Electronic Supplementary Information

Arsenite Oxyanions Affect CeO₂ Nanoparticle Dissolution and Colloidal Stability

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Summary: Total 8 Pages, including 6 Figures
S1. Effects of dissolved oxygen on the CeO$_2$ nanoparticle (NP) and arsenite system.

To determine potential effects of dissolved oxygen on the CeO$_2$ NP and arsenite system, settling tests were conducted outside of the anaerobic chamber, using deionized (DI) water whose oxygen content was equilibrated with the atmosphere. The settling trends of CeO$_2$ NPs for this system are shown in Figure S1. Settling over the first 8 hours was very similar for the aerobic systems and anaerobic systems, with only the $10^{-4}$ M As$^{3+}$ system undergoing significant settling (Figure S1A). Particle size and zeta potential data also showed that the largest size and the lowest zeta potential were in the $10^{-4}$ M As$^{3+}$ system, similar to measured values for the anaerobic system. Based on these results, very limited oxidation of aqueous arsenite ions by dissolved oxygen was expected.

**Figure S1.** Settling trends of CeO$_2$ NPs for (A) aerobic and (B) anaerobic arsenite systems. Particle size and zeta potential for CeO$_2$ NP aggregates were measured using Dynamic Light Scattering (DLS).
However, when the concentrations of arsenic in the anaerobic and aerobic systems were measured over the 8 hour reaction period (Figure S2), the concentrations were much lower in the $10^{-6}$ M As$^{3+}$ system for the aerobic case, in many cases falling below the detection limit for the instrument (Figure S2B, 2, 4, and 6 hours). This finding indicates that oxygen does impact these systems over the first 8 hours of reaction, potentially by oxidizing As$^{3+}$ to As$^{5+}$. As$^{5+}$ is expected to be less mobile and more easily sorbed at pH 5 because it has a negative charge, while the bare CeO$_2$ NPs

Figure S2. Aqueous total arsenic concentrations in (A) anaerobic and (B) aerobic systems. The results are from three replicates, and the error bars are smaller than the size of the symbols. Note that concentrations at 2, 4, and 6 hours in the aerobic system were below the detection limit.
are charged positively. Therefore, the total aqueous As concentration in the aerobic system decreased compared with the anaerobic system.

Settling in the $10^{-6}$ M As$^{3+}$ system was compared with that in the $10^{-6}$ M As$^{5+}$ system, and the settling trends were similar over the first 8 hours of reaction (Figure S3). The similarity further supports our hypothesis that the oxidation of As$^{3+}$ to As$^{5+}$ in the aerobic system accounts for the different As$^{3+}$ concentration trends (in particular, that of $10^{-6}$ M As$^{3+}$ in Figure S2) in anaerobic and aerobic conditions. Moreover, it also accounts for the similar settling trends in anaerobic and aerobic conditions (Figure S1). In other words, while the oxidation of As$^{3+}$ decreases the aqueous As$^{3+}$ concentrations in the aerobic system, there is no change in settling between the aerobic and anaerobic systems because the settling trends caused by $10^{-6}$ M As$^{3+}$ and $10^{-6}$ M As$^{5+}$ adsorption on CeO$_2$ NPs are similar.

Based on these results, it is clear that the presence of oxygen impacted As$^{3+}$ in our experimental system, particularly for the lowest concentration of $10^{-6}$ M. Therefore, to clearly elucidate direct redox interactions between As$^{3+}$ and CeO$_2$, further investigations focused only on

![Figure S3. CeO$_2$ NP settling in the arsenate system under the aerobic condition.](image-url)
anaerobic systems, in which any observed oxidation of As$^{3+}$ had to result from only interactions with Ce$^{IV}$O$_2$.

**S2. UV-Vis calibration for sedimentation experiments**

Although there may be contribution from Rayleigh scatter at low absorption wavelengths, the linear relationship between CeO$_2$ concentration and the 305 nm wavelength absorption was confirmed over a range of 2–100 mg/L of suspended CeO$_2$.

![Figure S4](image)

**Figure S4.** (A) Calibration curve for absorbance of 2-100 mg/L CeO$_2$ at 305 nm wavelength using UV-vis. (B) UV-Vis spectra of CeO$_2$ NP suspension showing absorbance peak at 305 nm. Figure reprinted with permission from Liu et al.\(^1\)

**S3. Potential secondary phase formation in the CeO$_2$ NP and arsenite system.**

To investigate whether secondary phases formed in the CeO$_2$/arsenite system, we used high resolution transmission electron microscopy (HRTEM, JEOL 2100F, MA). TEM samples were prepared as described in the manuscript. In addition to the large aggregates shown in Figure 2, lattice images were also taken to look for secondary phases in the $10^{-4}$ M As$^{3+}$ system and $10^{-5}$ M As$^{3+}$ system (Figures S5 and S6, respectively). All lattice spacings closely matched those of CeO$_2$.
nanoparticles, which have lattice spacings of 0.27 nm for (200) facets, 0.31 nm for (111) facets, and 0.21 nm for (511) faces.\textsuperscript{2,3} No additional lattice fringes from other solid phases were observed.

\textbf{Figure S5.} Lattice fringes of CeO\textsubscript{2} NPs for the 10\textsuperscript{−4} M As\textsuperscript{3+} system.
Figure S6. Lattice fringes of CeO₂ NPs for the 10⁻⁵ M As³⁺ system.
S4. Effects of aggregation on surface area.

Although the 10⁻⁴ M As³⁺ system has a higher As³⁺ concentration, more dissolution occurred in the 10⁻⁵ M As³⁺ system. This dissolution trend indicates that dissolution is related to the amount of exposed surface area in the system, since the 10⁻⁴ M As³⁺ system has a much larger aggregate size than the 10⁻⁵ M As³⁺ system. Where aggregate size is similar in the 10⁻⁶ M As³⁺ and 10⁻⁵ M As³⁺ systems, more dissolution occurs for the higher As³⁺ concentration (10⁻⁵ M As³⁺). It is difficult to measure the surface area of aqueous nanoparticle aggregates due to drying effects, which alter the aggregate morphology.² However, multiple studies have reported lower surface area for nanoparticle aggregates.²⁻⁴

References