Supplementary material

Effects of *myo*-inositol hexakisphosphate and phosphate adsorption on aggregation of CeO$_2$ nanoparticles: roles of pH and surface coverage

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Characterisation of CeO$_2$ nanoparticles, ATR-FTIR spectroscopy and nanoparticle–nanoparticle interactions and aggregation measurements

The powder XRD patterns were obtained on a Bruker D8 Advance diffractometer (Bruker AXS Gmbh, Germany) equipped with a LynxEye detector using Ni-filtered Cu Kα radiation (λ = 0.15418 nm). The diffractometer was operated at a tube voltage of 40 kV and a current of 40 mA with a scanning rate of 4° min^{-1} and at a step size of 0.02°. TEM analysis was carried out with a CM12 transmission electron microscope (Phillips, Eindhoven, the Netherlands) at 120 kV, and the samples were prepared by loading 10-μL aliquots of CeO$_2$ nanoparticles or reaction samples onto carbon-coated copper grids. The specific surface area of CeO$_2$ nanoparticles was calculated from N$_2$ sorption isotherms using the Brunauer−Emmett−Teller method with an Autosorb-1 N$_2$ absorption analyser (Quantachrome, Boynton Beach, FL).

   The ATR-FTIR spectra were recorded on a Bruker Vertex 70 FTIR Spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector (Bruker Optics Inc., Ettlingen, Germany). A single-reflection diamond ATR accessory (Pike Technologies, Inc.) was used to acquire spectra of *myo*-inositol hexakisphosphate (IHP) and orthophosphate (P$_i$) solutions prepared at various pH values. IHP and P$_i$ sorption onto CeO$_2$ surface was also probed with ATR-FTIR spectroscopy. A thin, evenly coated CeO$_2$ film was deposited onto a ZnSe crystal element in a horizontal 45° ATR cell. The film was prepared by placing a finely dispersed suspension of CeO$_2$ (2.0 mg CeO$_2$ in 1.0 mL of water) onto the crystal and drying overnight. The coated crystal was sealed in a flow cell,

placed on the ATR stage inside the IR spectrometer, and connected to a reaction vessel containing 500 mL of 0.01 mol L^{-1} KCl electrolyte adjusted to pH 7.0. A peristaltic pump was used to circulate solute from the reaction vessel through the flow cell at a rate of 1.0 mL min^{-1}. The flow cell effluent was collected as waste. The CeO_2 deposit was equilibrated with the background solution for ~1 h. At this time, a background spectrum consisting of the combined absorbance of the ZnSe crystal, the CeO_2 deposit and the reaction electrolyte was then collected as the average of 512 scans at a 4-cm^{-1} resolution in the spectral range of 1250–900 cm^{-1}, and the sorption experiment was started by pumping of 60 μmol L^{-1} IHP or 180 μmol L^{-1} P_i in 0.01 mol L^{-1} KCl electrolyte adjusted to pH 3.0, 5.0, 7.0 and 9.0 into the reaction vessel at a flow rate of 1.0 mL min^{-1}. The sample spectra at different times were collected as an average of 512 scans at 4-cm^{-1} resolution in the spectral range of 1250–900 cm^{-1}, where the bands associated with various P–O(H) vibrations can be found.

Nanoparticle–nanoparticle interactions and the aggregation behaviour of 20-nm CeO_2 particle suspensions at 0.01 mol L^{-1} ionic strength were examined at pH 3.0 and 7.0. Sedimentation experiments were conducted with a UV-Vis spectrometer by monitoring the changes in the light scattering when passing through CeO_2 suspensions (0.2 g L^{-1}) as a function of time. Suspensions were prepared in a 1-cm-path length cuvette, agitated, and placed in the UV-Vis instrument and the amount of transmitted light (λ = 376 nm) was measured over time. The solutions were left overnight to reach steady-state aggregation, and therefore, no aggregation was assumed to occur during the time of the measurement. Therefore, the sedimentation is solely attributed to gravitational settling depending on the particle size.

A commercial DLS instrument (Malvern Zetasizer ZEN3600) equipped with a 4-mW He-Ne laser (633 nm) was used to obtain the size distribution of aggregates in the absence and the presence of IHP and P_i. For DLS measurements, suspensions were prepared at 0.01-g L^{-1} solid loading of CeO_2 in appropriate pH solutions. The pH solutions were passed through a 0.22-μm syringe-driven filter to minimise the influence of unwanted dust particles. Samples were allowed to sit overnight to ensure the aggregation had reached its steady state. Before conducting DLS experiments, all samples were shaken well and allowed to settle for 3 min in order to rule out interference from other large particles. Aggregate sizes were studied over a range of IHP

concentrations (~0–0.9 µmol L^{-1}) or a range of P$_i$ concentrations (~0–2.7 µmol L^{-1}). In addition, the surface charge of the nanoparticles was measured using the zeta potential mode of the Malvern Zetasizer ZEN3600.

