

Adsorption of cesium from aqueous solution using graphene oxide grown on a porous substrate

Shiro Entani¹, Mitsunori Honda², Iwao Shimoyama², Songtian Li¹, Hiroshi Naramoto¹ Tsuyoshi Yaita², and Seiji Sakai¹

¹ National Institutes for Quantum and Radiological Science and Technology
Quantum Beam Science Research Directorate
2-4 Shirakata, Tokai, Ibaraki 319-1195, Japan
Phone: +81-70-3943-3443 E-mail: entani.shiro@qst.go.jp

² Japan Atomic Energy Agency
Materials Sciences and Research Center
2-4 Shirakata, Tokai, Ibaraki 319-1195, Japan

Abstract

Graphene oxide (GO) is expected to be one of the most promising adsorbents for radioactive nuclides in aqueous solutions. In this paper, studies were conducted for the electronic structure of Cs adsorbates on GO grown on porous alumina. Near edge X-ray absorption fine structure measurements make clear that Cs atoms bond to oxygen functional groups in the aqueous solution.

1. Introduction

Graphene has attracted wide attention in the field of environmental application because it has a potential prospect of using as the effective adsorbent [1]. Its low-cost and high chemical stability make its use feasible for large-scale application. However, pristine graphene without any chemical treatment shows hydrophobic nature, and hence it is difficult to adsorb ion species in aqueous solutions. Adopting graphene oxide (GO) instead of pristine graphene is able to resolve the above problem. GO is partially oxidized graphene and its surface and periphery are partially modified by epoxy, hydroxyl and carboxyl functional groups [2]. These functional groups increase the hydrophilicity of GO. Ramanchuk et al. have demonstrated that GO is effective in removal of actinides from nuclear wastewaters [3]. However, the adsorbing mechanism of relevant ions to GO surface is still uncertain.

In this study, we analyzed the electronic structure of Cs adsorbed on the GO surface in the aqueous solution. A porous alumina was used as the substrate for the chemical vapor deposition (CVD) graphene growth. The oxidation of the CVD grown graphene on the internal surface of porous alumina could allow us to obtain the GO sample with large surface area. This contributes to the improvement of enlargement of the adsorption amount of Cs and therefore to the improvement of the detection sensitivity in the electronic structure analysis. Adopting in-situ near edge X-ray absorption fine structure (NEXAFS) spectroscopy enables us to elucidate the electronic structure of Cs on GO in the aqueous solution. These fundamental aspects provide us important information for developing new adsorbent materials using GO.

2. Experimental

GO was formed on a porous alumina substrate in this study. Before synthesizing GO, a porous alumina film was grown on Si(100) substrate with a 300 nm thick oxide layer. Liquid alumisol (AlOOH, Kawaken Fine Chemicals Co., Ltd.) was used as precursor. A several micro-meter-thick alumisol film was deposited on the SiO₂ substrate by spin coating. After the pre-baking at 170 °C in the atmosphere, the alumisol film was introduced into a custom-designed vacuum furnace. The base pressure of the furnace was evacuated up to 6×10^{-6} Pa. After the evacuating, and then the alumisol film was heated at 1000 °C for 1 hour in order to convert alumisol into porous alumina. For the graphene growth, a methanol vapor was used as a precursor. Graphene was grown by introducing 200 Pa methanol vapor for 30 min [4]. After the graphene growth, the graphene in the sample was oxidized based on the modified Hummers method [5]. The GO surface was then dipped with 0.1 mol/l CsCl solution. Electronic structure of adsorbed Cs in the aqueous solution was investigated in situ by fluorescence-yield NEXAFS at the BL-27A station in KEK-PF. The details of the in-situ measurements were summarized elsewhere [6, 7]. The measurements were performed in a helium gas atmosphere by introducing the specimen into a NEXAFS apparatus immediately after the dropping of the CsCl solution onto the GO surface. For the measurements of the C and O K-edge NEXAFS (not shown here) and X-ray photoelectron spectroscopy (XPS) spectra, the CsCl solution was removed by a water-rinse and introduced into the vacuum chamber.

3. Results and discussion

Figure 1 shows an AFM image of GO/porous alumina. A lot of grains with 10-30 nm in diameter and with several nm in height are observed in the AFM image. The root-mean-square (RMS) value, evaluated from the AFM image, was 1.84 nm. Figure 1 (b) shows Cs 3d XPS spectrum of Cs-adsorbed GO. It is found that Cs is adsorbed on GO even after the water-rinse. The 3d_{5/2} peak of Cs adsorbed on GO (723.5 eV) is slightly shifted to higher binding energies compared with that of CsCl (723.9 eV) [8].

This indicates that the chemical state of Cs adsorbed on GO is different from that of CsCl. It is also found that the weight adsorption efficiency in the CsCl solution is estimated to be 1 Cs atom per 7-9 carbon atoms, which corresponds to approximately 70wt%, from the XPS analysis based on the peak intensity ratio between C 1s and Cs 3d [9].

