# Intrinsic formation of nanocrystalline neptunium dioxide in the neutral aqueous condition relevant to deep geological repositories

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# Intrinsic formation of nanocrystalline neptunium dioxide in the neutral aqueous condition relevant to deep geological repositories

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**The dilution of aqueous neptunium carbonate complexes induces the intrinsic formation of nanocrystalline neptunium dioxide ($NpO_2$) particles, which are characterised by UV/Vis- and X-ray absorption spectroscopy and transmission electron microscopy. This new route of nanocrystalline $NpO_2$ formation could be a potential scenario for the environmental transport of radionuclides from the waste repository (i.e. near field with alkaline conditions) to the geological environment (i.e. far field with neutral conditions).**

Owing to their high charge density, the aqueous chemistry of tetravalent actinides (An(IV)) is dominated by strong hydrolysis which often initiates the intrinsic formation of nano-sized oxide/oxyhydroxide particles.[1, 2] Under the geochemical conditions relevant to the repository and disposal of radioactive wastes, the An(IV) nanoparticles could occur as mobile colloidal species,[3, 4] the potential formation of which poses serious concerns for the safety management of radioactive wastes. For this reason, the An(IV) nanoparticles have attracted extensive attention over the past few years, particularly on the preparation and characterisation of pure phases of An(IV) oxide nanocrystals (NCs).[1, 5-7] In aqueous systems, the tetravalent state is a major concern for the early actinides, *i.e.* from $_{90}$Th to $_{94}$Pu,[8] except for $_{91}$Pa which shows a strong oxidation tendency to Pa(V).[9] Considerable efforts by precedent researchers have yielded success in identifying the fluorite-based oxide NCs originating from aqueous solutions of Th(IV),[10] U(IV),[11] and Pu(IV),[1, 6, 12] whilst no report has yet been released for Np(IV) NCs despite the longstanding prognostication of their formation.[13, 14] We herein report the first characterisation of nano-sized neptunium dioxide ($NpO_2$) obtained from a novel approach based on the dilution of an aqueous bicarbonate solution of Np(IV). A major isotope of Np, $^{237}$Np ($T_{1/2} = 2.14 \times 10^6$ y), is considered to be the predominant contributor to a potential radiation dose in radioactive waste repositories over an extremely long time frame of 1,000,000 years[15] and, hence, it is a significant cause of concern for the long-term safety assessment of radioactive waste repository and disposal. As such, this study not only completes a series of An(IV) NCs, but also would provide fundamental information required for the long-term safety management of radioactive wastes.

Precedent attempts to obtain aqueous-originated An(IV) NCs were based on the neutralisation of acidic An(IV) solutions.[6, 10, 16] Our Np(IV) NCs demonstrated here were, to the contrary, prepared from a weakly basic solution of Np(IV) in $NaHCO_3$ (pH = 8.6). The background of our synthetic strategy is to dissociate soluble Np(IV) carbonate species under a weakly basic condition to trigger olation/oxolation reactions which finally yield Np(IV) oxide clusters, whilst in the former neutralisation process the olation/oxolation reactions are induced by the hydrolysis of hydrated An(IV) species.[17] The dissociation process of Np(IV) carbonate species was monitored by UV/Vis absorption spectroscopy. The UV/Vis spectrum of the initial colloid-free solution of Np(IV) in

NaHCO$_3$ (solution **1** in Fig. 1) was consistent with that reported for Np(IV) carbonate species.[18] A tenfold dilution of this Np(IV) carbonate solution with ultrapure water (pH = 7.0) resulted in an immediate spectral change in UV/Vis with the emergence of a new absorption maximum at 742 nm (solution **2** in Fig. 1), which indicates the formation of colloidal Np species.[19] The diluted Np solution appeared to be clear for the first few hours, and yellow/brownish precipitate occurred (Fig. S1-(a) in Electronic Supplementary Information (ESI)). The redispersion of this precipitate in ultrapure water yielded an apparently transparent solution (Fig. S1-(b) in ESI). The UV/Vis spectrum of this transparent solution still showed the characteristic absorption maximum at 742 nm but with a significant increase in background (solution **3** in Fig. 1). The observed increase in background can be attributed to the light scattering from small particles,[20] suggesting the formation of Np colloidal particles in the solution **3**. The zeta potential ($\zeta$) of this Np colloid was determined to be 0 mV, which explains the tendency of the formed Np colloid to undergo precipitation within a few hours of redispersion. This precipitation-dispersion process was repeatable.

