

Editorial

Recent Advancements in Detection and Disposal of Radionuclides using Graphene Oxide

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Groundwater contamination due to accidental leakage is a major concern in nuclear fuel processing. Preemptive actions in terms of detection and sensing are needs of the hour before any unforeseen disaster such as the Fukushima-Daiichi accident strike to our ecosystem, where tons of tainted water leaked into the ocean. In a very promising work, Romanchuk et al. [1] showed experimentally that graphene oxide (GO) has a higher sorption capacity for U(VI) and Pu(IV) ions from waste solutions containing common ions such as Na⁺, Ca²⁺, NO₃⁻, Cl⁻, carbonates, and sulfates over a wide range of pH. Therefore, GO performs better than traditional materials such as activated carbon and bentonite for scavenging radionuclides from nuclear waste water. This result is of significant importance in nuclear waste treatment due to the fact that Pu(IV) is known to form strong complexes with the listed common anions.

In our earlier work [2], we analyzed a form of GO with a carbonyl functional group to detect radionuclides in nuclear waste water by calculating the current in the GO sensor induced by an external voltage when the waste water is in contact with the sensor. This analysis was performed using a combined DFT-Green's function approach [3] developed originally to analyze current-voltage characteristics in single molecule experiments [4-5]. Due to their interesting electronic properties [6-7], graphene has found huge interest in the academic community in several applications. Functionalized graphene can be used for variety of applications such as FRET biosensors [8], transparent conductive films [6], environmental pollution management [9], nuclear waste disposal [1], tunable optical devices [10], molecular devices [11] among several other applications. However, covalent functionalization can also lead to loss of those properties which make graphene so fascinating. The graphene plasmons (sea of π -electrons on the graphene surface) are highly sensitive and likely to be affected by the electrostatic field of a single molecule. The electrical and optical responses of graphene nanosheets depend on the interaction of those plasmons with any foreign molecule attached to the graphene surface. A significant change in the molecular electrostatic field of graphene was observed

when interacting with radionuclide complexes [2]. The change in electrostatic potential can be amplified into a current-voltage characteristic, which is the working principle behind graphene-based nanosensors [2,12].

A lot of work has been done in speciation of radionuclide complexes in water using both static ab-initio as well as Car-Parrinello methods. Most of these works make use of effective core potentials. Car-Parrinello molecular dynamics (CPMD) calculations performed on uranyl nitrate complex showed that mononitrate-hydrate complex may be the most predominant species present in aqueous phase [13]. Similarly, CPMD calculations for uranyl chloride complexes showed that monochloride-hydrates may be the most probable species present [14]. Classical molecular dynamics using polarizable force field as well as CPMD calculations done for Th(IV) chlorides and bromides indicate that Th(IV) is more likely to occur as completely hydrated structure in water [15]. Unlike Th(IV) ion, Pu(IV) ion has much higher affinity to attract counter-ions due to its open-shell ground state [2]. We studied in a great detail solvation of the actinide complex in water using polarizable continuum model [16]. Our results show that Pu(IV) ion has a higher tendency than the Th(IV) ion to form inner sphere complex with counter-ions [16]. Most of the ab-initio calculations also indicate that the radionuclides have a strong tendency to form complexes with common counter-ions present in nuclear waste water [2,17,18].

However, there are only few studies done to study interaction of these complexes with GO. GO is known to contain a variety of oxygen-containing functional groups on its edge and on its basal plane. Though the molecular formula can exhibit several variations, common functional groups present are epoxy, carbonyl, hydroxyl, and carboxylic groups [19-20]. The binding of hydrated uranyl cation with oxygen containing functional groups of GO was investigated by Wu et al. [21]. They also studied in a recent paper interaction of plutonium and neptunium with GO [22], but they did not consider the effect of counter-ions present in the system. Their study however show that PuO₂²⁺ and NpO₂²⁺ in cation form can covalently bond to oxygen containing functional groups. In our recent work, we showed that counter-ions if present can replace water molecules in the first coordination shell and hence it is less likely to exist in the form of completely dissociated cation solvated by water molecules [16]. In a very dilute system, however, these ions can exist in completely solvated forms. Thus, quantum chemistry calculations can help us to understand the mechanism of complexation for these radionuclides with graphene-based materials. The challenge however exists in making these sensors target-selective. GO has a higher affinity for heavy metals like Co(II), and Cd(II) ions [9], which are heavily abundant in nuclear power plants.