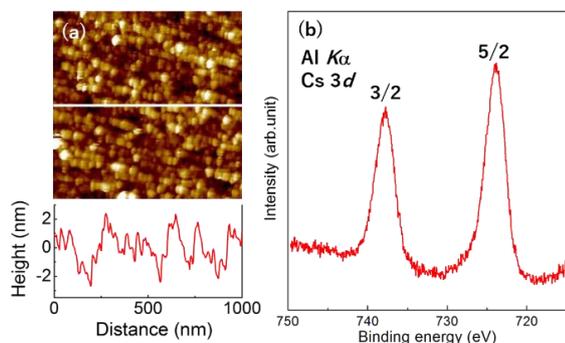


Fig. 1 (a) An AFM image of Cs adsorbates on GO/porous alumina. (b) Cs 3d core level XPS of Cs/GO/porous alumina.

Figure 2 shows Cs L_{III} -edge fluorescence NEXAFS spectra. Differences arise in the spectra between the CsCl solution (i) and the solution dropwise onto GO (ii). This indicates that the specimen of the CsCl solution after the dropwise on GO contains another Cs species with new electronic structure in addition to the Cs ions in the aqueous solution. It is also found that the difference spectrum (iii) is roughly similar to the spectrum of Cs adsorbed on GO after water-rinse (iv), in the points such as the absorption threshold and the spectral features. Although the peaks have not been assigned yet, it can be said that these changes are caused by the adsorption of Cs atoms on the GO surface in the aqueous solution from the comparison between the cases without and with GO. The spectral changes indicate that the Cs atoms are adsorbed with formation of bonding to oxygen functional groups on GO. By employing GO, it may be possible to efficiently collect radioactive Cs from waste waters.

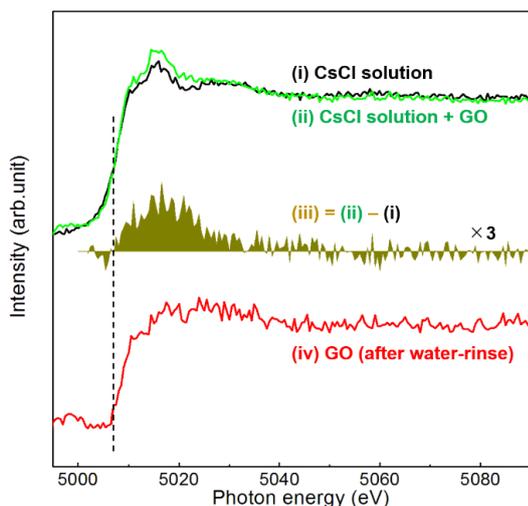


Fig. 2 Fluorescence NEXAFS spectra (i) of 0.1 mol/l-CsCl solution and (ii) of the solution dropwise onto GO. (iii) Difference spectrum

between (ii) and (i). (iv) Fluorescence NEXAFS spectrum of Cs adsorbed on GO after water-rinse.

4. Conclusions

The Cs adsorption on GO has been investigated by means of in-situ fluorescence NEXAFS. It is found that GO adsorbs the Cs atoms in the aqueous solution with formation of the bonding between oxygen functional groups and Cs. It is also indicated that GO shows the high Cs adsorption efficiency of 70wt%. This suggests that GO possesses surpassing properties for adsorption / recovery of radioactive Cs from waste waters. Employing CVD method, the any surface of GO can be prepared with porous structures. It is expected that the present technique is applicable to development of specially designed adsorption column with high adsorption efficiency.

Acknowledgements

A part of the present work has been performed under the approval of the Photon Factory Program Advisory Committee (PF PAC No. 2014G624).

References

- [1] L. Yu. Antipina, P. V. Avramov, S. Sakai, H. Naramoto, M. Ohtomo, S. Entani, Y. Matsumoto, P. B. Sorokin, *Phys. Rev. B* **86** (2012) 085435.
- [2] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. B. Nguyen, R. S. Ruoff, *Nature* **448** (2007) 457.
- [3] A. Yu. Romanchuk, A. S. Slesarev, S. N. Kalmykov, D. V. Kosynkin, J. M. Tour, *Phys. Chem. Chem. Phys.* **15** (2013) 2321.
- [4] S. Entani, L. Yu. Antipina, P. V. Avramov, M. Ohtomo, Y. Matsumoto, N. Hirao, I. Shimoyama, H. Naramoto, Y. Baba, P. B. Sorokin, S. Sakai, *Nano Res.* **8** (2015) 1535.
- [5] A. Lerf, H. He, M. Forster, J. Klinowski, *J. Phys. Chem. B* **102** (1998) 4477.
- [6] M. Honda, Y. Baba, I. Shimoyama, T. Sekiguchi, *Rev. Sci. Instrum.* **86** (2015) 035103.
- [7] M. Honda, I. Shimoyama, Y. Okamoto, Y. Baba, S. Suzuki, T. Yaita, *J. Phys. Chem. C* **120** (2016) 5534.
- [8] W. E. Morgan, J. R. Van Wazer, W. J. Stec, *J. Am. Chem. Soc.* **95** (1973) 751.
- [9] C. D. Wager, W. M. Riggs, L. E. Davis, J. F. Moulder, G. E. Muilenberg, *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer, Eden Prairie, 1979.