

## Electronic Supplementary Information

### Synthesis of Nearly Monodispersed Metal Oxide Nanoparticles in Water

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## S1 Detailed synthetic procedure for the synthesis of metal oxide nanoparticles

### S1(i) preparation of CeO<sub>2</sub> nanoparticles.

#### a. Synthesis of aqueous ammonium carbonate complex solution:

1 gm ammonium ceric nitrate was added to 3 ml water which gave a clear solution on stirring. Then, the ammonium ceric nitrate solution was added drop wise to a 7 ml saturated aqueous ammonium carbonate solution (pH 9) with constant stirring. Immediate after the addition of ammonium ceric nitrate a white precipitate appeared which was re-dissolved on stirring. During the addition process the pH of the ammonium carbonate solution was maintained to 9 by addition of solid ammonium carbonate. Finally, it gave a clear aqueous ammonium carbonate complex solution of cerium (IV).

#### b. Synthesis of Ceria in room temperature:

The clear aqueous ammonium carbonate complex solution of cerium (IV) was stirred for 5-6 h in ambient condition, which gave a light yellow precipitate. X-ray patterns of this powders indicated that the powders are crystalline and have fluorite cubic structure of CeO<sub>2</sub>, with crystallite size of 2-3 nm (Fig. S1). The TEM results confirm the presence of 2-3 nm particles (Fig. S2).

#### c. Synthesis in reflux condition

40 ml water was kept in an oil bath in 100 ml double necked round bottom flask fitted with a condenser. The temperature of oil bath was increased to 110°C and 1.9 gm decanoic acid was added to it and stirred for 5 min. Then, 10 ml solution of the ammonium carbonate complex solution of cerium (IV) was added to it and continued to heating in reflux condition with constant stirring for 12 h. X-ray patterns of this powders indicated that the powders are crystalline and have fluorite cubic structure of CeO<sub>2</sub> (Fig. S1). The TEM result confirms the presence of ~2 nm particles (Fig. S3).

5 nm agglomerated fluorite cubic structure of  $\text{CeO}_2$  was obtained when the same experiment was carried out in the absence of decanoic acid (Fig. S4).

#### **d. Synthesis in hydrothermal condition.**

In a beaker, 40 ml water and 0.6-4.7 gm decanoic acid was heated at  $100^\circ\text{C}$  with constant stirring for 5 min and to that solution of cerium ammonium carbonate was added slowly, which resulted a homogeneous milky white solution. Then 33 ml of this solution was transferred to a 50 ml autoclave and heated at  $130\text{--}180^\circ\text{C}$  for 12 h. Afterword, the system was cooled to room temperature and collected by precipitating and washing using ethanol. The purified product was separated by centrifugation and re-dispersed in nonpolar solvent like toluene, hexane, and chloroform. X-ray patterns of all the synthesized materials indicated that they are crystalline and have fluorite cubic structure of  $\text{CeO}_2$  but varied in size and shape.

#### **S1(ii) preparation of other metal oxide nanoparticles.**

Other metal oxide nanoparticles were synthesized only in the hydrothermal conditions.

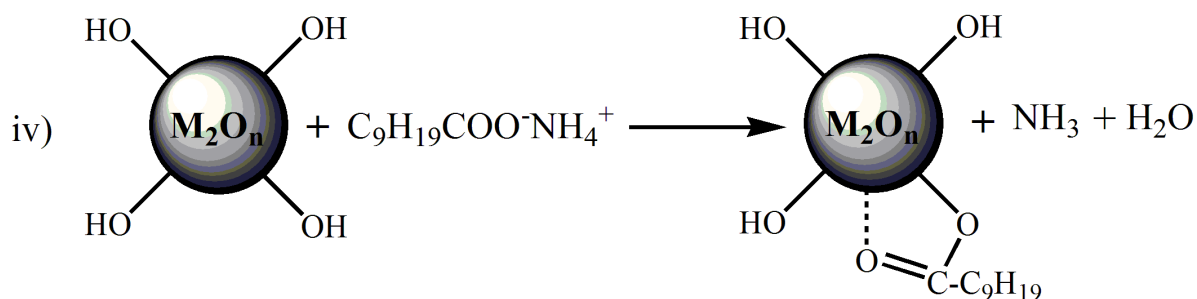
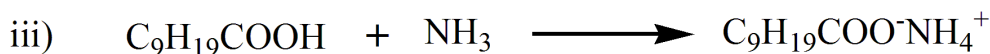
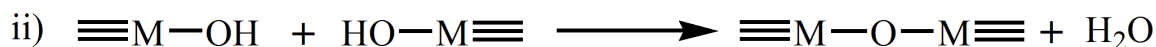
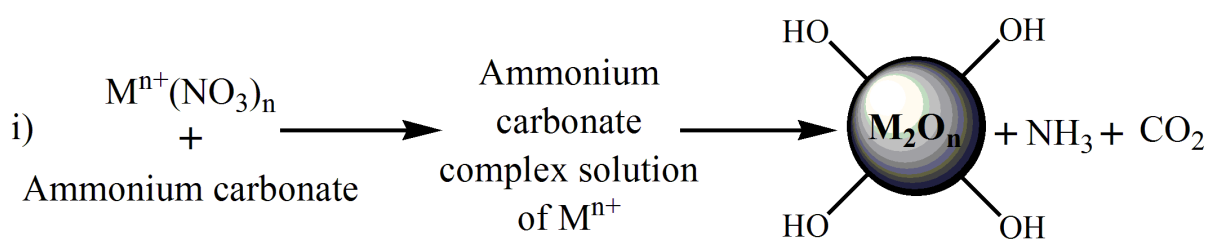
##### **a. Synthesis of aqueous metal ammonium carbonate complex solution:**

1 gm metal nitrate was added to 3 ml water which gave a clear solution on stirring. Then, the metal nitrate solution was added drop wise to a 7 ml saturated aqueous ammonium carbonate solution (pH 9) with constant stirring. Immediate after the addition of metal nitrate a white precipitate appeared which was re-dissolved on stirring. During the addition process the pH of the ammonium carbonate solution was maintained to 9 by addition of solid ammonium carbonate. Finally, it gave a clear aqueous ammonium carbonate complex solution of desired metal ion. For tin we have used tin (IV) chloride and for titania, titanium peroxo solution was used. The aqueous zirconium ammonium carbonate complex solution was synthesized following the procedure discussed in ref 12 (A. Tarafdar, A. B. Panda, N. C. Pradhan and P. Pramanik, *Micropor. Mesopor. Mater.*, 2006, **95**, 360)