Sun et al. synthesized GO-supported polyaniline composites for sorption of U(VI), Eu(III), Sr(II) and Cs(I) from aqueous solution

[23]. In acidic conditions, polyaniline-GO composite has a higher affinity for heavy metal ions due to presence of large number of amine and imine functional groups. Nitrogen-containing functional groups have a stronger chemical affinity than oxygen-containing functional groups towards radionuclides. As a result, radionuclides can be extracted from oxygen-containing functional groups more easily than nitrogen-containing functional groups due to irreversible adsorption [23]. This is however in contrast to the works done by Wu et al. where they showed that uranyl has a stronger binding with the graphene modified by hydroxyl and carboxyl groups than by graphene functionalized by $-\text{CONH}_2$ and $-\text{CONMe}_2$ groups [21]. It should also be noted that the sorption experiments were shown to depend on pH of the solution. More work needs to be done to clarify the binding nature of these radionuclides with GO.

Once we identify the common complexes present in nuclear waste water, we can obtain their optimized structure using a density functional and an appropriate basis-set. Our study indicated that B3PW91 functional along with Stuttgart effective core potential and associated basis-set ECP60MWB_SEG [24-25] yielded acceptable results when compared to very precise experimental data available [2,16]. Our calculations also show that An-O in actinyls and An-O_w (An - actinide) bond lengths are weakened on interaction with graphene. Other commonly used functional for lanthanides and actinides are B3LYP and PBE [26].

Our nanosensor consists of a GO molecule with a carbonyl group with two gold contacts attached to its two ends. The two contacts are further connected to an external voltage source and the current flowing through the circuit is measured. If any foreign molecule (uranium and plutonium complexes) comes in contact with the sensing molecule, we observe a change in the current value. The current-voltage characteristics are obtained using a combined DFT-Green's function approach [3]. The Hamiltonian and overlap matrices required for the formulation are obtained from the electronic structure calculation of an extended molecule (graphene-based molecule) attached to nano-contacts (as reference electrodes, gold atoms are used most of the times) at each end with and without a radionuclide. The two nano-contacts are coupled to continuous electronic state of gold slabs which are modeled as semi-infinite electrodes. All DFT calculations were performed using Gaussian-09 program [27]. An in-house program called GENIP based on Green's function was used to calculate the current-voltage characteristics. The detailed procedure is explained elsewhere [12]. The resulting current-voltage characteristic for hydrated $\text{PuO}_2(\text{NO}_3)_2$ on GO containing a $-\text{CO}$ group show a $1/6^{\text{th}}$ order reduction in average conductance after exposure to the radionuclide complex. The average conductance before and after exposure were calculated as 9.5 and 1.6 $\mu\text{A}\cdot\text{V}^{-1}$ respectively for an external applied voltage in the range of -1 to +1 V. Similar trends were observed for Eu(III) and U(VI) aquo-nitrate complexes. Preliminary experiments conducted using a graphene sheet (grown using CVD) on a silicon oxide wafer showed promising results when tested with Eu(III) nitrate solution {manuscript under preparation}. The change in the conductance can be explained qualitatively using molecular orbital's (MO). Fully localized MOs yield higher probability for electron transport which yields higher transmission function, thus, more number of transport channels available for electrons. The radionuclide complexes strongly affects π - π orbital's on GO causing

strong localization of the orbitals, hence the conductance is reduced. Instead of a neutral complex, if we chose to obtain current voltage for a cation adsorbed on GO, we expect the conductance to reduce even more. The challenge will then be to regenerate this material for next application. The radionuclide can be recovered however by burning the material or likewise [22]. An important factor is their selectivity towards lanthanides and actinides as compared to common heavy ions like Co(II), Fe(III), and Pb(II). More sorption experiments are needed to confirm the selectivity of GO in presence of heavy ions. Another major challenge is in synthesizing this material at large scale with low cost.

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