Table S1.   Langmuir fitting parameters for sorption of *myo*-inositol hexakisphosphate (IHP) and orthophosphate (P$_i$) on CeO$_2$ nanoparticles

	Q_{max} (µ mol m^{-2})	K (L µmol^{-1})	R^2
IHP	0.73	0.457	0.927
P$_i$	3.18	0.676	0.898

Table S2.   Fourier-transform infrared (FTIR) peak assignment for *myo*-inositol hexakisphosphate (IHP) solution

Wavenumber (cm^{-1})	Peak assignment	Reference
~1168–1185	v_{as}(P–O in HPO$_3^-$)	[1]
~1120–1130	v_{as}(P–O in PO$_3^{2-}$)	[1]
~1065–1071	v_s(P–O in HPO$_3^-$)	[1]
~977–991	v_s(P–O in PO$_3^{2-}$)	[1]
970	v_{as}(P–O–C)	[1]
935	v_{as}(P–O–H)	[1]

Table S3.   Fourier-transform infrared (FTIR) peak assignment for *myo*-inositol hexakisphosphate (IHP) and orthophosphate (P$_i$) adsorbed on CeO$_2$ NPs

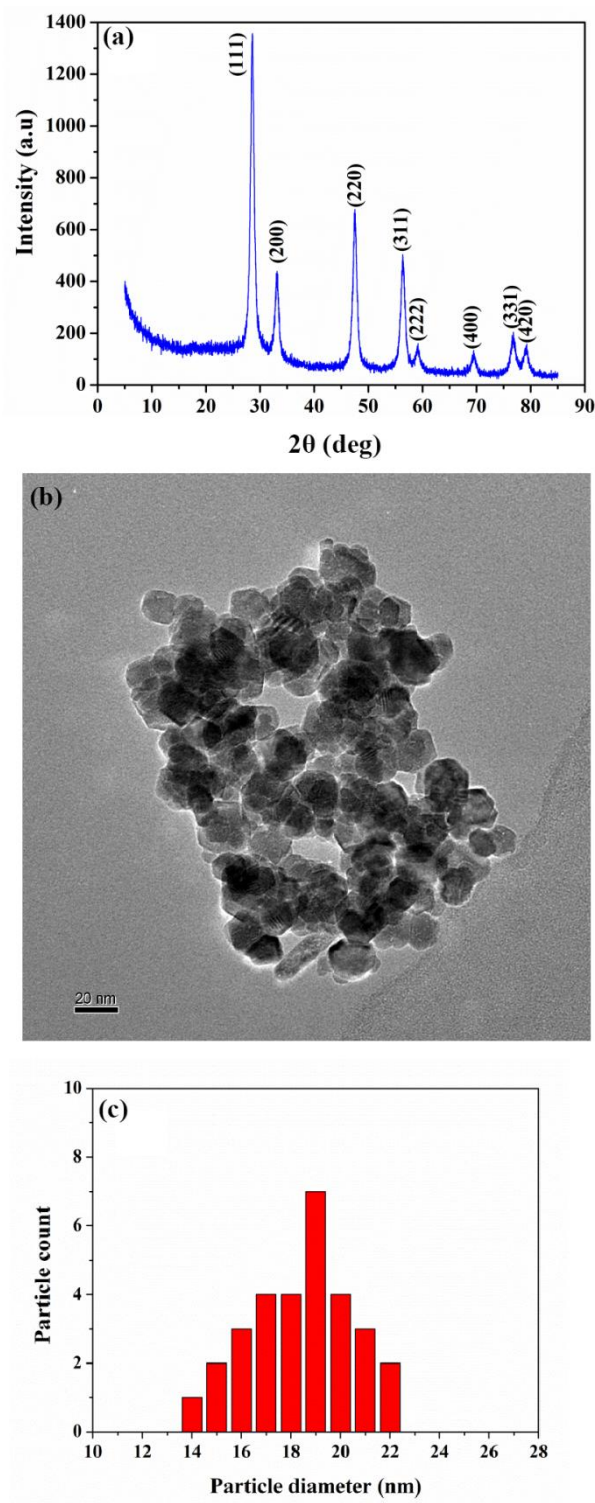|	Wavenumber (cm^{-1})	Peak assignment	References
IHP	~1171–1168	v_{as}(P–O in surface complexes)	[1]
	1131	v_{as}(P–O in PO$_3^{2-}$)	[1]
	1072	v_s(P–O in HPO$_3^-$)	[1]
	1010	v_s(P–O in PO$_3^{2-}$)	[1]
	984	v_{as}(P–O–C)	[1]
P$_i$	~1142–1116	v_{as}(PO$_2$ in surface complexes)	[2]
	1031	v_s(PO$_2$ in surface complexes)	[2]
	998	v_{as}(P–OH)	[2]
	958	v_{as}(P–O–Ce in surface complexes)	[2]
	927	v_s(P–O–Ce in surface complexes)	[2]

