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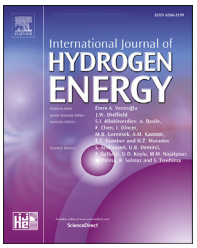

Short Communication

Optimum interlayer distance for hydrogen storage in pillared-graphene oxide determined by H_2 pressure-dependent electrical conductance

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ABSTRACT

To establish the relation between optimum interlayer distance for hydrogen storage and electrical conductance, we measured the electrical conductance (G) of 3-dimensional graphene oxide (GOA) depending on high H_2 pressure, from vacuum to 20 bar. The GOA was synthesized using diaminoalkanes with two lengths of alkyl chains, and the interlayer distance of GOA was modulated by thermal annealing. A decrease in G was observed as the H_2 pressure increased. The maximum variation in G was observed at 7.0 Å of interlayer distance. When the interlayer distance-dependent H_2 uptake was considered, we confirmed that the maximum variation in G as well as optimum H_2 uptake occurred at the same interlayer distance, 7.0 Å. The variation in G due to H_2 exposure provides understanding about the behavior of hydrogen molecules on these materials and on the modulation of the electronic structure of the materials.

Introduction

Fossil fuels have dominated the energy industry as the world's primary energy source over the past several decades. However, total fossil fuel production is limited and its consumption is environment-unfriendly. As a result, numerous studies to develop alternative energy sources have been actively pursued. Interest in eco-friendly energy sources in particular is growing. Among them, hydrogen has attracted wide attention as an energy source because of its renewable and inexhaustible characteristics [1–6]. In order to use hydrogen as an energy source, it will be necessary to overcome the current challenges of hydrogen storage and hydrogen production. Many studies seeking to solve these problems have been reported [7–15]. Graphene-based materials [16–19], which are two-dimensional carbon-based materials with light weight, large surface areas, and large pore volumes, have come into the spotlight as an efficient hydrogen storage material.

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Recently, it was reported that the interlayer distance in graphene-based materials is considered an important factor to enhance its hydrogen storage capacity. The optimum interlayer distance of multi-layer graphene oxide (GO) for hydrogen storage is 6.5 Å [16]. Using 3-dimensional GO (GOA) synthesized by GO and diaminoalkanes ($H_2N(CH_2)_nNH_2$) as a pillar, the optimum interlayer spacing of 6.3–7.0 Å was also reported [18]. In addition, the interaction between hydrogen and 2-dimensional materials has been studied as a function of H_2 pressure from vacuum to 24 bar, using electrical conductivity [17,20–27]. The variation in electrical conductivity due to H_2 exposure provides understanding about the behavior of hydrogen molecules on the materials, and on the modulation of the electronic structure of the materials. This will be helpful for designing hydrogen storage materials.

Herein, we report the electrical conductance (*G*) of GOA with respect to the H_2 pressure from vacuum to 20 bar. First, two GOA samples were synthesized using diaminoalkanes, $H_2N(CH_2)_nNH_2$ with different lengths of alkyl chains (n = 2, 6), Second, the interlayer distance of the two GOAs was controlled by thermal annealing process. Then, the H_2 pressure-dependent current-voltage (*I-V*) characteristics were measured from vacuum up to 20 bar. After that, to determine whether the electrical characteristics returned to their original state or not, the *I-V* characteristics were measured again in a vacuum (10^{-6} Torr). We found that physical adsorption as well as chemical adsorption occurred. Furthermore, it was confirmed that the maximum change in *G* was observed at the interlayer spacing which had the maximum hydrogen storage capacity.

Material and methods

GOAs were synthesized with different lengths of alkyl chains (n = 2, 6) [18]. They were designated GOA2 for n = 2 and GOA6 for n = 6. First, GO was prepared by the Hummers method [28]. Second, GO dispersed in deionized (DI) water was mixed with diaminoalkanes dissolved in methanol. The resulting product, GOA, was rinsed with DI water and methanol. 50 mg of GOA were dispersed in 30 ml of isopropyl alcohol (IPA) using an ultrasonicator. Then, the GOA was separated by centrifugation at 10000 rpm for 5 min to get the light and thin GOA. Using a micropipette, the GOA was dropped onto 300 nm thick SiO_2/Si substrate.

Result and discussion

Fig. 1(a) shows an optical image of the GOA on the substrate. We analyzed the GOA using Raman spectroscopy to confirm that the flake on the substrate was GOA (Fig. 1 (b)). Since the GOA is synthesized using GO and diaminoalkane, many defects are produced. As a result, the *D* band (approximately 1360 cm^{-1}) appears. In addition, the *G* band is shifted to 1600 cm^{-1} due to the reaction of the amines in diaminoalkanes with the epoxy groups in the GO [29]. The interlayer distance of GOA was modulated to observe the H_2 pressure dependence of *G* as a function of interlayer distance. First, the substrate with GOA was placed in a tube furnace and the furnace was evacuated under vacuum (10^{-3} Torr). After N_2 gas was flowed to purge the oxygen or water molecules, the tube furnace was evacuated under vacuum again. This process was repeated two times to remove any residue in the tube. Next, the temperature was increased by 2 K per minute and then was kept for 30 min at the target temperature. According to the previous research [18], the interlayer distances of GOA2 were 7.62 Å, 5.46 Å, and 5.12 Å when it was annealed at 358 K, 430 K, and 491 K, respectively. In the case of GOA6, the interlayer distances were 6.98 Å and 6.04 Å when GOA6 was annealed at 548 K and 573 K, respectively. Based on this result, these five GOAs with different interlayer distances were prepared. Since the hydrogen storage capacity depends on the interlayer distance of the GOA, it was expected that the H_2 pressure-dependent electrical characteristics would change with the change in interlayer distance.

In order to measure the *G* of the GOA, electrodes were fabricated on top of the GOA with Cr/Au (5/50 nm) with

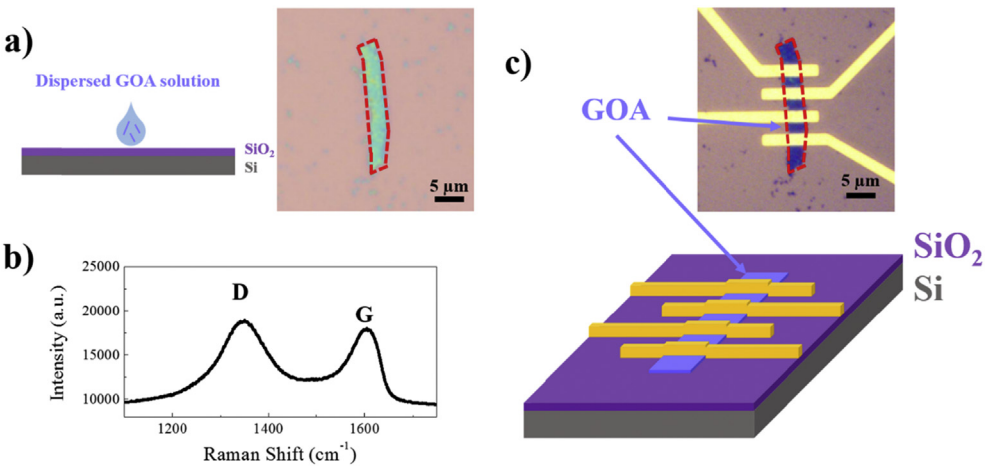

Fig. 1 – a) Image showing the dispersed GOA solution being dropped onto a 300 nm SiO_2/Si substrate using a micro-pipette, and its optical image. b) Raman spectrum of GOA. c) Au electrodes were fabricated on top of the sample using electron beam lithography and a thermal evaporator.

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