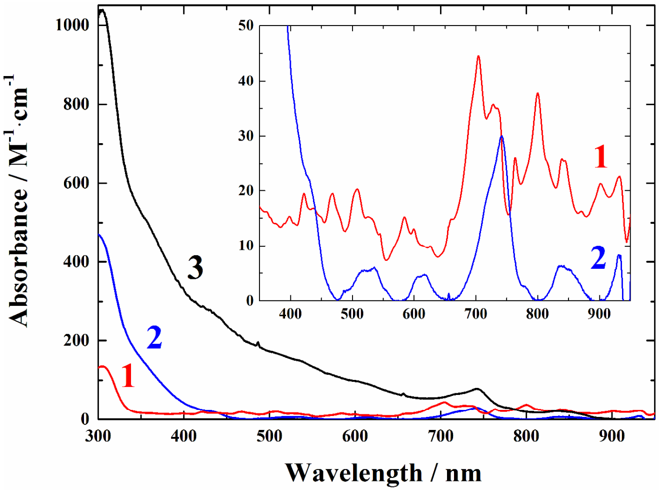


**Fig. 1.** UV/Vis absorption spectra of (**1**) the initial colloid-free Np(IV) solution in 1 M NaHCO$_3$ at pH = 8.6, (**2**) tenfold dilution of the solution **1** with ultrapure water, and (**3**) redispersion of precipitate obtained from the solution **2** in ultrapure water. The spectrum for the solution **2** was recorded immediately after dilution.

X-ray absorption spectroscopy, including both X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), was employed to characterise Np species in the solution and precipitate samples. The dilution of the initial Np(IV) solution and subsequent formation of Np colloids resulted in no significant shift in the Np L$_{III}$-edge XANES edge position (Fig. S2 and Table S1 in ESI), suggesting that the tetravalent state was preserved even after the colloid formation. The EXAFS structural parameters obtained for the initial Np(IV) solution (= solution **1** in Fig. 1) are well consistent with a pentacarbonate Np(IV) structure, $[Np(IV)(CO_3)_5]^{6-}$ (Table S2 in ESI), the coordination geometry of which is comparable to those reported for $[U(IV)(CO_3)_5]^{6-}$[21] and $[Pu(IV)(CO_3)_5]^{6-}$.[22] The EXAFS oscillation became intricate particularly in the higher $k$ range when $[Np(IV)(CO_3)_5]^{6-}$ was transformed into precipitate by dilution (Fig. 2-(a)). The main oscillation feature of this precipitate bore a close resemblance to that of reference NpO$_2$ powder, although the variation of their oscillation amplitude was different (Fig. 2-(a)). EXAFS structural analysis reveals that the nearest Np-O and Np-Np interatomic distances ($R$) obtained for the Np(IV) precipitate are well comparable to those for NpO$_2$, whilst the coordination numbers ($CN$s) for the precipitate are calculated to be much lower with larger Debye-Waller factors ($\sigma^2$) as compared with those for NpO$_2$ (Table S2 in ESI). Similar trends were also observed for UO$_2$ NCs[5] and a colloidal form of An(IV) oxide/hydroxide species (including polynuclear species),[2, 23, 24] indicating that the formed Np(IV) precipitate could be identified as either small particles of crystalline NpO$_2$ or structurally disordered Np(IV) oxide/hydroxide.

