Electronic Supplementary Information

A simple method to control the formation of cerium phosphate architectures

P. Pusztai,[a] E. Tóth-Szeles,[b] D. Horváth,[a] Á. Tóth,[b] Á. Kukovecz,[a,c] Z. Kónya*[,a,d]

[a] Department of Applied and Environmental Chemistry, University of Szeged, Rerrich Béla tér 1., H-6720 Szeged, Hungary

[b] Department of Physical Chemistry and Materials Science, University of Szeged, Aradi Vértanúk tere 1., H-6720 Szeged, Hungary

[c] MTA-SZTE "Lendület" Porous Nanocomposites Research Group, Rerrich Béla tér 1., H-6720 Szeged, Hungary

[d] MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, Rerrich Béla tér 1., H-6720 Szeged, Hungary

*Corresponding author: konya@chem.u-szeged.hu

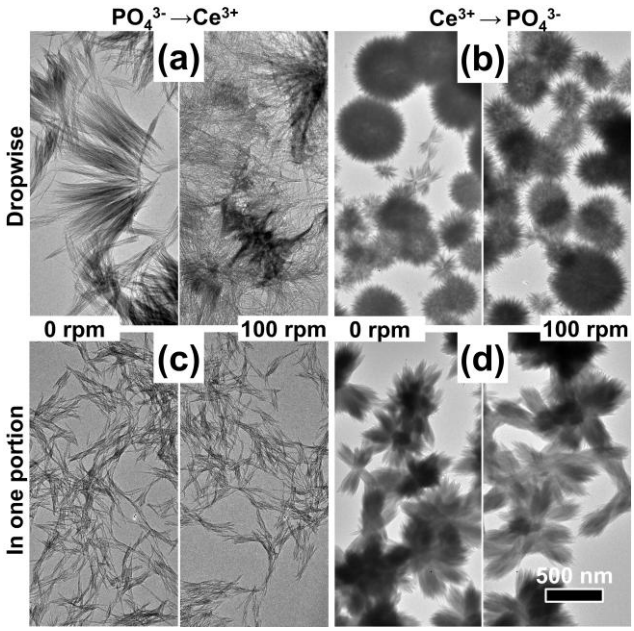

Figure S1. Conventional precipitation experiments of $CePO_4$ samples in batch system.

There are examples in the literature where stirring has a crucial impact on the developing nanostructures' morphology [1, 2]. According to Figure S1 one can clearly observe that stirring of the suspension in our case hardly affects the morphology of the nanostructures. Dropwise addition of phosphoric acid (2.3 mL) to cerium nitrate solution (60 mL) promotes the formation of 400-800 nm long nanowires with diameter of 5-8 nm shown in Figure S1a. Without stirring, the nanowires order into fan like structures, however, only randomly oriented nanowires are observed when stirring is employed. Some urchin like structures can also be found in the stirred sample which can be ascribed to the inadequate reaction time for their break up compared to our previous study. When the entire amount of phosphoric acid is poured in one portion to the cerium nitrate solution short nanorods with length of 100-200 nm and diameter of 5-8 nm are formed (Figure S1c). Stirring has no effect on the morphological parameters of these samples. Figure S1b and d demonstrates that reverse addition of the precursor solutions promotes the formation of urchin- (Figure S1b) and flower like (Figure S1d) nanostructures depending on the admixture rate. By dropwise addition without stirring, urchins with diameters from 300 up to 1000 nm are developed. Stirring though auspiciously affects the urchins' size distribution. In this case their diameter falls within the range of 300-500 nm. The flower like structures by addition in one portion possess similar morphology irrespective of whether stirring is applied or not. Their diameter varies between 700 and 900 nm.

