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# XAFS study of Ca adsorption on single-layer graphene oxide

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## 1 Introduction

Graphene oxide (GO) is oxidized graphene. Numerous oxygen functional groups are substantially attached on the surface and periphery of the single atomic graphene sheet [1,2]. Therefore, GO has a potential to be utilized in a variety of applications, including its use as an adsorbent for aqueous solutions. In this study, the adsorption mechanism of calcium (Ca) on GO has been investigated using single-layer graphene oxide (SLGO) as the model structure. SLGO is obtained through the process of oxidizing graphene grown by metal-free CVD on α-$Al_2O_3$(0001) [3], which prevents the aggregation and re-stacking during the Ca adsorption. Electronic states of adsorbed Ca on SLGO in the aqueous solution were investigated in situ by fluorescence-yield XAFS.

## 2 Experiment

Before synthesizing SLGO, single-layer graphene (SLG) was grown on an α-$Al_2O_3$(0001) substrate. Subsequently, the SLG was oxidized based on the modified Hummers method [4]. The SLGO film thus synthesized was washed with purified water and dried under nitrogen gas blow.

The Ca K-edge fluorescence-yield XAFS measurements were carried out using BL-27A station at KEK Photon Factory [5,6]. The SLGO surface was dipped with 1 μl-0.1 mol/l $CaCl_2$ aqueous solution. After the adsorption of Ca on SLGO, the $CaCl_2$ solution was removed by a water-rinse.

## 3 Results and Discussion

Figure 1 shows the Ca K-edge XAFS spectra of a 0.1 mol/l $CaCl_2$ aqueous solution and a Ca-adsorbed SLGO. For comparison, the spectrum of a $CaCl_2$ film was also included in the same figure. Three structures are observed in the spectra of the $CaCl_2$ film and the $CaCl_2$ aqueous solution. The intense peak observed at 4050.5 eV in the $CaCl_2$ film shifts to approximately 2 eV higher energy in the $CaCl_2$ aqueous solution. This is attributed to the full hydration of $Ca^{2+}$ in the aqueous solution. The pre-edge peaks denoted as P1 and P2 are assigned to $1s \rightarrow 3d$ and $1s \rightarrow 4p$ transitions, respectively. The P2 structure changes between spectra of the $CaCl_2$ film and the $CaCl_2$ solution. This comes from the formation of solvent-shared $Ca^{2+}$–$OH_2$–$Cl^-$ ion pairs, which slightly changes the $1s \rightarrow 4p$ transition [7]. In contrast, the XAFS spectrum of Ca adsorbed on SLGO displays an absence of structure (P1 and P2) in the pre-edge region. This suggests that the water on the SLGO is devoid of $Cl^-$ ions and that SLGO adsorbs exclusively $Ca^{2+}$ on the surface. Additionally, the quantitative estimation employing the peak analysis of XPS suggests that the amount of Ca adsorption on SLGO is contingent on the pH scale of the solution; the quantity of Ca adsorbed on SLGO is greater in solutions with higher pH value. From the discussion described above it is concluded that Ca adsorbs on SLGO by the substitution of H from oxygen functional groups, such as carboxyl and hydroxy groups.

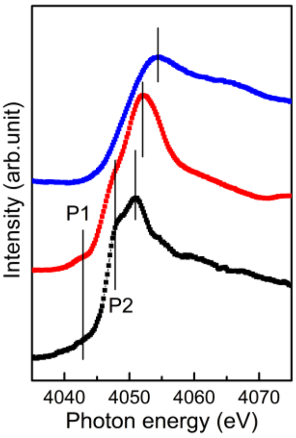

Fig. 1: Ca K-edge XAFS spectra of the $CaCl_2$ film (black), 0.1 mol/l $CaCl_2$ aqueous solution (red), and Ca-adsorbed SLGO in water (blue).

## References

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