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Hierarchical Graphene-Based Material for Over 4.0 Wt % Physisorption Hydrogen Storage Capacity

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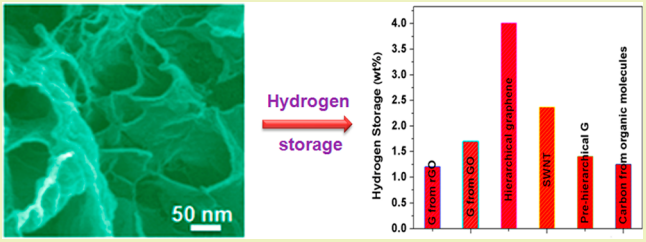
Supporting Information

ABSTRACT: A hierarchical graphene material composed of micropore (~0.8 nm), mesopore (~4 nm), and macropore (>50 nm) and with a specific surface area up to 1305 $m^2 g^{-1}$ is fabricated for physisorption hydrogen storage at atmospheric air pressure, showing a capacity over 4.0 wt %, which is significantly higher than reported graphene materials and all other kinds of carbon materials.



KEYWORDS: *Graphene, Hierarchical structure, Nanopores, Hydrogen storage, Physisorption*

Hydrogen is one of the most promising future sustainable energy fuels due to its abundance, high energy density, and environmental friendliness.[1−6] Nevertheless, its storage remains a great challenge for practical applications.[7−10] Carbon materials have recently attracted great attention in hydrogen storage in terms of their light weight, low cost, and unique chemical and physical properties related to the hydrogen storage.[8,11] Various carbons including activated carbons, mesoporous carbons, carbon black, and carbon nanotubes (CNTs) have been studied intensively.[12−16] Hydrogen storage by physisorption allows fast loading and unloading with low energy consumption and thus is a very promising approach in comparison to a chemisorption one.[17,18] However, the physisorption hydrogen storage of carbons at atmospheric air pressure is lower than 2.5 wt %, which is still far away from the target (6.5 wt %) set by the U.S. Department of Energy.[19]

Graphene-based materials are a relatively new member of the carbon family[20−22] and have very recently been explored for hydrogen storage.[17] As the physisorption interaction between graphene and hydrogen is dominated by weak van der Waals force, the amount of hydrogen stored in two-dimensional graphene nanosheets is relatively low (<2.0 wt %).[15] The theoretical studies of effects of nanostructures of graphene materials on hydrogen storage have predicted that nanopores less than 1 nm and a hierarchical structure are critical for the storage capacity improvement.[19,23] Inspired by the theoretical studies, herein we fabricated a hierarchical graphene-based material composed of micropore (~0.8 nm), mesopore (~4 nm), and macropore (>50 nm) with a Brunauer−Emmett−Teller (BET) surface area of up to 1305 $m^2 g^{-1}$. The hydrogen physisorption storage behavior on the hierarchical graphene-based material was investigated, showing a significantly enhanced capacity more than 4.0 wt % over the reported graphene materials and all other kinds of carbon materials as well.

The hierarchical graphene-based material was fabricated using a vacuum-based, low-temperature heating process followed by inert gas-protected thermal treatment. Graphite oxide was synthesized from graphite as reported.[20] Prehierarchical graphene-based material was prepared by placing the graphite oxide in a glass bottle to heat at 150 °C under vacuum for 45 min.[24,25] Hierarchical carbon-based material was then obtained by treating the prehierarchical graphene-based material in a quartz tube at 600 °C under Ar gas protection for at least 6 h, resulting in a highly loose and black powder.

The scanning electron microscopy (SEM) image in Figure 1a shows that the hierarchical graphene material is composed of micrometer-sized wavelike sheets. These wavelike sheets connect with each other to form a highly porous structure with pore sizes ranging from 50 to 200 nm. The detailed pore structure can be clearly seen from the high-magnification SEM image in Figure 1b, which has well-defined pores formed by waved and contacted ultrathin graphene-based sheets. The transmission electron microscopy (TEM) image in Figure 1c illustrates that the material has a transparent nature, further confirming that it is made up of ultrathin sheets. The thickness

