Correlation in Structure and Properties of Highly-porous Graphene Monoliths Studied with a Thermal Treatment Method

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Abstract: We prepared high surface area nanoporous graphene by reduction and KOH activation of graphene oxides and then heat-treated the nanoporous graphene up to 3073 K in Ar. The surface area of thus-prepared samples decreased remarkably from 1560 m²g⁻¹ to 10 m²g⁻¹ according to the subtracting pore effect (SPE) method. The transmission electron microscopic (TEM), X-ray diffraction (XRD), Raman spectroscopy and N₂ adsorption isotherms at 77.4 K clearly illustrate the evolution of morphology, crystallinity and porosity during the graphitization

process with increasing the heating temperature. The high temperature treatment shows a clear segregation of the disordered sp^3 carbon frames in addition to the growth of graphitic structure in the porous graphene monoliths, although overall changes in properties and structure of porous graphene monoliths with high temperature treatment are similar to those of other porous carbons. The electrical conductivity measurements indicate that heat-treated samples have an imperfect semimetallic property due to the crystallite boundaries. The cyclic voltammograms measurements indicate that the optimized pore size range of nanoporous graphene for specific capacitance with 2 M KCl aqueous solution as electrolyte is of $0.7 \text{ nm} < w < 2 \text{ nm}$.

1. Introduction

Graphene has shown fruitful and promising applications to sustainable technology. As graphene has excellent physical properties such as high electrical and thermal conductivities [1-6], many researchers have attempted to develop outstanding electrodes, membranes, catalysts and adsorbents [7-13]. Ruoff et al showed that highly porous graphene produced by the KOH activation showed an unusually high capacitance [14]. The graphene developed for these purposes possesses high surface area and nanoscale pores. Wang et al. developed the highly microporous and mesoporous graphene monolith through the KOH activation, which also has a unique macroscopic structure [15]. The nanoporous graphene monolith is produced from graphite through reduction of graphene oxide colloids; the KOH activation of the reduced graphene colloids can lead to a superhigh surface area of more than $2000 \text{ m}^2 \text{ g}^{-1}$. These highly porous graphenes consist of nanoscale less-crystalline graphenes, which come from the oxidation of graphite and the successive KOH activation. Now we can build up the porous carbon frameworks from nanographenes, which sheds light on the bottom-up graphene technology for well-designed porous carbon. However, both of the oxidation of graphite and KOH activation of

nanographitic colloids lead to defects in the formed nanographene units, deteriorating excellent physical properties. We must control the defects in the nanographene units to recover the physical properties. Heat treatment at high temperature is commonly used for improving the crystallinity and reducing the defects of carbon materials [16-18], although the mechanism of the structure change on the heat treatment is not well understood. Generally speaking, the heat treatment of porous carbons leads to a significant decrease of porosity due to the stacking of graphitic nanoscale units [19, 20]; the high temperature treatment brings about high crystallinity with less defects, accompanying with a serious destruction of pore structure. Even so, when we treat the high surface area graphene monoliths at high temperature to decrease the defects in the nanographenes and study the changes of structure and properties with the heat treatment carefully, we can answer an indispensable question whether the structural change of the graphene monoliths on the heat treatment is unique or not. In this work, we treated the highly porous graphene monoliths up to 3073 K under an Ar atmosphere to obtain porous graphene monoliths having both of high surface area and high electrical conductivity together with the fundamental understanding on the structural change on the high temperature treatment.

2. Experimental

2.1 Downsized route of graphite to highly porous graphene

Firstly the graphene oxide was prepared from graphite (Bay carbon graphite from Michigan City, U.S.) by an improved method using KMnO_4 , H_2SO_4 and H_3PO_4 [21]. The graphene oxide suspension was then mixed with KOH at a weight ratio of $\text{KOH/C} = 8$. The graphene oxide monoliths mixed with KOH were produced using unidirectional freeze drying method [22-24]. Then the monolith of graphene oxide and KOH mixture was heated from room temperature to 573 K at a heating rate of 1.5 K min^{-1} to reduce the graphene oxide. The reduced graphene

monolith with KOH was heated from 573 K to 1073 K at a heating rate of 30 K min⁻¹ and kept at 1073 K for 1 h for activation. Subsequently thus-activated graphene monolith was cooled down to room temperature under an Ar flow and then washed sufficiently by distilled water. This sample downsized from graphite is named the highly porous graphene monolith (PGM).