##### **b. Synthesis in hydrothermal condition.**

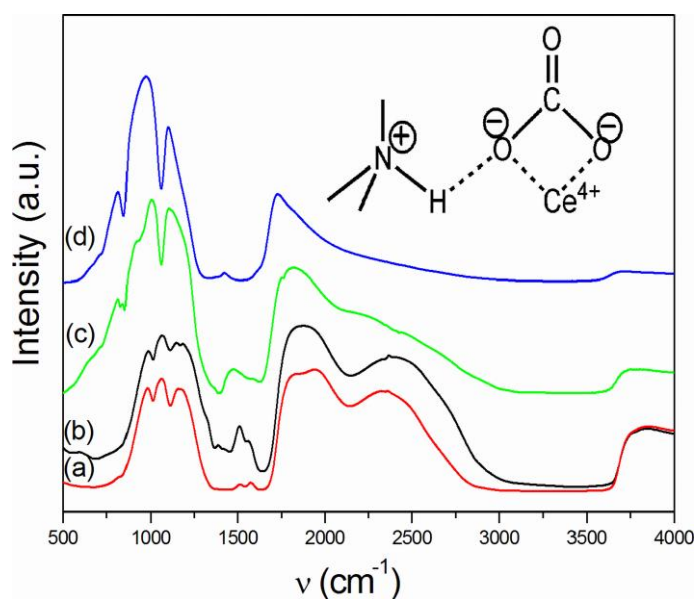
In a beaker, 40 ml water and 0.6-4.7 gm decanoic acid was heated at 100°C with constant stirring for 5 min and to that solution of metal ammonium carbonate solution was added slowly, which resulted a homogeneous milky white solution. Then 33 ml of this solution was transferred to a 50 ml autoclave and heated at 130--180°C for 12 h. Afterword, the system was cooled to room temperature and collected by precipitating and washing using ethanol. The purified product was separated by centrifugation and re-dispersed in nonpolar solvent like toluene, hexane, and chloroform. X-ray patterns of all the synthesized materials indicated that they are crystallile and phase pure.

## S2 Schematic representation of formation mechanism for the metal oxide nanoparticles.



### S3 Evidence of formation of cerium ammonium carbonate by FTIR spectroscopy.

The formation of cerium ammonium carbonate complex has been confirmed by recording FTIR spectra of clear solutions of ammonium carbonate, cerium ammonium carbonate, and the precipitates. A significant shifting of C=O stretching towards higher wave number and shifting of N-H stretching towards lower wave number in cerium ammonium carbonate solutions clearly indicate such complexation. The complexation occurs in such a way that  $\text{Ce}^{4+}$  interacts with negatively charged O of carbonyl group leading to weakening of hydrogen bonding between H of  $\text{NH}^{4+}$  and O of carbonyl group (schematic of the possible interactions prevailing in the complexation of  $\text{Ce}^{4+}$  to cerium ammonium carbonate are shown in inset of FTIR spectra).

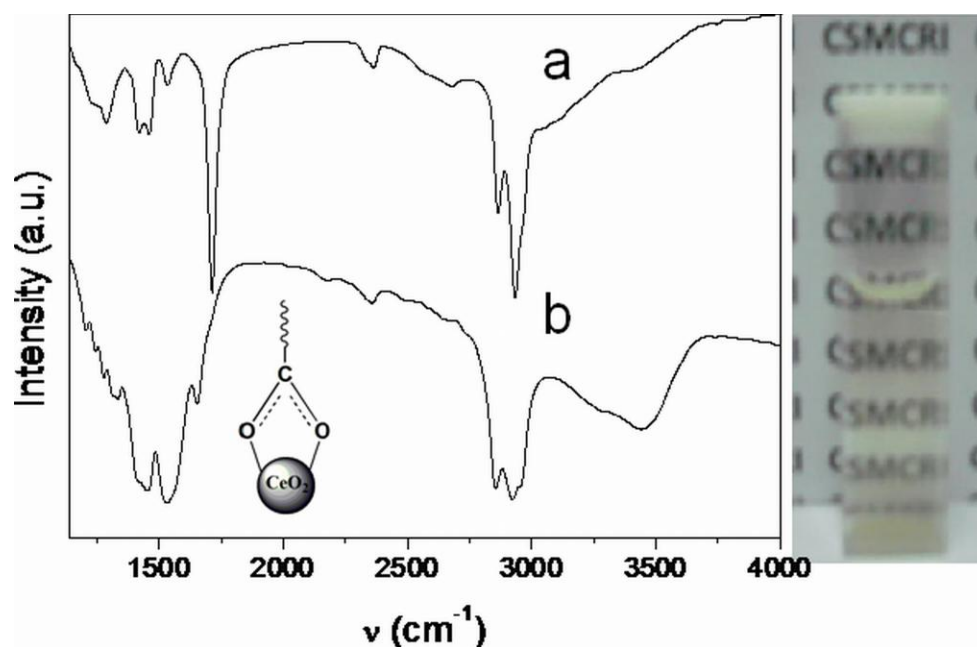


FTIR spectra of (a) clear aqueous solution of cerium ammonium carbonate, (b) aqueous solution of ammonium carbonate, (c) aqueous solution of  $\text{CeO}_2$  precipitate formed from cerium ammonium carbonate at ambient condition and (d) aqueous solution of  $\text{CeO}_2$  formed in reflux condition. Inset: the schematic diagram of bandings of cerium ammonium carbonate solution.