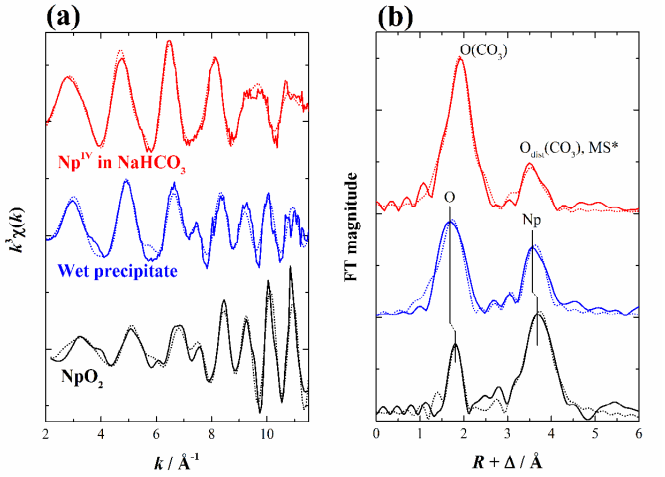
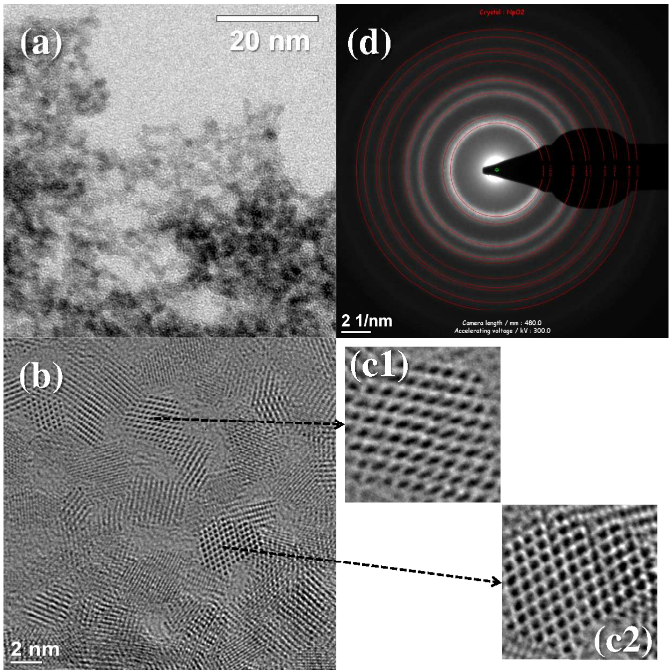


**Fig. 2.** (a) $k^3$-weighted Np L$_{III}$-edge EXAFS spectra for Np(IV) in 1 M NaHCO$_3$ / 1 M HNO$_3$ at pH = 8.6 (red), a wet precipitate obtained by the dilution of the Np(IV) NaHCO$_3$/HNO$_3$ solution with ultrapure water (blue) and reference NpO$_2$ powder (black), and (b) their corresponding Fourier transforms (FTs). Solid lines, experimental data; dotted lines, theoretical fit; phase shifts (Δ) are not corrected on FTs, MS*; multiple scattering paths. The magnitude of the data for NpO$_2$ is reduced by one forth relative to the $y$ axes for clear comparison of the spectra.

The Np(IV) precipitate was further characterised by high-resolution transmission electron microscopy (HR-TEM). Shown in Fig. 3-(a) is a TEM micrograph of the precipitate obtained from the solution **3** in Fig. 1, clearly demonstrating the agglomeration of uniformly sized particles with 2-5 nm in diameter. The relevant energy-dispersive X-ray (EDX) spectrum revealed the dominant presence of Np and O in the nanoparticles (Fig. S4 in ESI). When zooming in on some specific particles, clear lattice images could be acquired (Figs. 3-(b) and -(c)), the selected area electron diffraction (SAED) patterns of which are consistent with the fluorite-type NpO$_2$ structure ($Fm\bar{3}m$)[25] without the presence of secondary phases (Fig. 3-(d)). Note that the gentle drying process at room temperature to prepare TEM samples would not cause the formation of NpO$_2$ crystals, as the synthesis of crystalline NpO$_2$ generally involves calcination with high temperature.[26] Hence, it is highly likely that the observed NpO$_2$ NCs were already present in the solution phase. Another HR-TEM image for the precipitate obtained directly from the solution **2** in Fig. 1 (*i.e.* "non redispersed" precipitate) still showed clear lattice fringes compatible with the NpO$_2$ structure (Fig. S5 in ESI), confirming the formation of NpO$_2$ NCs even in the original precipitate before washing process. These results suggest that the dissociation of the initial soluble Np(IV) complex (*i.e.*



$[Np(IV)(CO_3)_5]^{6-}$) induces the intrinsic formation of nanocrystalline $NpO_2$ in the solution phase.

**Fig. 3.** (a) Bright field TEM micrograph of the dried precipitate obtained from the solution **3** in Fig. 1, (b and c) their HR-TEM images and (d) selected area electron diffraction (SAED) patterns. Red rings on (d) are the simulated diffraction patterns based on fluorite type $NpO_2$ structure (ICSD card 647176), demonstrating that the precipitate is composed of a pure phase of crystalline $NpO_2$.