2.2 Upsized route of highly porous graphene to graphite

PGM was thermally treated with a graphite-resistance furnace under an Ar flow of 1 L min⁻¹ to reconstruct the mother graphite structure. The heating rates were: 20 K min⁻¹ from room temperature to 2273 K, and 5 K min⁻¹ above 2273 K. The PGM samples were maintained at a given temperature for 30 min and then were cooled down to room temperature under the Ar flow. The porous graphene monolith treated at T K is named as PGM-T.

2.3 Structural characterization

As the essential difference between PGM and graphite is on the solid density, understanding of the graphitization process of PGM needs detailed porosity data. Porosity analysis was performed with a Micromeritics ASAP 2020 surface analyzer by N₂ adsorption at 77.4 K. The samples were pre-evacuated at 473 K for 3 h prior to adsorption. The surface area was determined by the subtracting pore effect (SPE) method [25, 26] using high resolution α_s -plots of the adsorption isotherms with carbon black (Mitsubishi Chem. Co. 32B) as reference sample. The N₂ adsorption isotherms were also analyzed with Brunauer-Emmett-Teller (BET) method in a relative pressure range of 0.05-0.30 for comparison. The micropore, mesopore volumes and pore size distribution were determined by use of the quenched solid density functional theory (QSDFT) using a slit pore model [27]. The micropore volumes were also determined by using Dubinin-Radushkevich (DR) equation [28] for comparison. The total pore volume was determined from the adsorption amount of N₂ at P/P₀ = 0.98 according to the Gurvitch rule.

The crystalline graphite structure change on reconstruction was examined by Raman spectroscopy and X-ray diffraction. The Raman spectra were obtained with a Raman spectrometer (Renishaw, inVia reflex 785S, UK) at room temperature using the 532 nm wavelength. X-ray diffraction (XRD) patterns of the samples were measured at room temperature using an X-ray diffractometer (Bruker AXS, D8, Germany) performed with CuK α radiation (0.1541 nm). Some samples were observed by a field emission scanning electron microscope (FE-SEM: JEOL, JSM-6330F, Japan) and a high-resolution transmission electron microscope (HR-TEM: JEOL, JEM-2100F, Japan).

2.4 Electrical conductivity and electrochemical performance

As the electrical conductivity sensitively depends on the crystallinity of the graphitic structure, the temperature dependence of the electrical conductivity over the wide temperature range was measured. The electrical conductivity measurements of PGM and PGM-T samples were performed by using a physical property measurement system (model 600: Quantum Design) with four probe method over the temperature range of 2 to 370 K. The electrochemical capacitive behavior of highly porous graphene monoliths were evaluated by cyclic voltammetry using a HZ-3000 system (Hokuto Denko Corp.) with an Ag/AgCl (sat. KCl) as the reference electrode and a Pt-mesh as the counter electrode. The cyclic voltammetry were carried out at room temperature in 0.5 M H₂SO₄ and 2 M KCl aqueous solution at a scan rate of 5 mV s⁻¹. A commercial activated carbon (Kuraray YP-50) was also tested for comparison.

3. Results and discussion

3.1 Nanomorphology changes of highly porous graphenes on reconstruction to graphite

Figure 1 shows the SEM images of PGM and PGM samples treated at 1873, 2273 and 2673 K. PGM consists of corrugated and conglomerated graphene sheets, as shown in Figure 1(a). No

significant change is observed on PGM-1873, as shown in Figure 1(b). The graphene sheets of PGM-2273 and PGM-2673 become more crumple comparing with those of PGM without the heat-treatment, as shown in Figure 1(c) and (d). Besides, the surface of the assembled graphene sheets become more uniform and smooth through the high temperature heat-treatment.