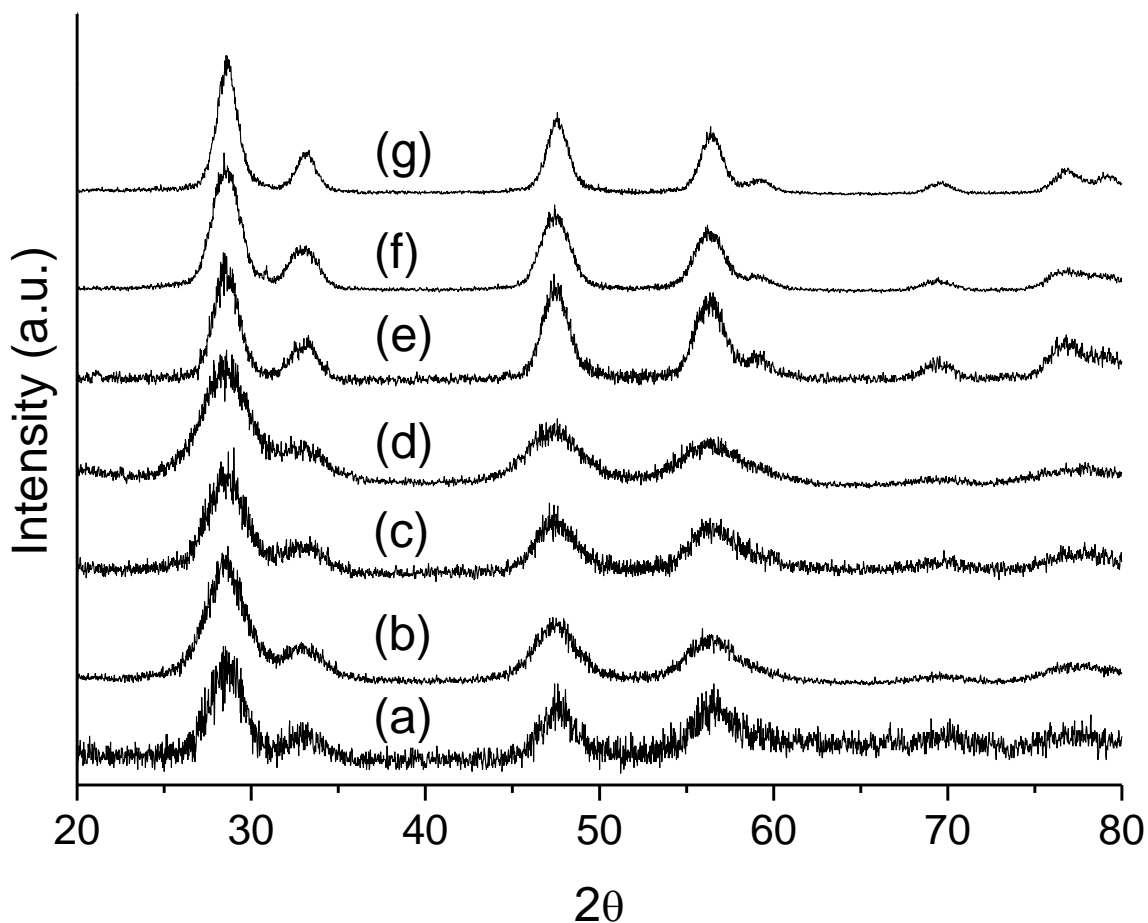
### S4 Evidence of the surface modification of $\text{CeO}_2$ nanoparticles by decanoic acid through carboxylate group co-ordinated in a bidentated fashion

FTIR spectra of free decanoic acid and synthesized nanoparticles was recorded. The absorption maxima due to vibrations of the aliphatic chain of decanoic acid are identical in both the spectra. However, the

IR absorptions due to the carboxyl group do change drastically. A strong band as singlet around 1716 of localized carbonyl group in decanoic acid disappears in nanoparticle and replaced by the symmetric and asymmetric stretching vibrations of the carboxylate group ( $\text{COO}^-$ ) around 1530 and 1410, giving a splitting of  $\Delta\gamma = \gamma_{\text{as}} - \gamma_{\text{s}} = 120 \text{ cm}^{-1}$ . Nakamoto and McCarthy [K. Nakamoto, P. J. McCarthy, *Spectroscopy and Structure of Metal Chelate Compounds*. New York, NY, USA: John Wiley & Sons; 1968.] reported that if the coordination is monodentate the  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  will be shifted to higher and lower frequencies, respectively. Whereas, if the coordination is chelating bidentate or bridging bidentate both  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  frequencies will change in the same direction. This is because the bond orders of both  $\text{C}=\text{O}$  bonds would change by the same amount. Based on these facts and comparing the  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  frequencies of the metal-decanoate complex we can say that carboxylate group coordinate in a bidentated fashion. A broad peak of medium intensity appears in the range  $3500\text{--}3300 \text{ cm}^{-1}$ , centered at  $3540 \text{ cm}^{-1}$  due to OH stretching. This supports a hydrate structure.