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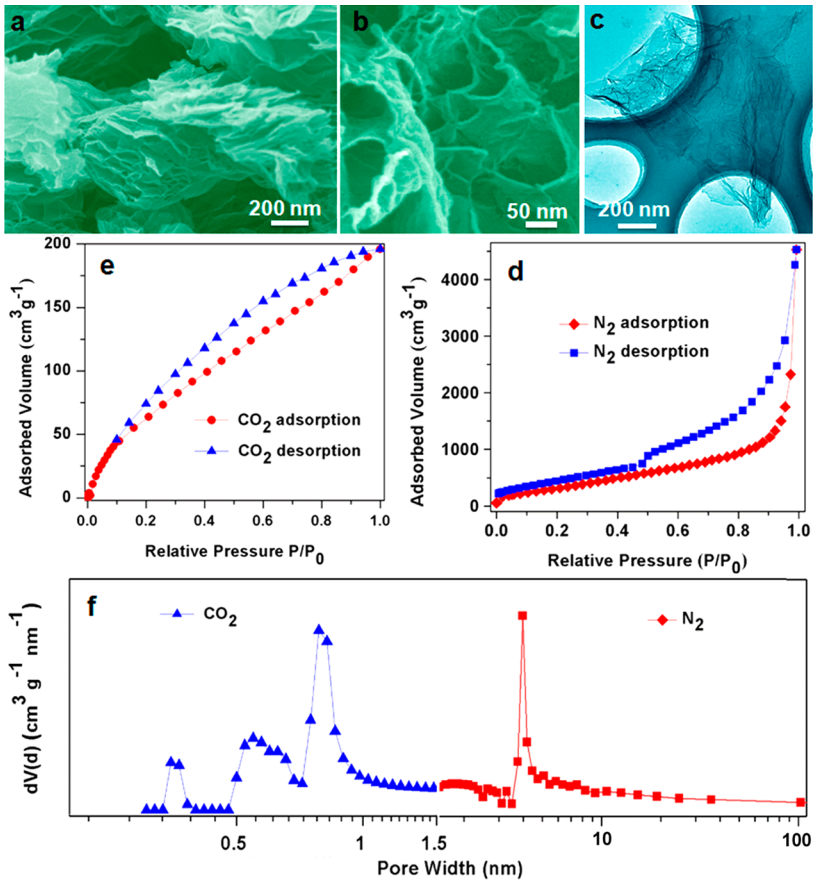

Figure 1. Characterizations of the hierarchical graphene-based material. (a, b) SEM and (c) TEM images. (d) N_2 adsorption/desorption at 77 K. (e) CO_2 adsorption/desorption at 273 K. (f) The corresponding pore size distributions.

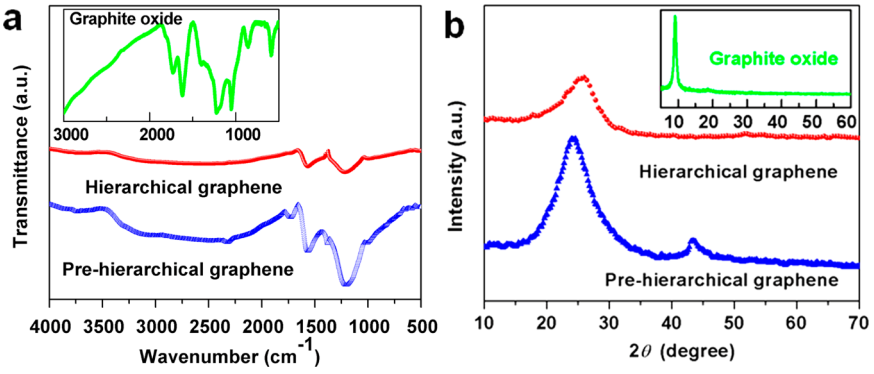

Figure 2. (a) Fourier transform infrared (FTIR) spectra and (b) X-ray diffraction (XRD) patterns of the hierarchical graphene-based material and prehierarchical graphene-based material.

of some individual graphene sheets obtained from sonication was examined by atomic force microscopy (AFM), exhibiting an average thickness of 0.9 nm (Figure S1, Supporting Information), which is the typical thickness of a graphene nanosheet.[20]