Fig. 1 - SEM images of (a) PGM, (b) PGM-1873, (c) PGM-2273, and (d) PGM-2673.

The high-resolution TEM images clearly indicate the growth of uniformly stacked graphene sheets through the heat treatment, as shown in Figure 2. Figure 2(a) shows that the PGM mainly consists of entangled and crumpled carbon sheets of monolayer to few layers of graphene, being markedly different from activated carbons (or activated carbon fibers), which have no well-defined graphene sheet structure [29-31]. Figure 2(b) shows the high resolution TEM image of PGM-1873. The stacking of distorted graphene layers in small bricks with wrinkled surface can be observed, which comes from the collapse of the nano-frameworks supported by graphene sheets. The degradation of these nano-frameworks should lead to a marked decrease of surface area and microposity, as described later. PGM-1873 is in a transitional state between highly

entangled graphene networks and partially graphitic ordered structures. Elevation of the heating temperature to 2273 K gives rise to a local graphite structure, as shown in Figure 2(c). We can see the stacking layers consisting of well-aligned graphene sheets with a large-scale of uniformity instead of small scattered pieces, being indicative of the reconstruction to the graphite structure. The well-crystalline graphitic layer structure with much less defects develops in a longer range and the disordered graphitic parts coexist each other in PGM-2673, as shown in Figure 2(d). Consequently, the growth of better graphitic layers should consume preferentially only crystalline parts, leaving the disordered structures. Supplementary TEM images of PGM-T are available in Figure S1.

Fig. 2 - HR-TEM images of (a) PGM, (b) PGM-1873, (c) PGM-2273, and (d) PGM-2673.

3.2 Evolution of reconstructed graphite crystallites in highly porous graphenes

Raman spectral examination shows an explicit feature of the growth of the local graphitic units in the distorted graphene-based structure. Figure 3 shows the comparison of Raman spectra of PGM-T samples. Two overlapping broad bands locating at ~ 1350 and ~ 1590 cm^{-1} can be

Fig. 3 - Raman spectra of PGM and PGM-T samples.

observed, being associated with the disordering of the sample (D band) and stretching vibration in the aromatic planes (G band), respectively. No significant variation of Raman spectra on both bands is detected at the treating temperature below 1873 K, while the treating above 1873 K leads to the decrease of D band and increase and sharpening of the G band. The intensity ratio of D band and G band, I_D/I_G , decreases continuously from 1.52 to 0.11, as shown in Table 1, suggesting a continuous growth of the localized graphitic structure on heat treatment. The second-order bands, which correspond to the overtones and combination of the D and G band, can also be detected in the spectra, as shown in Figure 3. A peak at 2450 cm^{-1} can be observed on the spectra of samples heated at temperatures above 2073 K, being assigned to the overtone mode longitudinal optical (LO) phonons (2LO) [32]. The 2D band (also called G' band) locating at 2700 cm^{-1} , which can provide a very sensitive probe for characterizing specific sp^2 carbons [33], becomes more distinct with increasing the temperature above 1873 K. A less distinct peak at around 2930 cm^{-1} , which is attributed to (D + G) combination mode [34], becomes weaker and

finally disappears with increasing the treating temperature. All these results indicate that thermal treatment lead to the local reconstruction of graphite. The in-plane size of graphitic crystallites, L_a , can be evaluated from I_D/I_G by using the Tuinstra-Koenig equation [35, 36]:

$$I_D / I_G = C(\lambda) / L_a$$

Where $C(514.5 \text{ nm})$ is $\sim 4.4 \text{ nm}$ according to reference [37] and the L_a value are derived, as shown in Table 1. The in-plane size of graphitic crystallites doesn't change with the elevation of heating temperature up to 1873 K and then increases with the heating temperature above 1873 K.

Table 1. Parameters obtained from X-ray diffraction patterns and Raman spectra.