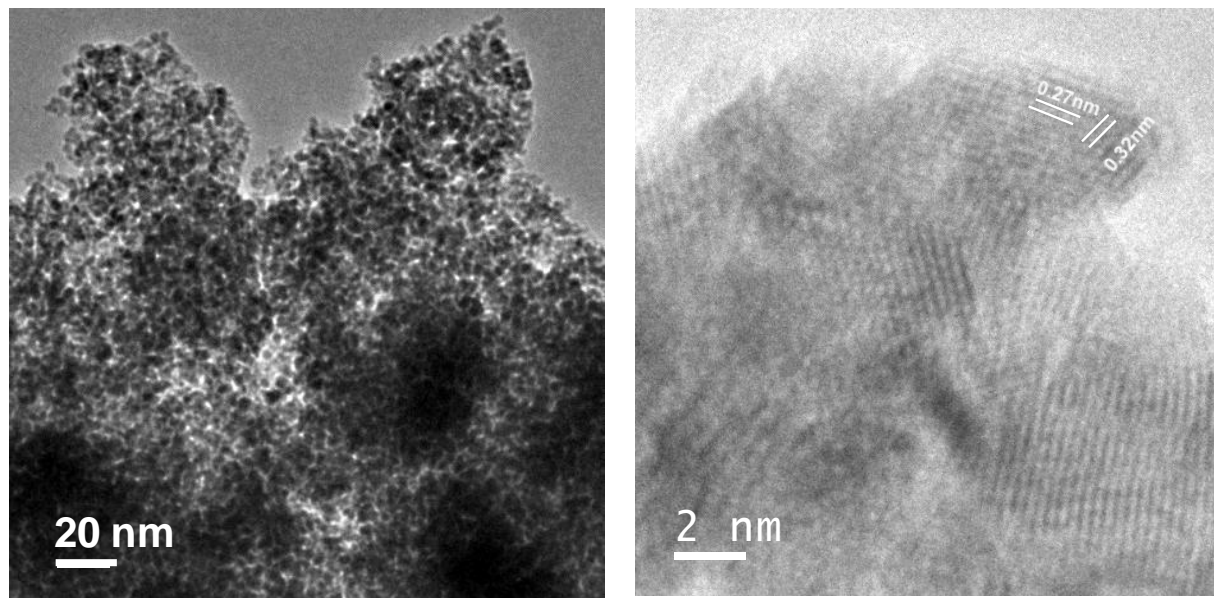


Left: FTIR spectrum of pure decanoic acid(a) and 2nm ceria nanoparticles synthesized in reflux condition in the presence of decanoic acid (b). Right: The transparent ceria nanoparticles with a concentration of 0.5 (w/w) in toluene.

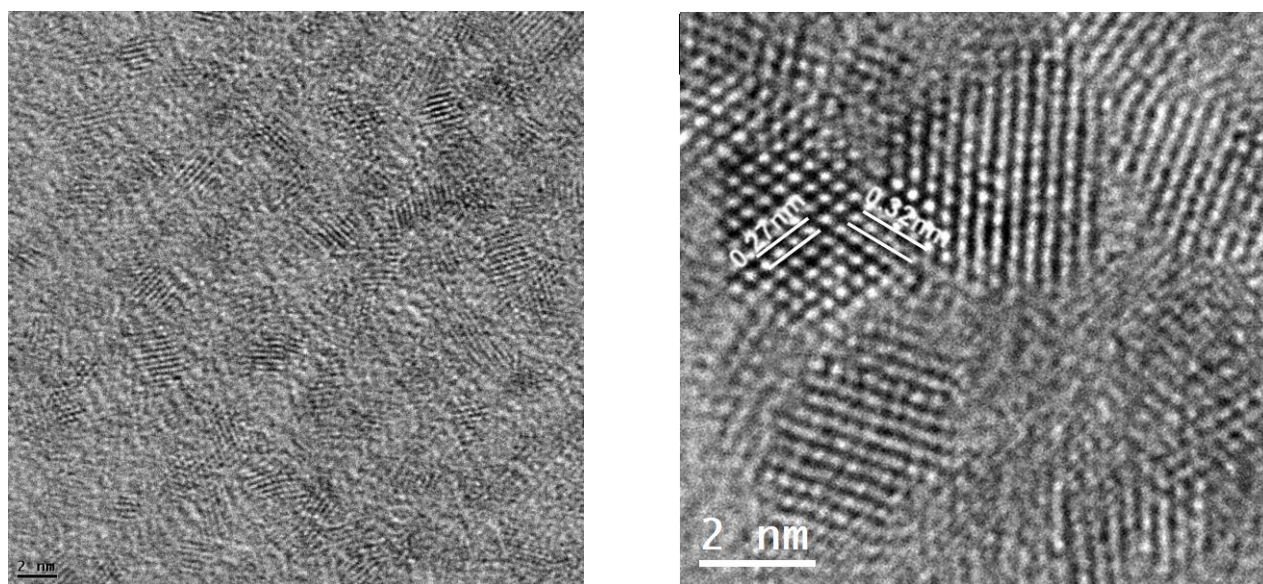


**Fig. S1** XRD patterns of synthesized CeO<sub>2</sub> synthesized in different condition. (a) in ambient condition and (b) at 100°C (reflux condition) without decanoic acid; (c) at 100°C (reflux condition), (d) at 130°C (hydrothermal condition), (e) at 160°C (hydrothermal condition), (f) at 180°C (hydrothermal condition) with molar ratio of decanoic acid to caria precursor 6:1; (g) at 160°C (hydrothermal condition) with molar ratio of decanoic acid to caria precursor 4:1.