The precipitation of aqueous An(IV) species under circumneutral conditions could also involve the formation of amorphous oxides/hydroxides.[13, 27] These amorphous phases often show a similar EXAFS pattern as observed for the pure dioxides, but their *CN*s for the neighbouring coordination shells (*i.e.* nearest An-O and An-An) are calculated to be much smaller than those for the dioxide together with larger $\sigma^2$ values stemming from their amorphism.[2, 23, 24] The *CN*s and $\sigma^2$ values obtained for the Np(IV) wet precipitate follow this trend (Table S2 in ESI). Therefore, the Np(IV) precipitate formed in solution can be identified as a mixture of amorphous Np(IV) oxides/hydroxides and nanocrystalline $NpO_2$, only the latter of which could be characterised by TEM. The redispersion of the original precipitate into water removes soluble species/phases from the precipitate, finally helping purify $NpO_2$ NCs from the amorphous phases. Indeed, image acquisition for the redispersed precipitate (Fig. 3) barely suffered from the presence of amorphous phases.

It has been reported that some An(IV) and Ce(IV), a chemical analogue of An(IV), have an intrinsic nature to form uniformly sized (2-3 nm) oxide NCs in solution phase,[1, 7, 28] which is in accordance with the $NpO_2$ NCs observed in Fig. 3. Therefore, the original precipitate ("Wet precipitate" in Fig. 2) could be identified as the aggregation of 2-3 nm sized $NpO_2$ NCs agglomerated *via* amorphous oxide/hydroxide phases. This amorphous phase tie is removed by the redispersion process, which finally yields uniformly sized $NpO_2$ NCs observed in Fig. 3-(a).

Soluble An(IV) species formed in alkaline conditions, such as $[Np(IV)(CO_3)_5]^{6-}$ in the present case, have been considered to be stable. This study demonstrates, however, that the hydrolysis of An(IV) is strong enough to dissociate these stable species by simple dilution and the subsequent marginal change in pH, which finally yields crystalline $AnO_2$ nanoparticles. This study also simulates the plausible transport scenario of An(IV) from waste repositories (near field with alkaline conditions) to the surrounding environment (far field with neutral conditions) involving diffusion processes (dilution). The observed drastic change in chemical form from soluble species to stable nanocrystalline oxides would have a significant impact on understanding the behaviour of An in natural aquatic environments. This is of particular importance in terms of long-term prediction of radionuclide transport in geological environments, as $AnO_2$ NCs are expected to be stable for a long period of time and the co-existing amorphous phases could even transform into $AnO_2$ NCs over time.[29]

This study also highlights the importance of further investigation into the formation of An(IV) NCs from alkaline conditions as well as their properties as colloids, both of which are still unexplored. With a general knowledge of chemistry, one would expect the same hydrolysis product regardless of whether the initial solution is neutralized from acidic or from basic. As a matter of fact, the precedent works on An(IV) hydrolysis have focused primarily on the former neutralisation route from the acidic condition. This would reflect the fact that the leakage of An contaminants (*e.g.* Pu) was often found under acidic–circumneutral conditions at shallow ground waste disposal sites (*e.g.* pH > 1.9 at the Maxey Flats disposal site, Kentucky, USA;[30] pH = 3.9–6.8 at the Savannah River Site, South Carolina, USA;[31] and pH = 5 at the Little Forest Legacy Site, New South Wales, Australia[32]). However, as demonstrated in Fig. S3 in ESI, the EXAFS spectrum for the present alkaline-originated Np(IV) precipitate is obviously different from that for the precipitate obtained from an acidic condition,[33] implying that the alkaline-originated precipitate would be more amorphous than the acid-originated one. Although further study is required to fully characterise these Np(IV) precipitates, this difference in chemical form would finally cause a significant impact on their chemical behaviour in actual environmental and engineered systems.

In addition to the environmental implication discussed above, this study also demonstrates a new synthetic concept for producing metal dioxide ($MO_2$) NCs *via* simple dilution of alkaline M(IV) solutions. The existing routes to $MO_2$ NCs, such as $TiO_2$[34] or $ZrO_2$,[35] are generally based on the hydrolysis of aquo M(IV) species. However, the alkaline-originated synthesis demonstrated in this study is potentially applicable to the production of $MO_2$ NCs for these transition metals.[36]

## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, sample photos, XAS spectra and TEM images not shown in the main text. See DOI: 10.1039/c000000x/

