

# ATR-FTIR Spectroscopic Investigation on the Interaction of U(IV) Nanoparticles With Organic Molecules

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## 1. Introduction

In deep groundwater systems, tetravalent uranium (U(IV)) is a dominant redox form of uranium because of the anaerobic condition [1]. Natural organic complexing agents present at contaminated sites may not only affect the mobility of uranium, but also its microbial transformation and reductive precipitation. It is thus very important to understand the behaviors of U(IV) interacting with organic molecules in order to assess the geological migration of actinide species in the groundwater environment.

## 2. Results and Discussions

In this study, we developed a hydrothermally-induced U(IV) nanoparticle preparation method using acidic U(IV) aqueous solutions (pH ~2) to investigate the complexation of phosphoester on the surfaces of U(IV) nanoparticles (U(IV)<sub>NPs</sub>)

employing surface-enhanced infrared absorption (SEIRA). SEIRA is a near-field phenomenon where IR absorption of molecules adsorbed on or in the vicinity of small metal-/metal oxide-clusters is enhanced by a factor of 10 to 1000 due to the electromagnetic fields produced by the surface plasmon of clusters [2]. Herein, we report that U(IV)<sub>NPs</sub> induces SEIRA for *p*-nitrophenyl phosphate (NPP). As demonstrated in Figure 1, the overall IR absorption of 5 mM NPP is enhanced in the presence of 1 mM U(IV)<sub>NPs</sub>. The strong band (indicated by '\*' in Figure 1) at 1350 cm<sup>-1</sup> has been assigned as a symmetric NO<sub>2</sub> stretching vibrational mode in previous SEIRA studies and is used to examine the molecular orientation of the ligand adsorbed on noble metal-based and metal oxide-based nanoparticle systems [3]. Overall, such SEIRA effects indicate that the crystalline primary particles of U(IV)<sub>NPs</sub> possessing UO<sub>2</sub>-like semiconductor

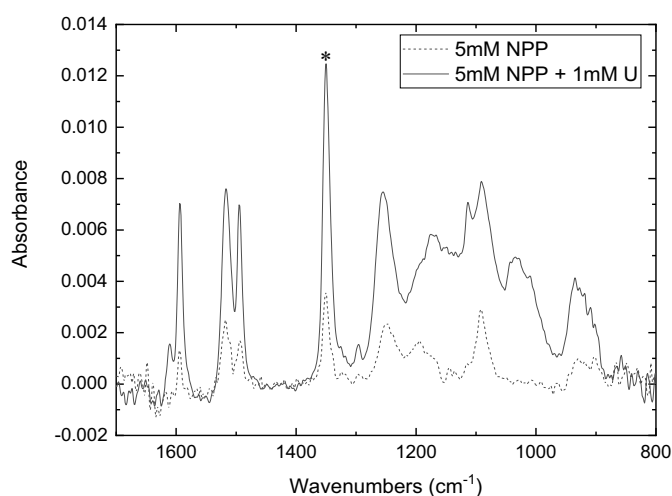


Fig. 1. ATR-FTIR spectra of reaction mixture exhibiting SEIRA effects at pH 5.2; dashed line: 5 mM NPP without U(IV)<sub>NPs</sub>; solid lines: addition of 1 mM U(IV)<sub>NPs</sub> to 5 mM NPP.

properties can effectively create polarized local electromagnetic fields interacting with the oscillating dipoles of the adsorbed molecules. Notably, the synthesized  $U(IV)_{NPs}$  display unique colloidal properties, as measured by dynamic light scattering (DLS, Fig. 2) and transmission electron microscopy (TEM): (i) highly positive zeta-potential values (+35 - +40 mV), which is a strong indicator of the presence of partially hydrolyzed surface structures such as  $\equiv U(OH)^+$  on the crystalline primary particles; (ii) high surface areas originating from the rough cluster morphology composed of primary particles. We believe that the inter-particle Coulombic repulsion

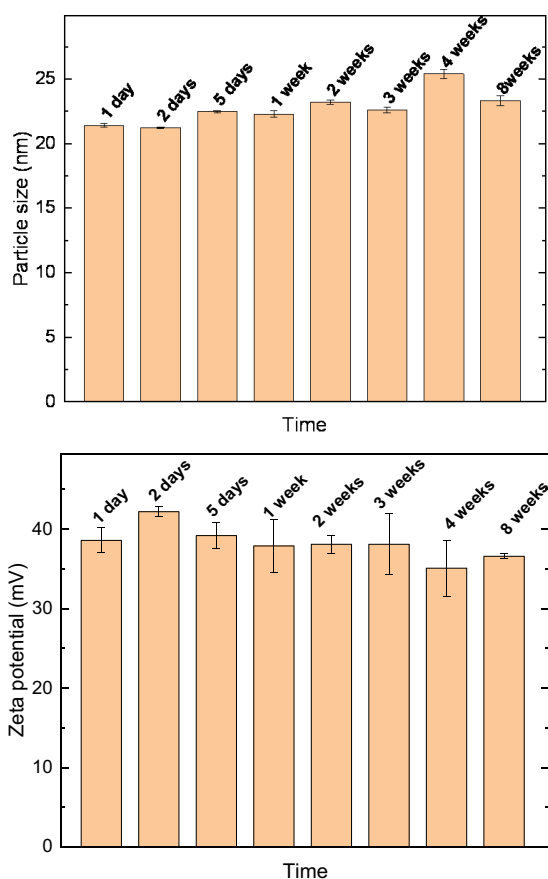


Fig. 2. Size and zeta potential measurements of 1- mM  $U(IV)_{NPs}$  over time by DLS. The data were collected using the average values of three measurements. The measured size of the particles was  $23 \pm 6$  nm and the same size was constantly observed for up to 8 weeks.

resulting from the surface charges is a critical

interfacial determinant of the colloidal stability of  $U(IV)_{NPs}$  and gives rise to reproducible particle/cluster sizes. These properties are the major factors facilitating the surface adsorption of NPP anions on  $U(IV)_{NPs}$ .

### 3. Conclusion

We conclude that the SEIRA effects of the NPP- $U(IV)_{NPs}$  system provide strong evidence for the inner-sphere surface complex formation of NPP on  $U(IV)_{NPs}$ , and more specifically, its molecular orientation perpendicular to the surface in a bidentate fashion for surface coordination. The SEIRA of a variety of nitrophenyl derivative ligands such as carboxylates, oxalate, and sulfates with  $U(IV)_{NPs}$  also will be discussed.

### ACKNOWLEDGEMENT

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