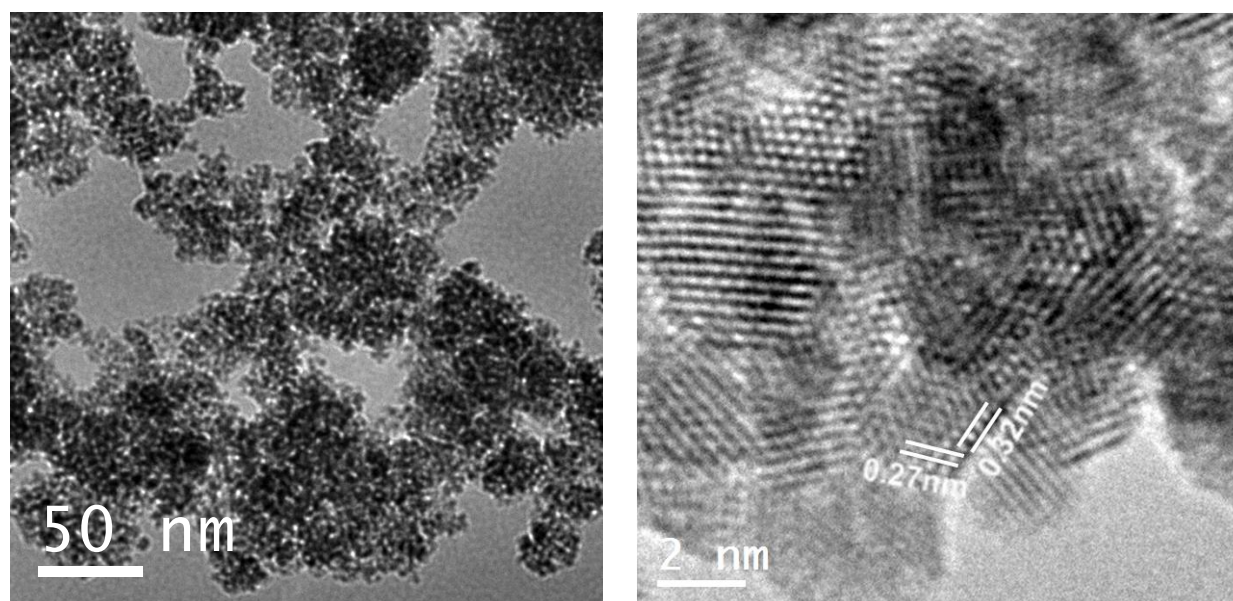




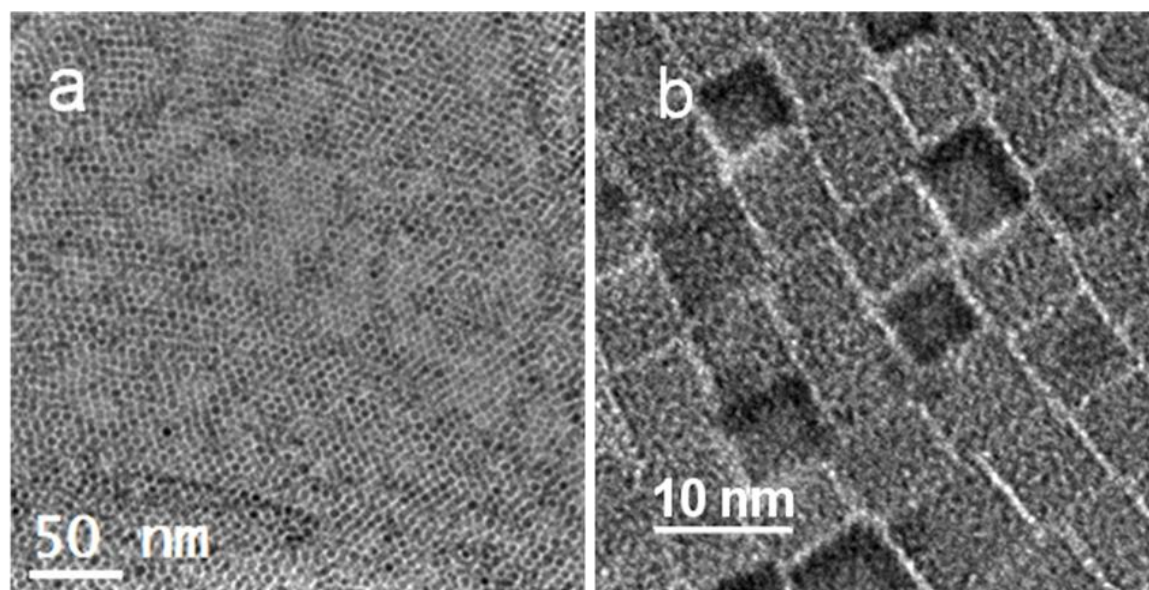
**Fig. S2** CeO<sub>2</sub> synthesized in ambient condition.



**Fig. S3** CeO<sub>2</sub> synthesized in reflux condition with decanoic acid (molar ratio to ceria precursor 6:1).

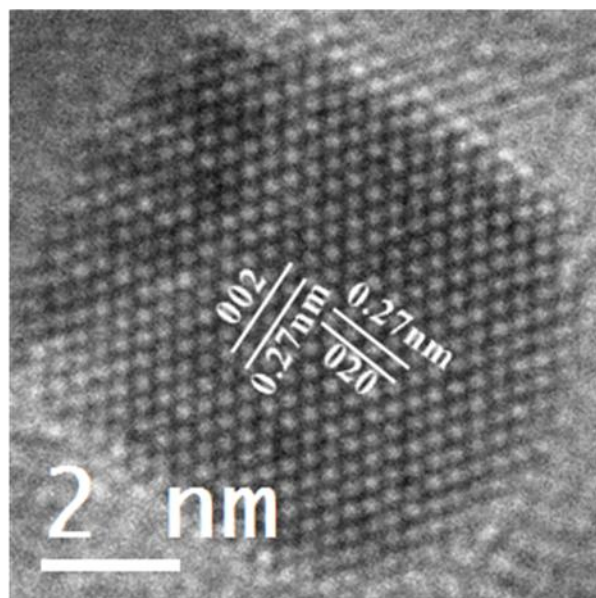


**Fig. S4** CeO<sub>2</sub> synthesized in reflux condition without decanoic acid.

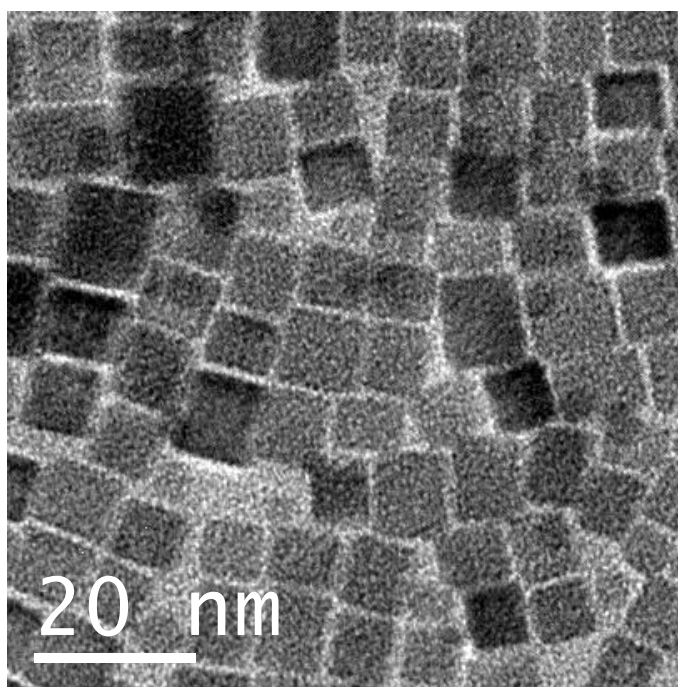


**Fig. S5** (a) Three dimensionally arranged (b) two dimensionally assembled CeO<sub>2</sub> nano cubes synthesized in hydrothermal condition with decanoic acid (molar ratio to ceria precursor 6:1) at 160°C.

