

## Synthesis of the Pore-free Graphene Oxide and Application for Flexible Barrier Thin Films

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### Abstract

Graphene oxide (GO) membranes have been attracting intensive attention as a promising flexible barrier film however, provides no barrier for proton transfer due to its exceptionally high proton conductivity based on nanoscale defect (pore) with various oxygen functional groups. In the present study, we report that a pore-free GO with controlled oxygen functional groups exhibits unexpected proton blocking behavior.<sup>[1]</sup>

### 1. Introduction

Graphene oxide (GO) is a two-dimensional material composed of carbon and oxygen with a thickness of approximately 1 nm. The presence of the oxygen functional groups on the surface makes GO dispersible in various solvents, easy to composite and exhibiting many properties, making it a material that can be used in a wide range of applications. On the other hand, GO reported so far has a complex structure with many types of functional groups and carbon-defects (pores), which has considerably hindered research. The formation of the pores in the GO surface is caused by breaking the C-C bonds in the graphene backbone during the oxidation process, which introduces COOH and C=O groups. In other words, the introduction of oxygen functional groups in the plane while maintaining the C-C bond will theoretically get in a pore-free GO. The oxygen functional groups that achieve these results are C-O-C (epoxy group) and C-OH (hydroxy group). It has been reported that the oxygen functional groups of Brodie's method graphite oxide with Fuming HNO<sub>3</sub> or KClO<sub>3</sub> exist almost as epoxy groups and such GO are considered pore-free. However, the graphite oxide prepared by the Brodie's method was known to be difficult to exfoliate into water. In this study, monolayer GO nanosheets were successfully obtained with high efficiency using weakly basic solvents with ammonia, and its detailed structure has been revealed.<sup>[2]</sup> Pore-free GO (Pf-GO) are expected to exhibit unique properties as graphene-like materials, different from conventional GO.

### 2. Experiment

Pf-GO was prepared using modified Brodie's method. 1 g of graphite powder and 40 mL of fuming HNO<sub>3</sub> were mixed in an ice bath, and 8 g of KClO<sub>3</sub> was slowly added. The resulting mixture was washed with water, dried in an oven at 50 °C. Ammonia aqueous solution adjusted to pH 12.5 was added the graphite oxide. After stirring at room temperature for 5 days, the mixture was sonicated by the ultrasonication for 30 minutes. Finally, the resulting GO dispersion was washed with pure water and Pf-GO water dispersion was obtained.

### 3. Results and discussion

Nanosized pores in the nanosheets were confirmed by HAADF-STEM. Fig. 1a show that a lot of pores were observed in conventional GO (circled white line). On the other hand, pores were not observed in a Pf-GO (Fig. 1b). Thus, the structure of the Pf-GO differs substantially in terms of pores when compared with conventional GO nanosheets. In particular, the 020 spot was clearly observed in electron diffraction patterns of Pf-GO (Fig. 1d), whereas it could not be observed in conventional GO (Fig. 1c). The calculated  $d$ -spacings from 010 and 110 spots were larger than those for graphene and GO. These might be explained by the introduction of oxygen functional groups without breaking the regularity of the graphene honeycomb structure. The proton permeation properties of the pore-free GO membrane were compared with those of a GO membrane by the proton permeation test using a U-shaped cell. In the case of the GO membrane, the pH of the permeate side rapidly decreased with time (Fig. 2). The high proton permeability of the GO membrane is attributed to its large pore concentration. By contrast, in the case of the pore-free GO membrane, the pH of the permeate side hardly changed over 8 h. These results indicate that the concentration of pores in the pore-free GO was substantially lower than that in the GO membrane.

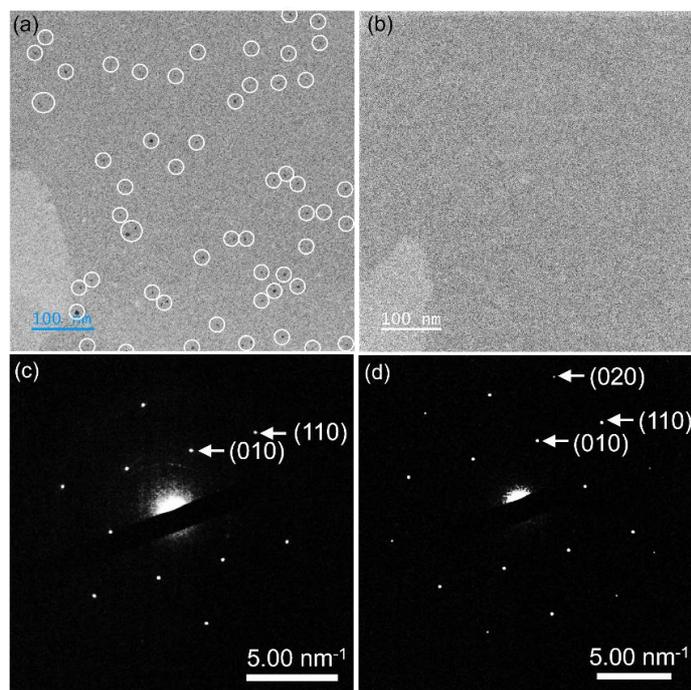


Fig.1 HAADF-STEM images of (a) conventional GO and (b) Pf-GO, and electron diffraction patterns of (c) conventional GO and (d) Pf-GO.

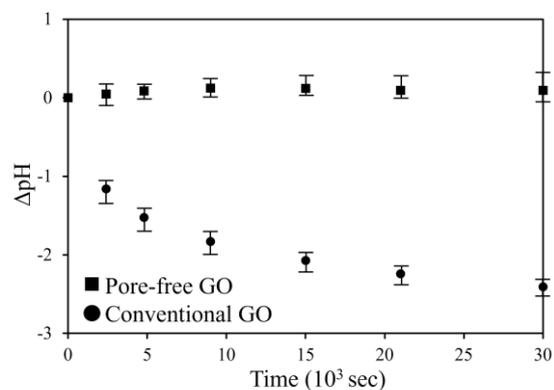


Fig. 2 Results of proton permeation tests using the conventional GO and the Pf-GO membranes.

### 4. Conclusion

The pore-free GO developed in the present study is expected to be used not only to enhance proton-impermeable barrier performance but also as a barrier thin-film material with high mechanical strength and compatibility with complex shapes. In addition, we expect it to be introduced into various applications such as research and development of flexible barrier films based on two-dimensional materials with finely controlled structures

### References

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