Fig. S1. (a) XRD patterns, and (b) TEM image of CeO$_2$ nanoparticles (scale bar 20 nm); (c) size distribution of CeO$_2$ nanoparticles
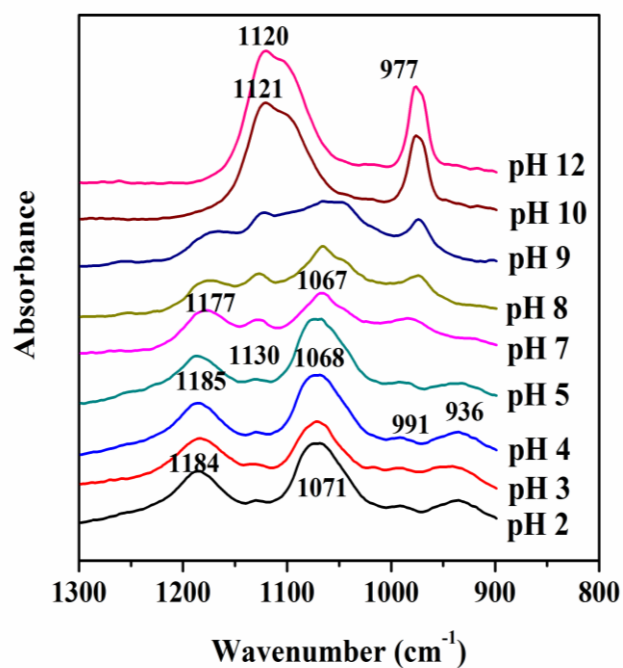
Fig. S2. ATR-FTIR spectra of 6 mmol L^{-1} *myo*-inositol hexakisphosphate (IHP) solution as a function of pH in 0.01mol L^{-1} KCl.
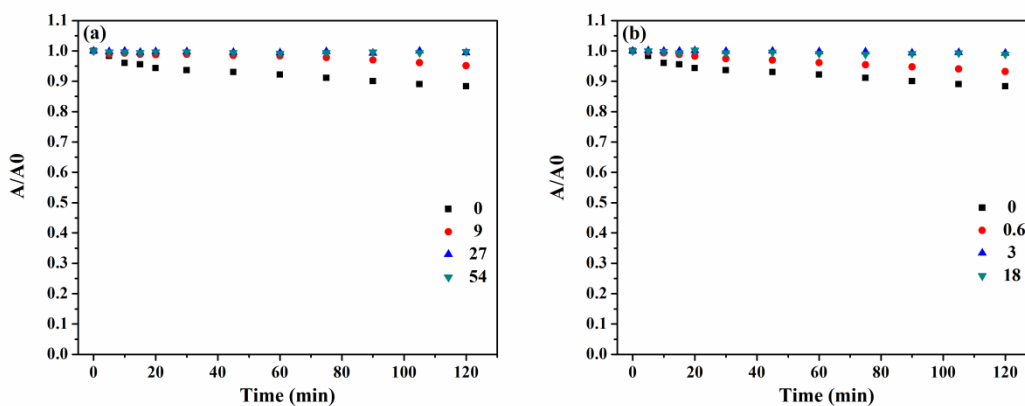