Sample	XRD				Raman			
	d_{002}	d_{002}^*	L_c	L_c^*	N_c	N_c^*	I_D / I_G	$L_a \text{ (nm)}$
	(nm)	(nm)	(nm)	(nm)				
PGM	0.368	--	0.650	--	1.77	--	1.82	2.4
PGM-1073	0.369	--	0.667	--	1.81	--	1.79	2.5
PGM-1373	0.366	--	0.669	--	1.83	--	1.87	2.4
PGM-1473	0.371	--	0.674	--	1.82	--	1.79	2.5
PGM-1673	0.365	--	0.664	--	1.82	--	1.75	2.5
PGM-1873	0.369	--	0.642	--	1.74	--	1.52	2.7
PGM-2073	0.368	0.338	0.645	3.8	1.75	11.2	0.83	5.3
PGM-2273	0.368	0.338	0.659	5.9	1.79	17.5	0.38	11.6
PGM-2473	0.368	0.337	0.669	12.7	1.82	37.5	0.19	23.2
PGM-2673	0.368	0.337	0.659	17.5	1.79	51.9	0.14	31.4
PGM-3073	0.369	0.337	0.652	22.1	1.77	65.6	0.11	40.0

d_{002} , L_c and N_c are the interlayer spacing, the mean crystallite size along the c axis and the average atomic layer number of turbostratic graphene layers in PGM-T. Symbols with an asterisk indicate the corresponding parameters of well-crystallized graphite in PGM-T.

L_a is the in-plane size of graphitic crystallite.

I_D/I_G is the intensity ratio of D band and G band.

Fig. 4 - X-ray diffraction patterns of PGM and PGM-T samples.

Figure 4 shows X-ray diffraction patterns of PGM and PGM-T samples. The PGM has only a broad peak at 22.6° without any other peaks of graphite, being indicative of the non-crystalline structure of PGM. Little change of the X-ray diffraction patterns is observed with elevation of the heating temperature up to 1873 K, suggesting the high energy barrier for the mutual ordering of non-crystalline structures. A distinct (002) peak appears at 26.4° and becomes sharper with elevation of the heating temperature above 2073 K, indicating the growth of well-ordered graphitic structure. However, a broad peak at 22.6° still remains on PGM-3073; the highly graphitic structure and noncrystalline structure coexist. This X-ray diffraction result agrees well with the TEM image of Figure 2(d), which shows the coexistence of the graphite structure and irregular one. The irregular structure which is difficult to be graphitized under high treating temperature is ascribed to the strong cross-linking which immobilized the graphitic units in a rigid mass [38]. When the treating temperature is higher than 2473 K, the peak (100) and (101) locating at around 44° , peak (004) locating at around 55° , peak (110) locating at around 78° and

peak (112) locating at around 83.5° start to appear, showing a slight recovery of the graphitic structure [39]. This is because the X-ray diffraction patterns in the angle higher than 35° , being magnified by 7 times of those in the lower angle region, are very weak.

The interlayer spacing d_{002} and d_{002}^* for the broad and sharp peaks can be obtained according to Bragg's equation, as collected in Table 1. The d_{002} values are in the range of 0.366 to 0.371 nm, showing that these broad peaks come from the turbostratic structure. It is noteworthy that d_{002}^* values are almost constant at around 0.337 nm irrespective of the heating temperature, being very close to the d -spacing of a well-crystalline graphite (0.3354 nm). The mean crystallite size along the c axis, L_c and L_c^* , can be determined by using the Scherrer's equation with the half width of the (002) peak of the broad and sharp peaks [40]. The average number of atomic layers N_c and N_c^* can be determined from d_{002} and L_c (or d_{002}^* and L_c^*) by means of the simple equation $N_c = L_c / d_{002}$ [41], and the calculated results are collected in Table 1. It can be seen that the mean crystallite size along the c axis L_c^* and the average atomic layer number N_c^* of the well-crystallized part in PGM-T increase with the elevation of heating temperature above 1873 K, while disordered structures are difficult to be graphitized, showing no change. Briefly speaking, the growth of graphitic structure in the porous graphene monolith follows the general tendency of various kinds of carbon materials; we need to study the change in the coexistent structure of graphitic and disordered carbon frames with the heat treatment to extract the characteristic of the porous nanographenes [42].

