

Electrochemical Analysis of Alkaline Metal Cation Adsorption on a Graphene Interface by Electrochemical Surface X-ray Diffraction

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Understanding electrochemical behavior of the alkaline metal cation–graphene interface in electrolyte is essential for understanding the fundamental electrochemical interface and development of graphene-based technologies [1]. However, most studies have been mainly conducted based on typical electrochemical analysis and computational evaluation, and the fundamental properties of cations on graphene at the electrified interface by the experimental approach still remain poorly understood. Here, we report analysis of the electrochemical behavior of both alkaline metal cations and graphene using electrochemical surface X-ray diffraction (EC-SXRD) in which the interfacial structure of cations can be elucidated [2]. As an model interface, monolayer graphene synthesized on an atomically flat Au(111) electrode (graphene/Au(111)) was employed. Crystal truncation rod (CTR) surface diffraction measurements of EC-SXRD were conducted on the graphene/Au(111) electrodes at BL14B1, SPring-8 using a κ -diffractometer.

Figure 1a shows the $(0, 0, L)$ CTR profile of the graphene/Au(111) electrode in 0.1 M KOH at 0 V vs Ag/AgCl, and one intense Bragg peak is clearly observed at $L = 3$. When the potential is set from 0 to -1.15 V where the adsorption of K^+ ions occurs, dips in CTR profile around $L = 2$ and 4.5 are clearly changed (Figure 1b). These changes in the profile only appear at a more negative potential where the adsorption of K^+ ions occurs and is eliminated when the potential is subsequently set to more positive potential where the desorption of K^+ ions occurs. Each profile is fitted using a three-layer structural model (first layer, adsorbates, such as ions and water; second layer, graphene; third layer, reconstructed Au(111) surface) to understand the potential-induced profile change. The model analysis revealed that the water structural layer is formed on graphene at 0 V, while the electrochemical dehydration of hydrated K^+ is involved at -1.15 V, and resultant cationic adsorbed layer structure is formed on the graphene surface. In addition, electrochemical analysis (date not shown here) found that the charge density for the K^+ adsorption can be estimated to be $\sim 17 \mu\text{C cm}^{-2}$, which corresponds to $\sim 0.1 \times 10^{15} K^+ \text{ cm}^{-2}$, and is equivalent to $\sim 1 \text{ nm}^2$ per one potassium ion. This value is close to the estimated value from the EC-SXRD diffraction data ($\sim 0.14 \times 10^{15} \text{ atoms cm}^{-2}$) and seems very reasonable for the diameter of hydrated K^+ , indicating that the adsorption and desorption behavior is based on one potassium ion with one positive charge. Interestingly, electrochemical-Raman spectroscopy also revealed that under K^+ adsorption potential, graphene becomes a highly electron doped state with lattice expansion, which is a similar feature of the potassium–graphite intercalation compound (data not shown here).

From these results, we can consider the mechanism of the cation adsorption and desorption on graphene and the associated electron high doping in graphene. Figure 2 shows a schematic illustration of electrochemically driven adsorption and desorption of cations on graphene proposed by our analyses. When the potential is set around a more positive potential than a potential of zero charge (PZC) in which the value is located at -0.6V for our electrochemical system, the positively charged

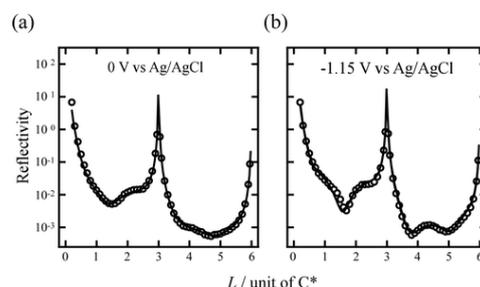


Fig. 1 CTR profiles of the graphene/Au(111) electrode in 0.1 M KOH at (a) 0 V and (b) -1.15 V vs Ag/AgCl. Circles and solid lines denote experimental data and the fitted curve, respectively.

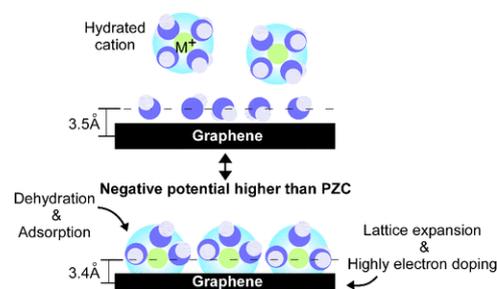


Fig. 2 Schematic illustration of electrochemically driven adsorption and desorption of cations involved in dehydration and hydration process.

graphene would prevent the approach of hydrated cations to the surface, and thus the water layer structure is mainly formed on the graphene interface. The hydrated cations attract negatively charged graphene at a more negative potential than the PZC and would approach the graphene surface at the more negative potential. When the potential reaches a certain value where it attracts sufficient energy to overcome the hydration energy, partial dehydration of cations electrochemically occurs, and the dehydrated cations are adsorbed on the graphene surface. The partially dehydrated cation adsorption is also considered to trigger the high electron doping in graphene with lattice expansion. Because the dehydrated cations are adsorbed on the graphene surface, electrons would be simultaneously doped in the graphene from the Au electrode to compensate for the positive charge by the cation adsorption, reaching a high doping level. When the potential is swept positively back to the PZC, the adsorbed cations would be hydrated again, desorbing from the graphene surface because the attractive energy becomes lower than the hydration energy. These findings have not been reported so far and provide a fundamental understanding of the electrochemical electrolyte–graphene interface and development of novel catalytic and sensing graphene-based carbon electrode applications.

References

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