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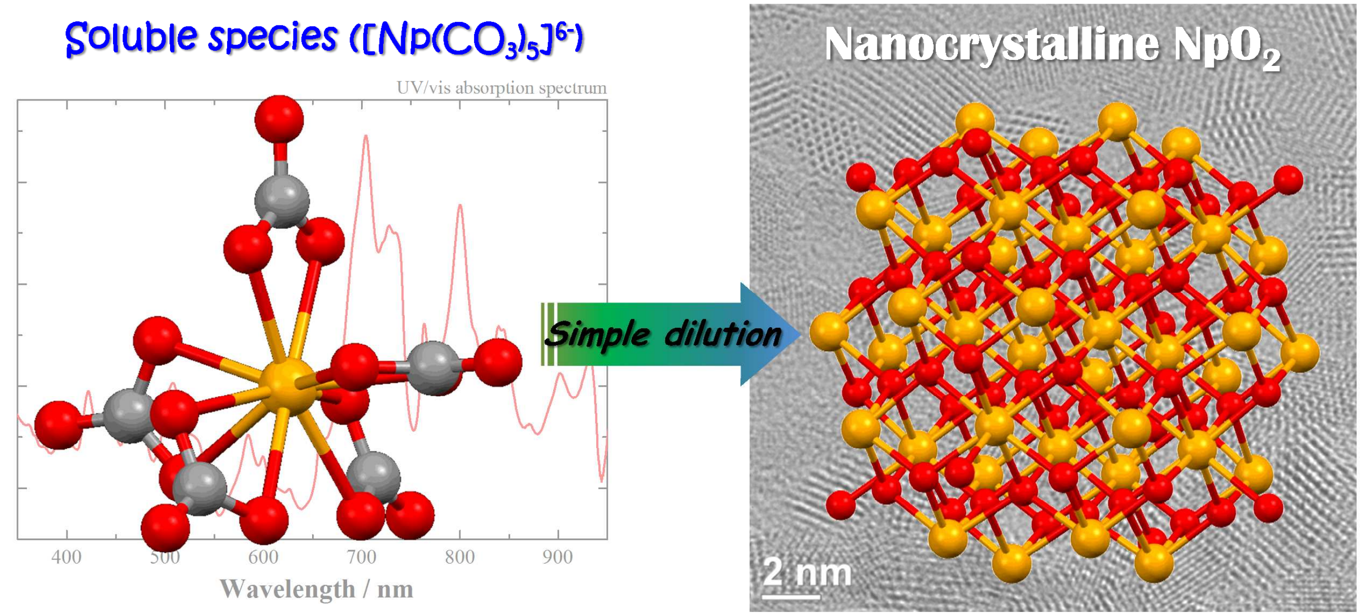
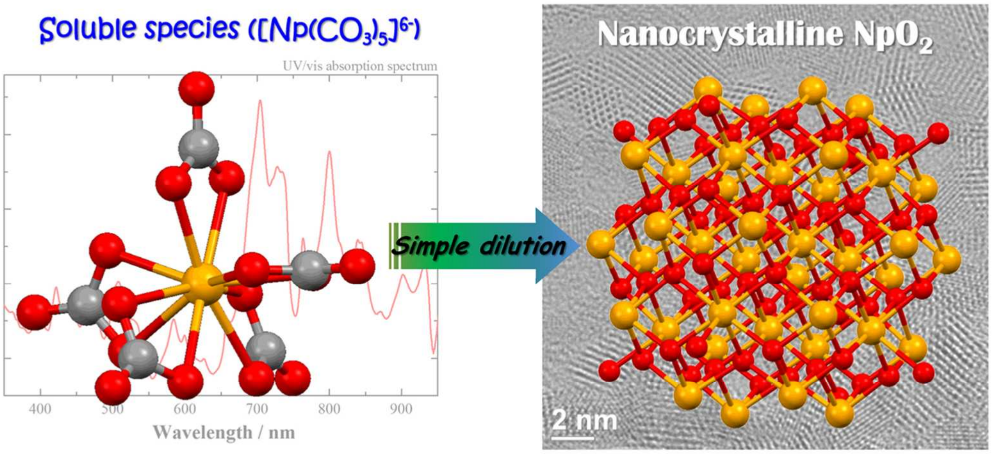


Abstract: Simple dilution of an aqueous Np(IV) bicarbonate solution triggers the intrinsic formation of nanocrystalline neptunium dioxide ($NpO_2$). This new formation route could be a likely scenario in the repository and disposal of radioactive wastes.



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