The van't Hoff equation can provide a direct estimation of enthalpy change ΔH during the crystallization in a thermodynamic equilibrium, which is expressed as

$$(\partial \ln K / \partial T)_P = \Delta H / RT^2$$

Where R is the gas constant, T is the corresponding absolute temperature, and K represents the equilibrium constant, which is the ratio of crystalline carbon and non-crystalline carbon of PGM-T. Here the ratio can be determined from the deconvolution of XRD patterns, as shown in Figure S2 and Table S1.

Fig. 5 - The van't Hoff plot of PGM-T samples.

As the PGM-T samples obtained from one time of thermal treatment have similar XRD patterns to those from two times of thermal treatment at temperature of T , as shown in Figure S3, the thermodynamic reaction for preparing PGM-T can be considered to have already reached the equilibrium. Then a linear plot of $\ln K$ and $-1000/RT$ can be obtained, as shown in Figure 5. The nanographenes have many sp^3 carbon atoms at the edges and thereby the observed growth of graphitic structure should stem from a collective rearrangement of nanographenes accompanying with chemical bonding changes. The determined enthalpy change is 135 kJ mol^{-1} , which should be associated with the change in the chemical bonding of carbon atoms from the single bonding into the conjugated bonding. The enthalpy difference of 1 mol carbon atoms of graphene structure and diamond structure is evaluated to be 45 kJ mol^{-1} according to Figure S4, being about one third of the observed enthalpy change of 135 kJ mol^{-1} . Hence, a collective rearrangement and chemical bonding change in which three sp^3 carbon atoms in the

nanographenes are involved is indispensable to the graphitic structure growth. If the requirement of this collective change is not satisfied, the graphitic structure cannot grow from amorphous state, agreeing with the observed X-ray diffraction results on high temperature treating.

3.3 Nanoporosity degradation on reconstruction of graphitic structure

Figure 6 shows N₂ adsorption isotherms at 77.4 K of PGM and PGM-T samples. The isotherm of PGM is of combination of type I and type IV according to the IUPAC classification [43, 44], with significant N₂ uptake at low P/P₀ and a distinct hysteresis loop at P/P₀ above 0.4, indicating the presence of both microporosity and mesoporosity. No significant difference is observed on N₂ adsorption isotherms for PGM and PGM thermally treated at 1073 K ~ 1373 K. The surface areas determined by SPE method are 1560, 1580, and 1590 m² g⁻¹, respectively, as listed in Table S2. The N₂ uptake in the low P/P₀ region decreases dramatically, when the heating temperature is elevated above 1473 K, being indicative of the degradation of micropores. At P/P₀ above 0.4, the hysteresis loop doesn't change obviously through treating up to 1373 K, and the desorption branch is explicitly deviated from the adsorption branch, giving the hysteresis loop of type H4, which is often associated with narrow slit-like pores [43]. The PGM-1473 shows a slower upward structure on desorption branch, suggesting its characteristic of H4 become weaker and that of type H2 becomes more distinct. The hysteresis loops become typical type H2 on treating above 1473 K, as shown for PGM-1673, PGM-1873 and PGM-2073. The H2 loop may be attributed to 'ink bottle' pores, although the network effects must be taken into account [43]. The hysteresis loop becomes less evident for PGM-2273 and it almost disappears for PGM-2473. Figure 6(b) shows the detailed N₂ adsorption isotherms in the submonolayer region. We cannot observe an explicit step in the relative pressure region of 10⁻³ to 10⁻², which gives the information on the presence of well-grown graphite surfaces [45-47]. The comparative pore

structure study of PGM and PGM-T samples with adsorption of N₂ (77.4 K) and of Ar (87.3 K and 77.4 K) was reported elsewhere [48].

Fig 6 - (a) N₂ adsorption isotherms at 77.4 K and (b) their corresponding logarithmic curves at $P/P_0 < 0.1$ for PGM and PGM-T samples. N₂ adsorption isotherms of PGM-2673 and PGM-3073 are not shown.

