

Raman Spectroscopic Investigation of Proton Penetration Properties of Graphene/Au under Electrochemical Potential Control

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Recently, it has been highlighted that proton transport through graphene occurs in electrolyte solution.¹ We have also investigated that proton penetration properties of graphene/Au electrode through the in-situ electrochemical Raman spectroscopy.² To the best of our knowledge, proton penetration properties have been investigated for single layer type compounds such as hexagonal boron nitride, MoS₂ and mica.² However, molecular level control of proton penetration behavior has been difficult. Here, we show that molecular modification of graphene surface can alter the proton penetration properties.

We prepared Au (111) surface by the Cavalier method, and graphene was prepared through the chemical vapor deposition on Au (111) surface. The presence of monolayer graphene on Au(111), denoted as G/Au, was characterized from the Raman spectroscopy.³ Molecular modification of graphene was accomplished by the electrochemical oxidation of phenylhydrazine derivatives. Electrochemical measurements were conducted in 0.1 M NaClO₄ in the presence or absence of 2 mM phenylhydrazine. In the absence of phenylhydrazine, anodic current was not observed. On the other hand, in the presence of phenylhydrazine, anodic current was observed from -0.2 V vs. Ag/AgCl. The anodic feature was different from second cycle suggesting that deposition of phenyl groups on G/Au electrode (Ph-G/Au). G band (1580 cm⁻¹) and 2D band (2700 cm⁻¹) were observed for the as-prepared G/Au electrode. On the other hand, D band (1350 cm⁻¹) was additionally observed for Ph-G/Au. Spectral analysis showed that molecular groups were introduced with several nanometer spacing without any vacancy type defects. It suggests that successful modification of graphene surface by phenylhydrazine. We studied the electrochemical potential dependence of G band and 2D band position of G/Au and Ph-G/Au electrodes (Fig. 1). G band and 2D band positions remain similar at different electrochemical potential modulation. 2D band suddenly dropped at -1.8 V for G-Au and -1.6 V for Ph-G/Au reversibly. The observed 2D band shift is due to the intercalation of H₂ molecules between graphene and Au by through the proton penetration, which was induced by control of electrochemical potential. This study highlights that molecular level control of graphene to induced and modulate the proton permeability of graphene.

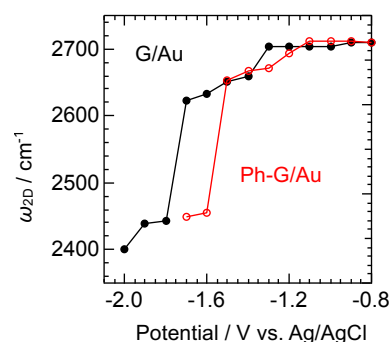


Fig.1 Dependence of 2D band peak position on electrochemical potential.

(1) M. Lozada-Hidalgo, H. A. Wu *et al.*, *Nature* **2014**, 516, 227. (2) T. Fukushima, K. Murakoshi, *Current Opinion in Electrochemistry* **2019**, 17, 158. (3) T. Fukushima, K. Murakoshi *et al.*, *Journal of Physics Conference Series*, **2019**, 1220, 012016.