The specific surface area and mesopore structure (2−50 nm) of the material are investigated by N_2 adsorption/desorption (77 K) experiment with the isotherms shown in Figure 1d. On the basis of the multipoint Brunauer−Emmett−Teller (BET) method, the calculated specific surface area is 1305 $m^2\ g^{-1}$, which is much higher than that of graphite (38 $m^2\ g^{-1}$),[24] CNTs (<200 $m^2\ g^{-1}$),[25] and other kinds of graphene materials.[26] The pore size distribution of the material has a pronounced mesoporosity centered at 4 nm (Figure 1f). The BET method based on N_2 adsorption/desorption is not suitable to characterize a small microporous structure (<1 nm).[27] Thus, CO_2 adsorption/desorption experiment at 273 K was performed to investigate the ultramicropore (pores of width <1 nm) structure as shown in Figure 1e. The ultramicropore size was analyzed from CO_2 adsorption/desorption isotherms by applying a Monte Carlo method.[27] The obtained pore size distribution from both CO_2 and N_2 adsorption/desorption isotherms indicates that the carbon material has significant ultramicropore (0.6−0.8 nm) and mesopore (4 nm) distributions. Combining with macropore (>50 nm) sizes ranging from 50 to 200 nm observed from the SEM characterizations shown

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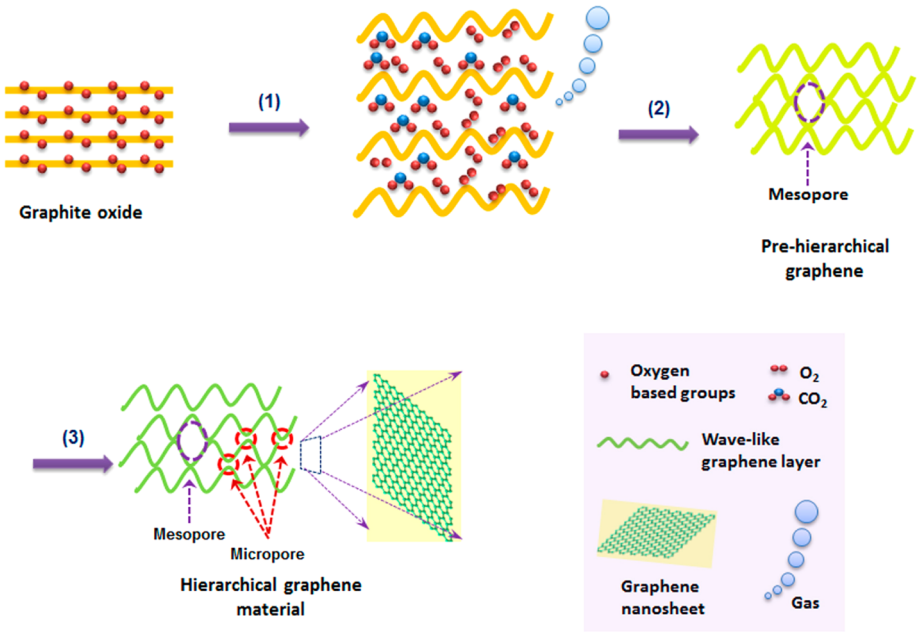

Figure 3. Scheme for the formation process of the hierarchical graphene-based material.

in Figure 1a and 1b, the material is indeed very distinctively hierarchically nanopore structured with a series of micro-, meso-, and macropores.

