Dehydration behaviour and structural evolution of graphene oxide membranes on silicon substrate

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Abstract

The dehydration kinetics of graphene oxide (GO) were investigated by in-situ two-dimensional grazing incident X-ray diffraction. We found that the interlayer spacing of the GO membrane gradually decreased as the annealing temperature increased and as time elapsed. Surprisingly, we observed the formation of an intermediate “water-rich” GO layers at 25 °C with an interlayer spacing of approximately 15.2 Å, which was caused by the intercalation of two additional layers of water into the interlayers of the GO membrane. Moreover, three types of water trapped in GO were clearly distinguished upon isothermal annealing at various temperatures. Below 160 °C, the removal of “bulk water” and “confined water” resulted in a smaller interlayer spacing and the preservation of oxygen-containing functional groups. At 160 °C or higher, “bound water” was removed and oxygen-containing functional groups were lost, which contributed to the reduction of GO. The dehydration behaviour and structural evolution of GO investigated here is useful for understanding and controlling the properties of GO membranes for permeation, separation and electronic applications.

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1. Introduction

Because of its unique 2-dimensional structure, graphene oxide (GO) membranes have attracted much attention in the scientific community and exhibit great potential in filtration, sieving and separation applications [1–3]. GO is a nonstoichiometric material produced by strong oxidation of graphite with a periodic layered structure that is similar to that of graphene [4–6]. The hydrophilic nature of GO is considered to be its most outstanding feature, which causes the swelling of the interlayer spacing under certain conditions and in various solutions [7–11]. It has been reported that the molecules and ions travel through a “labyrinth path” in GO interlayers [12,13]. Therefore, the study of the GO interlayer spacing modified by hydration is important to explain and predict the permeation and separation properties of GO membranes.

Until now, many authors have investigated the hydration behaviour and kinetics of water molecules in GO, and they found that the hydration behaviour can be changed by varying certain factors, such as the solvent, humidity, temperature, pressure and grain size [7,8,12,14–23]. The degree of GO hydration is typically evaluated by X-ray diffraction or neutron scattering [15]. The interlayer spacing of the GO (001) reflection provides information about the distance between “graphene skeleton” planes, and therefore, an increase or decrease in the interlayer spacing can reflect the intercalation or removal of water molecules in the interlayers of GO [14]. The interlayer spacing of hydrated graphite oxide is found to increase gradually by 30% upon compression to 1.3–1.5 GPa [18] at ambient temperature due to the pressure-induced insertion of additional water. This interlayer spacing gradually increases from approximately 8 Å to 11.5 Å when the relative humidity increases in a range of 45%–100% [8]. Moreover, it is reported water is very hard to be removed completely from the
structure of GO even under humidity-free conditions. Water is always present because of the strong hydrogen bonding between water molecules and the surface of GO [17], and hydrated GO has been observed of the phase transition in solvents, such as methanol, alcohol, and acetonitrile [18,19]. These works show that complex hydration behaviours exist in GO systems. However, the dehydration behaviour of GO is rarely mentioned. In particular, a dehydration process normally occurs during the manufacturing of GO membranes [2,3]. Therefore, it is necessary to study the dehydration behaviour to understand and control the structure and properties of GO membrane.

In this work, we investigated the dehydration kinetics of GO membrane by in-situ two-dimensional grazing incident X-ray diffraction (GIXRD) and X-ray photoelectron spectroscopy (XPS). The chemical evolution of GO during the dehydration is observed by Fourier transform infrared spectroscopy (FTIR) measurement. We observed two types of GO structures with different interlayer spacing at room temperature. Moreover, three types of water [7] ("bulk water", "confined water", "bound water") trapped in GO can be clearly distinguished upon isothermal annealing at various temperatures due to three different dehydration behaviours. Then, we compared the results of the dehydration processes of GO membranes with different average grain sizes, thicknesses and relative humidity.

2. Experimental

GO solution (2 mg/ml) was purchased from Xian Feng NANO Co., Ltd. This is a single layer graphene oxide water dispersion. It was prepared from graphite powder using a modified Hummers method [24]. GO flakes with two different grain sizes (with an average diameter >500 nm and <500 nm) were used for the experiments. GO membranes were deposited onto hydrophilic silicon substrates cleaned by piranha solution by drop-casting.

GIXRD experiments were performed at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) with a wavelength of 1.2387 Å. A MarCCD detector was used to acquire two-dimensional GIXRD signals, which can track the continuous evolution of the interlayer spacing of GO with a sub-second time resolution. Moreover, GO membrane is a laminar material, the stacking properties of GO flakes can be easily obtained by two-dimensional GIXRD method. The entire experimental setup is depicted in Fig. 1A. The sample was dehydrated through different isothermal processes via a heating procedure at a rate of 10 °C/min from 25 °C to 190 °C. The heating processes at 25 °C, 50 °C, 80 °C, 130 °C, 160 °C and 190 °C formed the complete isothermal process. The isothermal process at 25 °C lasted for 40 mins, while each of the other processes (50 °C, 80 °C, 130 °C, 160 °C and 190 °C) lasted for 20 mins.

XPS measurements were performed using an Al-Kz radiation (1486.6 eV) at a 3 × 10⁻¹⁰ mbar background pressure. The XPS peaks were fitted using Voigt functions with 80% Gaussian and 20% Lorentzian characteristics after Shirley background subtraction was performed. The FWHM values were fixed at a maximum limit of 1 eV for all of the peaks. FTIR measurements were carried out using a PerkinElmer Spectrum Spotlight 300 with reflectance mode. Each spectrum was collected with an average of 60 repetitive scans.

3. Results and discussion

The in-situ GIXRD experiment was initiated after a 15 μL GO solution (with a grain size >500 nm) was drop-cast on a hydrophilic piranha-cleaned Si substrate in air at room temperature (Fig. 1A). The data from the MarCCD detector were continuously recorded every 12 s. At room temperature, hydrated GO layers are first formed in the water solution as shown in Fig. 1B, a diffuse circle emerged at qz = 0.008 Å⁻¹, which is associated with the surrounding water molecules in aqueous solution [12]. After the membrane is exposed to air for 3 mins, a weak peak emerges in the qz direction, which clearly indicates that the GO layers self-assemble in the solution [21]. After 5 mins of further exposure to air, an intense peak emerges at qz = 0.007 Å⁻¹, which indicates the well-stacking of GO on Si. After twenty more mins, the water in the aqueous solution was completely removed, and a weak peak appeared at a lower qz value (Fig. 1D). This peak becomes slightly intense over time (marked as the circle in Fig. 1E) and corresponds to the layers with a larger interlayer spacing.

To analyse the structural evolution of the dehydration process, the 1-dimensional data obtained from MarCCD images along the qz direction are illustrated in Fig. 2. As the water in the aqueous GO solution gradually evaporated, the intensity of the GO (001) peak obviously increases and the peak position shifts from approximately 7.79° to 8.58° at 25 °C. According to Bragg’s equation, the calculated d (001) value decreases from approximately 9.12 Å to 8.28 Å. The detailed evolution of the GO (001) interlayer spacing is illustrated in the inset of Fig. 2. The continuous decrease of d (001) over time is attributed to the squeezing out of water from the GO interlayers during the evaporation of the solution [25].

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