Fig. S3. Sedimentation of CeO_2 NPs in the absence or presence of orthophosphate (P_i) with various concentration (0, 9, 27 and 54 µmol L^{-1}) (a), and *myo*-inositol hexakisphosphate (IHP) with various concentration (0, 0.6, 3 and 18 µmol L^{-1}) (b) at pH 9.0. A/A0 is the normalised nanoparticle turbidity where A and A0 are the turbidity at time *t* and 0 respectively.
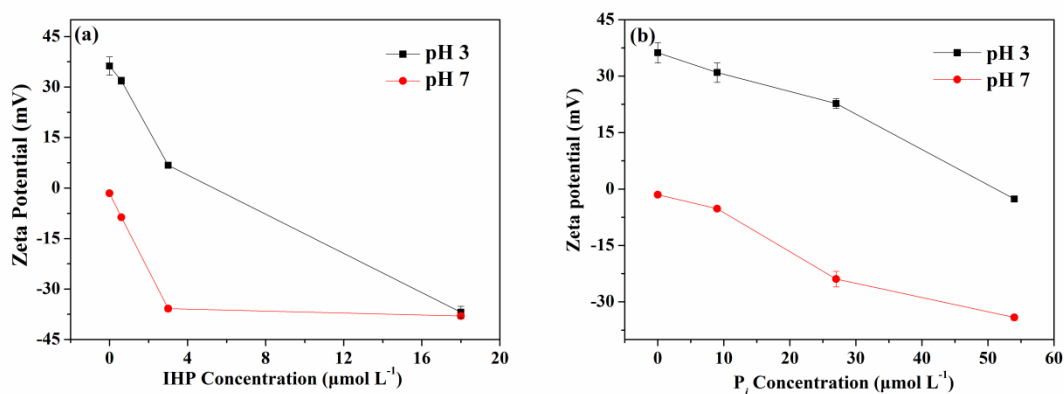
Fig. S4. Zeta potential of CeO_2 in the presence of *myo*-inositol hexakisphosphate (IHP) (a) and orthophosphate (P_i) (b) at various concentrations at pH 3.0 and pH 7.0.
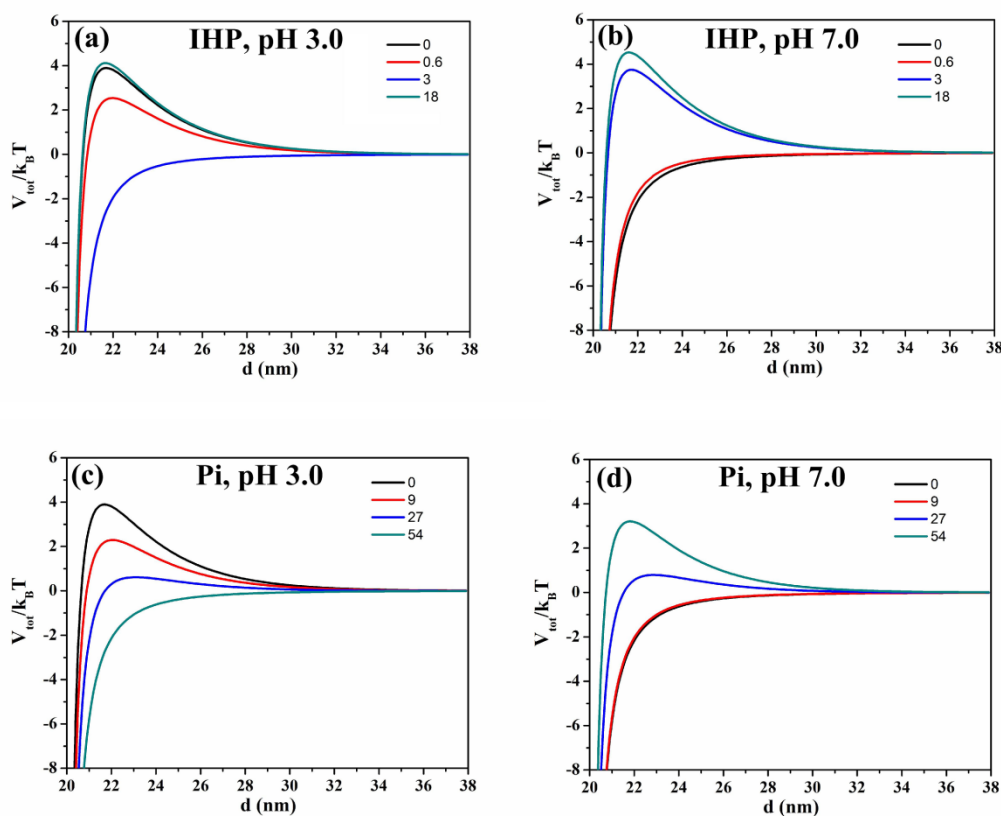

Fig. S5. Derjaguin–Landau–Verwey–Overbeek (DLVO) interaction energy ($k_B T$) between CeO_2 NPs *v.* separation distance (*d*, nm) at different *myo*-inositol hexakisphosphate (IHP) and orthophosphate (P_i) concentrations and pH values (pH 3.0 and 7.0). The coloured lines in graph legend represent the concentrations of IHP at 0, 0.6, 3 and 18 μmol L^{-1} and the concentrations of P_i at 0, 0.6, 3 and 18 μmol L^{-1}. The concentration of CeO_2 suspension is 0.2 g L^{-1}.

References

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[2]   E. J. Elzinga, D. L. Sparks, Phosphate adsorption onto hematite: an in-situ ATR-FTIR investigation of the effects of pH and loading level on the mode of phosphate surface complexation. *J. Colloid Interface Sci.* **2007**, *308*, 53. doi:10.1016/j.jcis.2006.12.061