The formation mechanism for the hierarchical graphene-based material is analyzed based on the structure and surface property characterization results. The starting material of graphite oxide has abundant oxygen functional groups such as carboxyl and hydroxyl groups (inset of Figure 2a).[28−30] Heat treatment at a temperature of 150 °C under vacuum exfoliates graphite oxide, which is indirectly confirmed by the observation on an explosive-like phenomenon for dense graphite oxide to fluffy black powder. It is well-known that graphene sheets are flexible and have a very low density.[27] Under the exfoliated state, it is difficult for them to remain flat in a solid state, but rather maintain a bended form. We can reasonably argue that some oxygen functional groups under high temperature and vacuum could be converted to gas molecules such as O_2 and/or CO_2. The gas escape can create pores between graphene sheets to form a wavelike structure. The release of gas molecules also can be directly proved from the increased pressure inside the glass tube that is connected to a pressure meter. The removal of most oxygen functional groups is also supported by the FTIR results shown in Figure 2a. During the exfoliation and cooling processes, wavelike graphene sheets collapse due to the strong $\pi-\pi$ interaction, resulting in the formation of prehierarchical graphene-based material with nanopores. The prehierarchical graphene-based material has a specific surface area around 480 $m^2\ g^{-1}$ and a pore distribution of 4 nm (Figure S2, Supporting Information), while displaying almost negligible pores less than 1 nm (Figure S3, Supporting Information). Hierarchical carbon is obtained by further heat treatment of the prehierarchical carbon at a temperature of 600 °C under Ar gas protection. The further heat treatment reduces the surface functional groups (Figure 2a) and greatly increases the amount of micropores less than 1 nm in comparison to the prehierarchical graphene material for significantly increased specific surface area (1305 versus 480 $m^2\ g^{-1}$). The micropores are very likely to be formed from the space originally occupied by the surface functional groups (Figure 2a). In addition, powder X-ray diffraction results shown in Figure 2b show that the (002) peak of the hierarchical graphene-based material has a markedly reduced intensity and is broadened, indicating that the hierarchical carbon is composed of many single- and several-layer nanosheets, which is consistent with the AFM characterization for graphene sheets observation (Figure S1, Supporting Information), which has a significantly different structure from that of expandable graphite materials. The formation process of the hierarchical carbon is schematically summarized in Figure 3.

Figure 4a presents hydrogen adsorption and desorption isotherms of the hierarchical carbon at 77 K with pressure up to 106.66 kPa. To better understand the hydrogen storage behavior on the hierarchical carbon, isotherms of the prehierarchical carbon are also shown in Figure 4a. The purity of the used hydrogen gas in the experiments is above 99.999%. Both materials exhibit an almost linear hydrogen uptake with respect to the pressure. The reversibility is assessed by measuring the desorption branch down to a very low pressure. From the isotherms in Figure 4a, it can be seen that the desorption branch nearly coincides with the adsorption branch, indicating that chemisorption is not the main mechanism for the hydrogen storage because a large desorption hysteresis loop is usually the prominent feature of chemisorptions.[5] The hierarchical carbon shows a higher hydrogen storage capacity of up to 4.01 wt %, which is almost three times higher than that of the prehierarchical carbon (1.40 wt %). In addition, the capacity is much higher than that for graphene prepared from exfoliated graphene oxide (1.70 wt %),[14] graphene-like nanosheets from reduced graphene oxide (1.20 wt %),[15] single-walled carbon nanotubes (2.37 wt %),[13] and carbon derived from chlorine-containing small organic molecules (1.25 wt %)[16] at similar testing conditions (Figure 4c).

To evaluate the interactions between the hierarchical carbon and hydrogen, the isosteric heats of adsorption are calculated from the adsorption isotherms at different temperatures of 77 and 87 K and are analyzed by Van't Hoff equation,[31] with the results shown in Figure 4b. The isosteric heat of adsorption on the prehierarchical carbon is also presented for comparison. It can be seen that, at low hydrogen coverage, the adsorption

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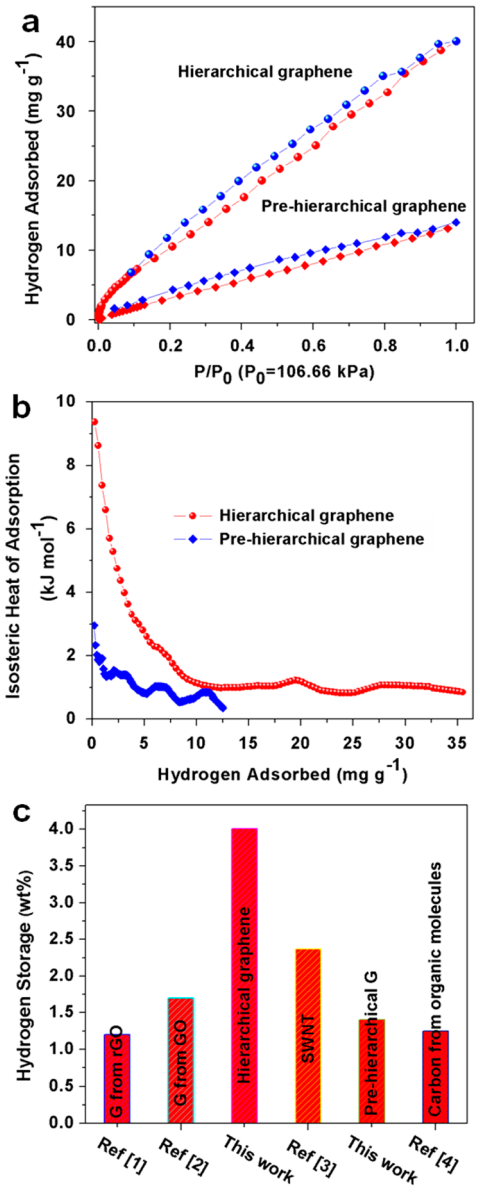