Fig. 7 - (a) Surface area and graphene layer number and (b) Pore volume evolution of PGM during heat treatment at different temperatures. Surface area: ●, graphene layer number: ■, total pore volume: ◆, mesopore volume: ▲, micropore volume: ▼.

The porosity parameters of the PGM thermally treated at different temperatures are shown in Table S2. Figure 7 shows the change of the surface area and pore volume of samples with heating temperature. The surface area doesn't change with heating temperature up to 1373 K, suggesting the porous graphene frameworks are considerably stable. The surface area remarkably decreases with elevation of the temperature above 1373 K; the heating at 2473 K gives $20 \text{ m}^2 \text{ g}^{-1}$ of surface area. The decrease of pore volume with the heating temperature is similar to that of the surface area. All of the total pore volume, mesopore volume and micropore volume decrease in a similar way with the heating temperature. Consequently the stacking of graphene layers should occur very uniformly.

Approximately we can evaluate the number of the stacked graphene layers from the surface area, as shown in Figure 7(a) and Figure S5. The increase of the number of the stacked graphene layers with the heating temperature well corresponds to the crystallite size change from X-ray diffraction and Raman spectroscopy. Elevation of the heating temperature leads to the stacking of the graphene layers, losing the pores.

Fig. 8 - Comparison between the crystallite size parameters and pore volume at different heating temperatures. Mesopore volume: ■, micropore volume: ●, in-plane size of graphite crystallites L_a : ▲, mean crystallite size along the c axis L_c^* : ★.

The changes of micropore volume, mesopore volume, the mean crystallite size along the c axis (L_c) and in-plane size of graphite crystallites (L_a) with heating temperature are compared in Figure 8. Four distinct regions can be observed: (A): $T < 1373$ K, (B): $1373 \text{ K} < T < 1873$ K, (C): $1873 \text{ K} < T < 2473$ K, and (D): $T > 2473$ K. No change occurs in region (A). In region (B), the porosity starts to decrease, whereas the graphitic crystallites still do not change. Then the stacking of the graphene layers has a lower activation process than the crystallite growth. This is plausible, because the in-plane graphene crystallite growth needs reconstruction of the edge chemical bonding for coalescence of the in-plane graphene crystallites [49, 50], whereas the partial stacking of the graphene crystallites can be possible by slight translational motion and partial arrangement of the graphene crystallites. The thermal energy at region (C) enables recombining the mutual edges of the graphene crystallites to give the in-plane graphene growth. At the same time, the well-developed graphene sheets combine and stack each other in this temperature range. In the highest temperature region (D), further stacking and coalescence of graphene crystallites are brought about. However, even the graphene samples heated at 2673 K and 3073 K have the mixed structure of the well-crystalline graphite and the disordered graphitic parts as shown in X-ray diffraction data. Consequently, even nanographene units produced by graphite crystals cannot be reversibly restored to the original structure by heating treatment above 2473 K. As the D-band is negligibly small compared to the G-band for these samples, graphene units must be well-crystalline and these should be mismatching in the graphene-graphene stacking; a partial intrusion of the graphene should provide the larger d_{002} spacing, as shown in Table 1.

Fig. 9 – Structural evolution model of PGM thermal treated at different temperature regions. (a) $T < 1373$ K, (b) 1373 K $< T < 1873$ K, (c) 1873 K $< T < 2473$ K, and (d) $T > 2473$ K.

A simplified structure model for growth of graphitic structures through high temperature treatment of the porous graphene monolith is shown in Figure 9. Here this model only describes the graphitizable part in the porous graphene monolith, although the non-graphitizable parts tend to be segregated from the graphitic structure with high temperature treatment. The non-treated PGM consists of randomly bridged nanographene sheets, as shown in Figure 9(a). The interspaces constructed by such nanographene sheets provide micropores and mesopores in PGM. Heat treatment below 1373 K doesn't change this structure, while heat treatment above 1373 K induces the stacking of the nanographene layers, consuming both micropores and mesopores, as shown in Figure 9(b). However, the nanographenes do not coalesce with each other at this temperature region due to the insufficient thermal energy. The coalescence of nanographenes begins above 1873 K, inducing growth of graphitic crystallites and further consumption of micropores and mesopores, as shown in Figure 9(c). The well-crystalline graphite structure is