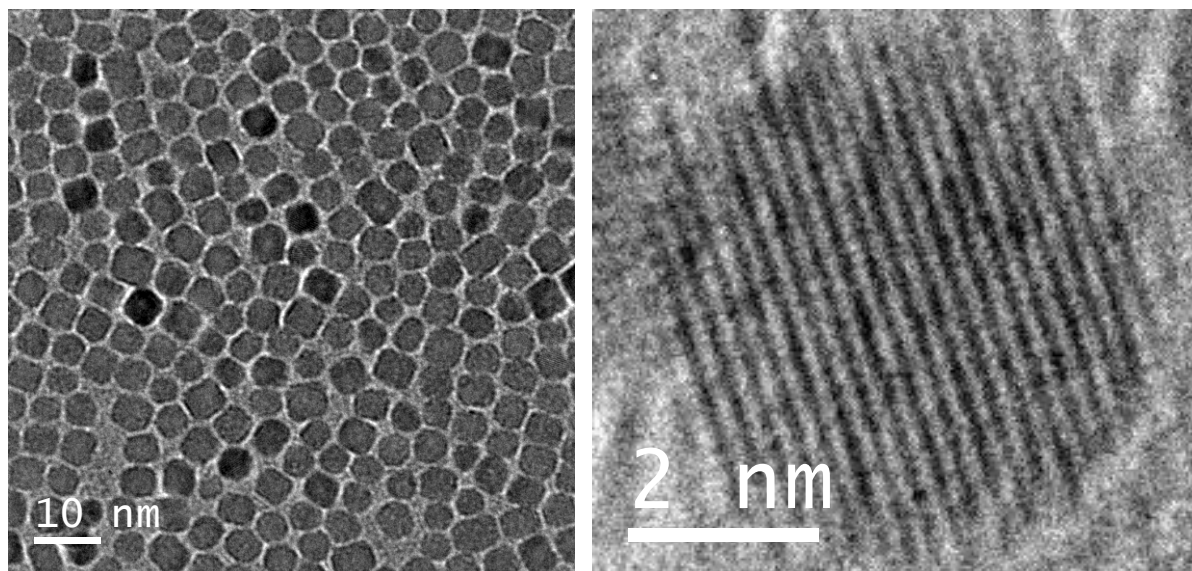




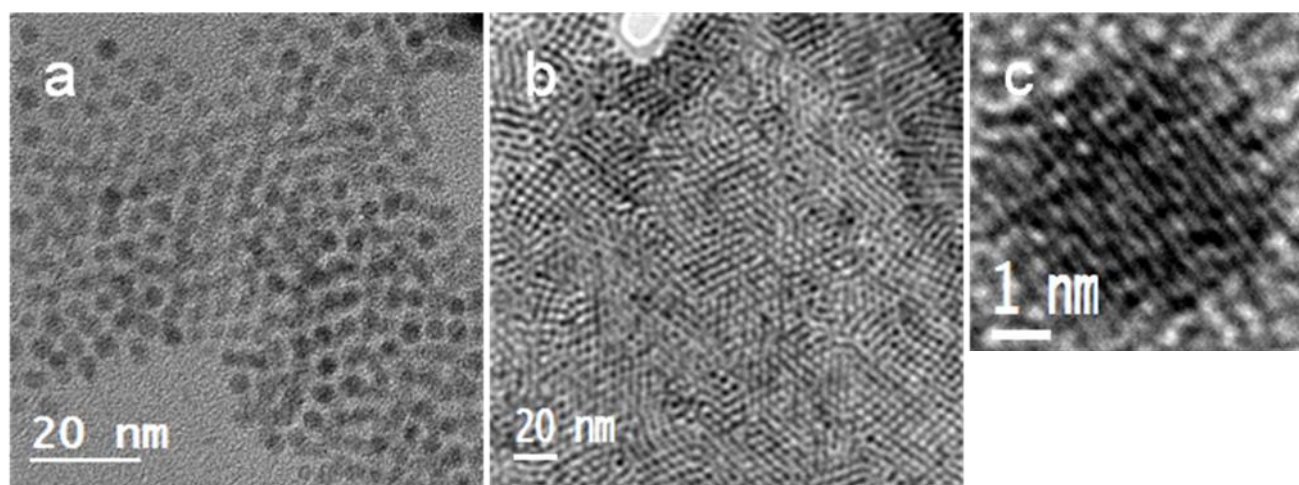
**Fig. S6** HR-TEM image of 5 nm CeO<sub>2</sub> Cube



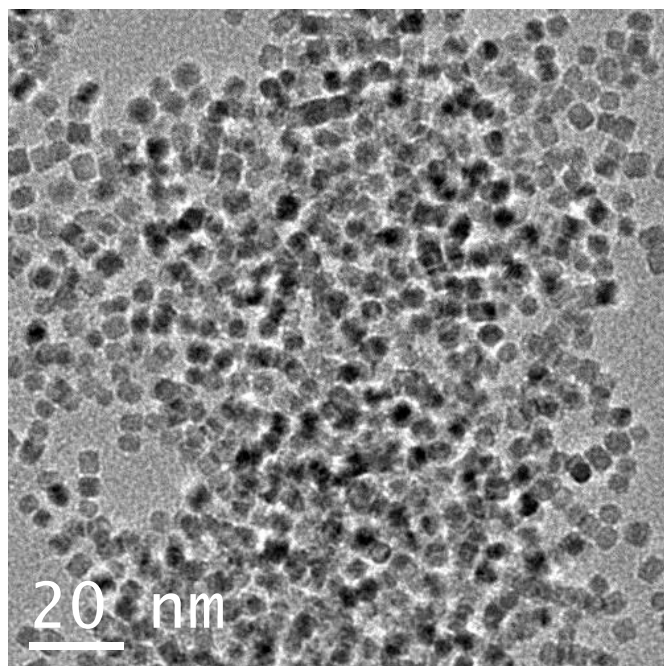
**Fig. S7** Two dimensionally assembled CeO<sub>2</sub> nano cubes (8 nm) synthesized in hydrothermal condition with decanoic acid (molar ratio to ceria precursor 6:1) at 180°C.



