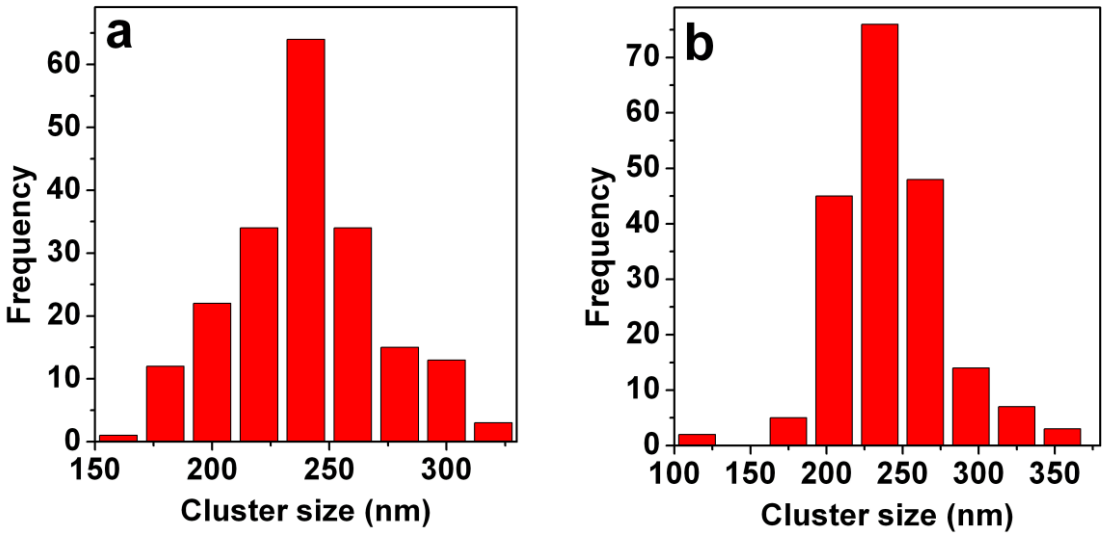

Figure S14. (a) and (b) are the histograms showing the cluster size distribution of as synthesized TiO_2 aggregates and TiO_2 annealed at 600°C.

1. X. Liang, X. Wang, Y. Zhuang, B. Xu, S. Kuang and Y. Li, *J. Am. Chem. Soc.*, 2008, **130**, 2736-2737.
2. B. Viswanath, S. Patra, N. Munichandraiah and N. Ravishankar, *Langmuir*, 2009, **25**, 3115-3121.
3. S. Y. Ho, A. S. W. Wong and G. W. Ho, *Cryst. Growth Des.*, 2009, **9**, 732-736.
4. H. G. Yang and H. C. Zeng, *J. Phy. Chem.B*, 2004, **108**, 3492-3495.