formed by heating above 2473 K, as shown in Figure 9(d); the above-mentioned X-ray diffraction and TEM results indicate the coexistence with non-graphitic carbon structure, although it is not illustrated in the figure, as mentioned above. Briefly speaking, this structural change of highly porous graphene monoliths with heat treatment is close to that of other carbons. We must elucidate the change in the boundary structure of graphitic and disordered units to find out a better crystallinity control of nanographenes without collapse of pore structure. However, the porous graphene monolith does not shrink irrespective of the stacking and coalescence of nanographenes even by heating at 3073 K, being quite unique. This should be ascribed to the rigid linkage between nanographenes which is supported by the non-graphitizing units.

3.4 Changes of electrical conductivity and electrochemical property on graphitization treatment

Fig. 10 - The temperature dependence of electrical conductivity of graphene samples. PGM: ■, PGM-1673: ●, PGM-2073: ▲.

We showed the structural restoring process of the highly porous graphene monoliths to graphite with the high temperature treatment. The structural restoring proceeds should be deeply associated with electrical and electrochemical properties having information on the electronic structure. Figure 10(a) shows the temperature dependence of the electrical conductivity of the

porous graphene monolith PGM and the heat-treated samples (PGM-1673 and PGM-2073). The $\log_{10}\sigma$ vs $1000/T$ plot of PGM is not linear over the wide temperature range. On the other hand, the plots of PGM-1673 and PGM-2073 are almost horizontal except for the high temperature range and their electrical conductivities are much higher than that of PGM; PGM-2073 has the highest electrical conductivity. The temperature dependence of the electrical conductivity of PGM-1673 and PGM-2073 is similar to that of polycrystalline graphite, then those PGM treated at high temperature have a semimetallic nature [51, 52]. Nevertheless, their semimetallic property is not perfect and their electrical conductivity is governed by the crystallite boundaries, which induce an increase in the electrical conductivity at the higher temperature range. Also the magnified $\log_{10}\sigma$ vs $1000/T$ plots at the high temperature range in Figure 10(b) have breaking points, indicating the mixing state of the different crystallite boundaries.

Fig. 11 - The 3D variable range hopping plots of PGM.

The temperature dependence of the electrical conductivity of PGM can be well described by the 3D variable range hopping mechanism, as shown in Figure 11, although the linear plot upward deviates slightly at 110 K. Electrons can hop from one nanographene to another in the highly porous graphene monolith. The heat-treatment of the PGM sample at the high temperature

leads to the nonuniform graphitization, which is shown by the Raman spectroscopic and X-ray diffraction studies, agreeing with the electrical conductivity results.

The graphene materials having high porosity and crystallinity are promising for better science and various applications. Unfortunately the high temperature treatment brings about the opposite effect on crystallinity and porosity; crystallinity is improved, whereas porosity is lost. At this moment still we cannot solve this contradiction. Even so, this work reveals that we can trade a certain degree of porosity to obtain a high electrical performance. For example, PGM-1673 shows 18% lower surface area compare to pristine PGM, but its electrical conductivity at 273 K, 77.4 K (liquid N₂) and 4.2 K (liquid He) are 36%, 52% and 200% higher, respectively (Figure S6 and Table S2). PGM-2073 shows 64% lower surface area compare to pristine PGM, but its electrical conductivity are 56%, 102% and 400% higher. The increase of electrical conductivity without losing too much porosity should give a new application in addition to a new scientific perspective.