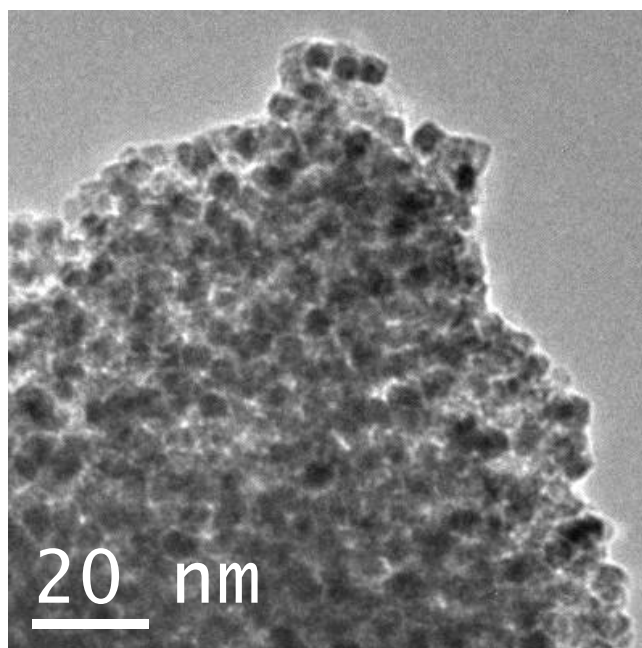
**Fig. S8** CeO<sub>2</sub> synthesized in hydrothermal condition with decanoic acid (molar ratio to ceria precursor 9:1) at 160°C.



**Fig. S9** (a) two dimensionally arranged (b) three dimensionally assembled and (c) HRTEM CeO<sub>2</sub> spherical particles synthesized in hydrothermal condition with decanoic acid (molar ratio to ceria precursor 15:1) at 160°C.

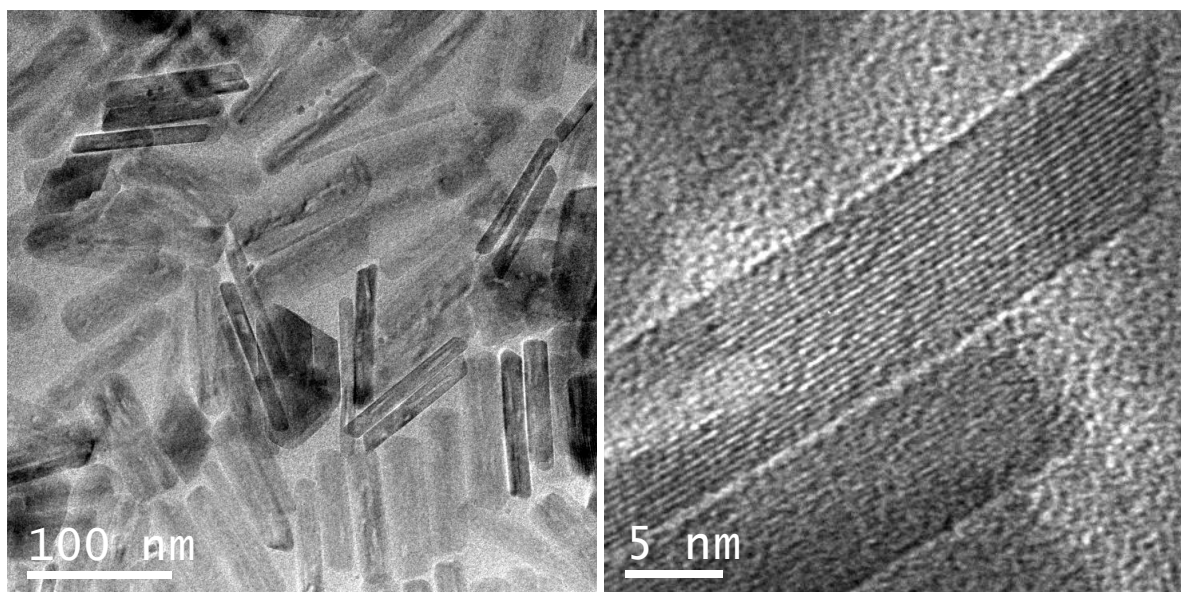


**Fig. S10** Agglomerated CeO<sub>2</sub> nano cubes synthesized in hydrothermal condition with decanoic acid (molar ratio to ceria precursor 4:1) at 160°C.

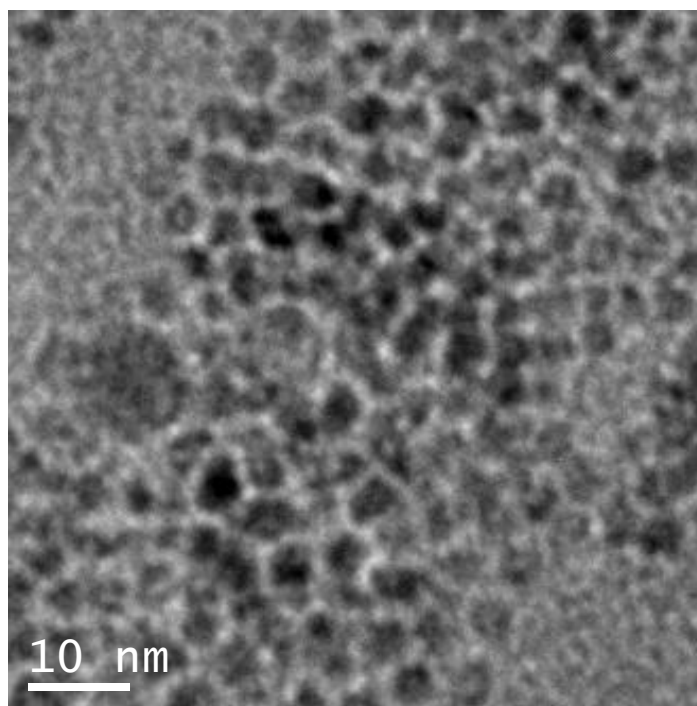


**Fig. S11** More agglomerated CeO<sub>2</sub> nano cubes synthesized in hydrothermal condition with decanoic acid (molar ratio to ceria precursor 2:1) at 160°C.