Figure 4. (a) Hydrogen adsorption and desorption isotherms of the hierarchical graphene and prehierarchical graphene. (b) Isosteric heat of hydrogen sorption. (c) Physisorption hydrogen storage capacity comparison between the hierarchical graphene and various carbon materials.

heats for both hierarchical and prehierarchical carbon are large. With the increased hydrogen coverage, the adsorption heat decreases quickly. This phenomenon corresponds to the adsorption in small pores with small volume fraction where the adsorption potential is high. The prehierarchical carbon has an adsorption heat of 2.9 kJ mol^{-1} at a hydrogen capacity of 0 mg g^{-1} and becomes relatively constant at ~1 kJ mol^{-1} or less when hydrogen capacity is ~4 mg g^{-1}. The hierarchical carbon has an adsorption heat of 9.5 kJ mol^{-1} at a hydrogen capacity of 0 mg g^{-1} and keeps relatively constant at ~1 kJ mol^{-1} after hydrogen capacity exceeds 10 mg g^{-1} until very high hydrogen coverage. The adsorption heats for both hierarchical and prehierarchical carbon are much lower than those reported for materials with chemisorptions.[32] It is also obvious that the hydrogen storage capacities for the two carbon materials do not result from the hydrogen spillover process because no active catalyst is added. Thus, we can conclude that the hydrogen storage mechanism is mainly physisorption.

The hydrogen storage capacity of the hierarchical carbon (4.01 wt %) is nearly three times that of the prehierarchical carbon (1.40 wt %), which corresponds to their BET surface ratio, in which the BET surface area of the hierarchical carbon (1305 versus 480 m^2 g^{-1}) is about 3 times that of the prehierarchical carbon. This correlation is in agreement with the reported conclusion that there is a linear relationship between the hydrogen storage capacity and the BET surface area for a physical adsorption mode.[12] This observation further confirms the physisorption in principle for the hierarchical carbon. Compared with prehierarchical carbon, the hierarchical material exhibits a much higher adsorption heat (9.5 versus 2.9 kJ mol^{-1}) at the initial hydrogen coverage, possibly indicating that the small micropores (<1 nm) greatly enhance its hydrogen storage capacity. Therefore, the high hydrogen storage capacity of the hierarchical carbon should mainly result from the ultrahigh specific surface area and hierarchically nanoporous structure, in particular the small micropores less than 1 nm. The hierarchical nanopore structure including mesopore (~4 nm) and macropore (>50 nm) also should be helpful in hydrogen storage and release by providing efficient paths. Nevertheless, energetic sites including defect sites and edge sites (i.e., armchair and zigzag edge sites) and some functional groups on the hierarchical carbon should not be ruled out, which may partially contribute to the higher hydrogen storage capacity as compared with other carbon materials as shown in Figure 4c. Further experiments are designed and carried out in our lab for understanding their roles in the hydrogen storage capacity enhancement.

In summary, we report a graphene-based material with hierarchical nanopore structure comprising micropore (~0.8 nm), mesopore (~4 nm), and macropore (>50 nm) and with a specific surface area of up to 1305 m^2 g^{-1}. The hierarchical graphene material demonstrates a physisorption hydrogen storage capacity of more than 4.0 wt %, which is significantly higher than that of reported graphene materials and all other kinds of carbon materials measured at the similar conditions. The hydrogen storage capacity for the hierarchical graphene material could further be improved by metal doping, surface functionalization, and edge-site tailoring for the practical applications, and these are currently underway in our lab.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

‡These authors contributed equally. The manuscript was written through contributions of all of the authors, and all of the authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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