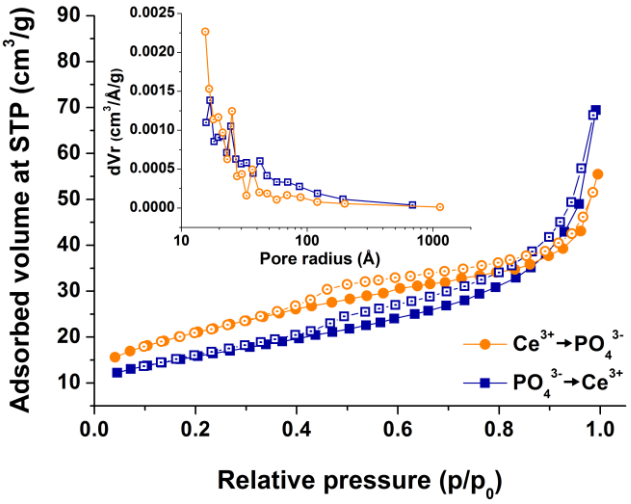

Figure S2. Nitrogen adsorption-desorption isotherms and the corresponding BJH pore size distributions (inset) of (PO_4^{3-}→Ce^{3+}) and (Ce^{3+}→PO_4^{3-}) samples representing abundant mesopores.

Table S1. Summary of the parameters obtained from nitrogen sorption measurements. Calculated SSA values are also provided as a comparison to the measured ones.

	SSA_{N2} BET (m^2/g)	**SSA Calc (m^2/g)**	**Total Pore Volume (cm^3/g)**	**Average Pore Radius (nm)**
PO_4^{3-}→Ce^{3+}	54.5	0.93	$1.07 \cdot 10^{-1}$	3.9
Ce^{3+}→PO_4^{3-}	73.4	0.57	$8.6 \cdot 10^{-2}$	2.3

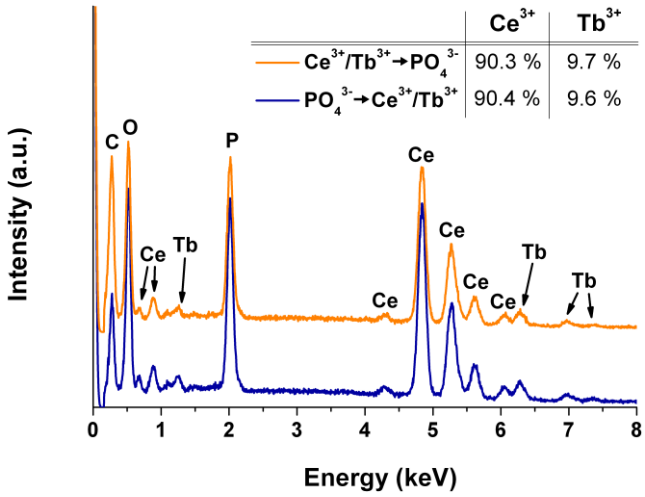

Figure S3. Energy dispersive X-ray spectra of terbium doped (PO_4^{3-}→Ce^{3+}/Tb^{3+}) and (Ce^{3+}/Tb^{3+}→PO_4^{3-}) samples. Both samples consist of Ce, Tb, P and O without any detectable impurity. The C peak is a feature of the sample holder carbon tape. The terbium content in both samples correlate well with the desired atomic ratio of Ce^{3+}:Tb^{3+} = 9:1.

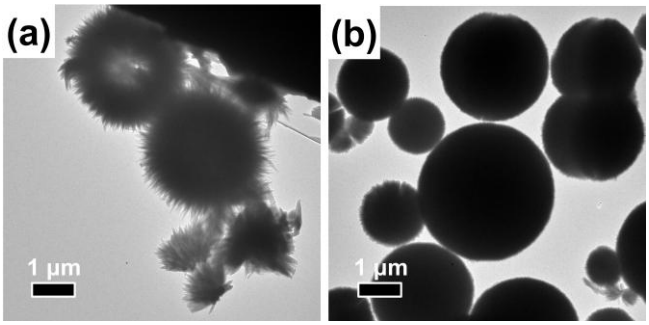

Figure S4. TEM images of terbium doped (PO_4^{3-}→Ce^{3+}/Tb^{3+}) (a) and (Ce^{3+}/Tb^{3+}→PO_4^{3-}) (b) samples.

1. J. Tang and A. P. Alivisatos, *Nano Lett.*, 2006, **6**, 2701–2706.
2. K. Liu, Y. Zheng, G. Jia, M. Yang, Y. Huang and H. You, *CrystEngComm*, 2011, **13**, 452–458.