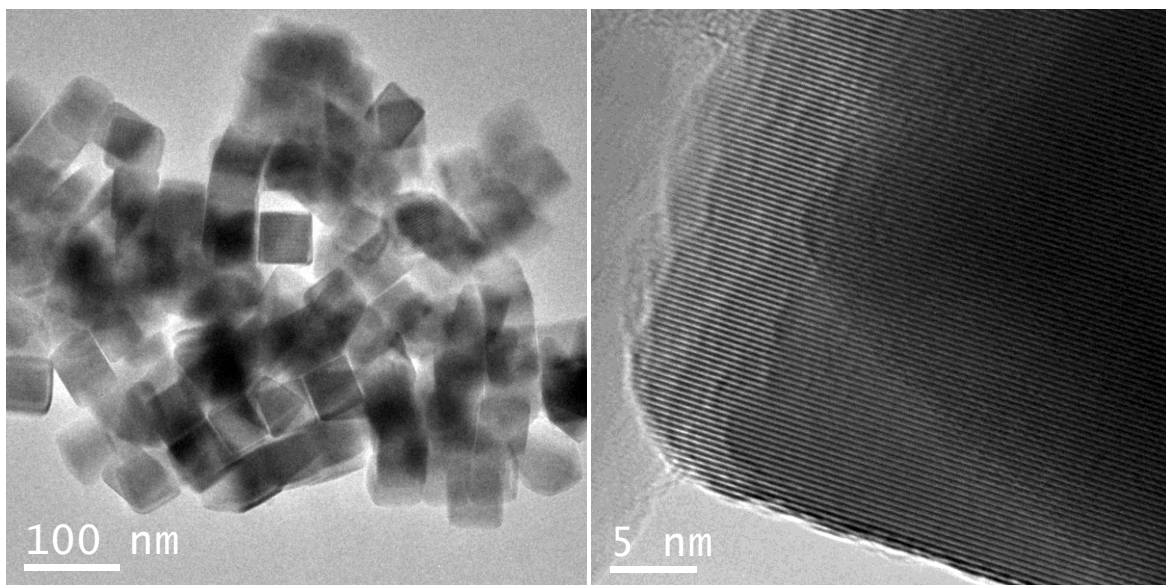




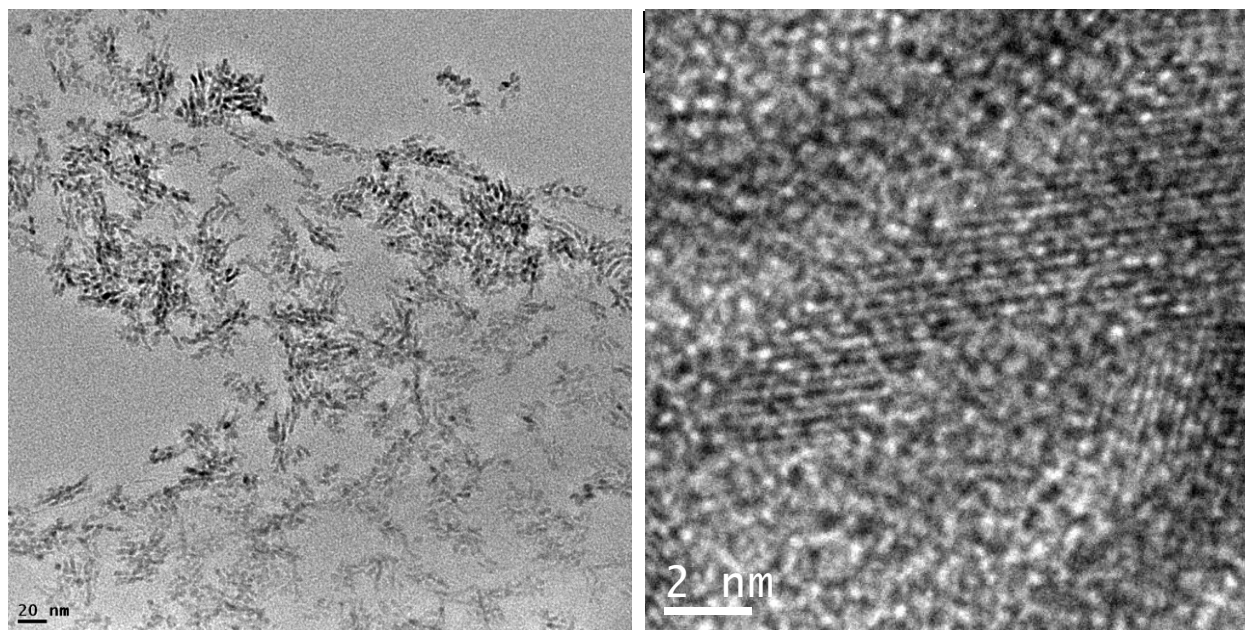
**Fig. S12** TEM image of FeOOH rods synthesized at 150°C



**Fig. S13** TEM image of Fe<sub>2</sub>O<sub>3</sub> spherical particles synthesized at 180°C with metal to ligand ratio of 1:15.

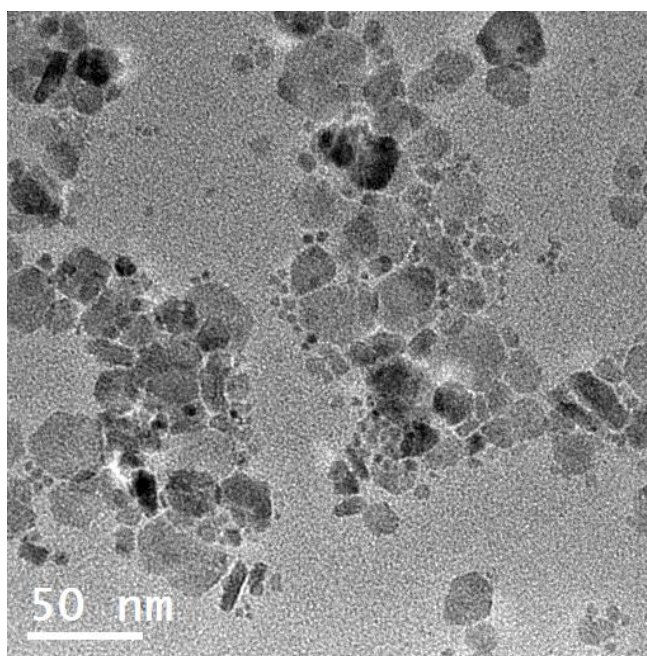


**Fig. S14** TEM image of Fe<sub>2</sub>O<sub>3</sub> nano cubes synthesized at 180°C with metal to ligand ratio of 1:6..



**Fig. S15** TEM image of ZrO<sub>2</sub> nano rods synthesized at 180°C.





**Fig. S16** TEM image of Ga<sub>2</sub>O<sub>3</sub> nano plates synthesized at 180°C.