Determining the optimum pore size of the electrode material is of significant importance on designing the supercapacitors. The PGM-T samples have a wide range of pore structure derived from the reconstruction of graphitic structure at different temperatures, appearing to be an excellent model on the evaluation of pore size effect on the electrochemical performance. In this work, the cyclic voltammograms of PGM, PGM-1673, PGM-2073 and activated carbon (AC) in 0.5 M H₂SO₄ at a scan rate of 5 mV s⁻¹ are studied, as shown in Figure 12(a). AC used in this work has a similar surface area ($S_{\text{SPE}} = 1760 \text{ m}^2 \text{ g}^{-1}$) and micropore volume ($V_{\text{micro}} = 0.63 \text{ cm}^3 \text{ g}^{-1}$) to those of PGM. A redox peak was observed at around 0.6 V on the cyclic voltammograms of all samples in H₂SO₄ solution, which comes from the redox reaction of oxygen-containing functional groups of sample [53]. The redox peak of AC is stronger than that of graphene derived

materials, indicating the higher content of oxygen-containing functional groups of AC than others. The obtained specific capacitance of PGM is 164 F g^{-1} , being close to that of AC, which is 167 F g^{-1} . A decrease in specific capacitance is observed on thermally heated samples of PGM-1673 and PGM-2073, of which the specific capacitances are 125 and 48 F g^{-1} , respectively. The cyclic voltammetry measurement was also carried out in a neutral solution of 2 M KCl , as shown in Figure 12(b). The obtained cyclic voltammograms in KCl solution are rectangular for all samples, and no redox peaks is observed, suggesting a pure capacitive behavior for all samples in the neutral solution. The specific capacitance of PGM is 122 F g^{-1} , being 50% higher than that of AC in the KCl solution (81 F g^{-1}); AC shows a significant pseudocapacitance of AC in H_2SO_4 solution due to its oxygen-containing functional groups [54]. Thus, graphene-based materials can provide the capacitance behavior stemming from the graphene walls. The specific capacitances of PGM-1673 and PGM-2073 obtained in KCl solution are 75 and 27 F g^{-1} , respectively.

Fig. 12 - Cyclic voltammetry curves of PGM, heat treated PGM and AC in electrolyte solutions of (a) $0.5 \text{ M H}_2\text{SO}_4$ and (b) 2 M KCl at 5 mV s^{-1} . PGM: $-\cdot-$, PGM-1673: $\cdots$, PGM-2073: $--$, AC: $—$.

Fig. 13 - Pore size distribution of AC and PGM-T samples determined from QSDFT method. PGM: —, PGM-1673: --, PGM-2073:

Shi [55] reported a model for evaluating the different contributions of the specific capacitances from micropores and mesopores using the following equation.

$$C = S_{\text{meso}}C_{\text{meso}} + S_{\text{micro}}C_{\text{micro}},$$

where S_{meso} and S_{micro} are the mesopore and micropore surface areas, respectively. We extended this analysis to get detailed information on capacitances contributed from ultramicropores ($w < 0.7$ nm), supermicropores ($0.7 \text{ nm} < w < 2$ nm) and small mesopores ($2 \text{ nm} < w < 4.5$ nm). The surface areas in each pore size region were determined with QSDFT method by using a slit pore model. The porosity parameters are shown in Figure 13 and Table S3. In order to minimize the effect of pseudocapacitance, only the specific capacitances of PGM and PGM-T samples measured with the neutral solution of 2 M KCl are employed. The relationship between the specific capacitance and surface area of different pore sizes are proposed as following.

$$\sum K_i S_i = C$$

Here S_i is the surface area at a specific pore size region, K_i is the coefficient between the surface area S_i and capacitance contributed from corresponding pore size region, and C is the

total capacitance. By employing the porosity value given in Figure 13 and Table S3, the extended relationship of the above equation can be obtained as follows.

$$0.003S_1 + 0.162 S_2 + 0.016 S_3 = C$$

Here S_1 , S_2 , and S_3 are the surface areas of ultramicropores, supermicropores, and small mesopores, respectively. It is obviously that the supermicropores contribute the most efficiently to the capacitance with 2 M KCl aqueous solution as electrolyte. This result qualitatively agrees with the reported work [56]. However, we need to do systematic study using porous graphene monoliths having more controlled pore structures in order to give conclusive information on the optimum pores for higher capacitance in future.

3.5 Crystallinity control of nanographene units in highly porous graphene monolith

Although highly porous graphene monoliths are produced from nanographene units, reduction of graphene oxide colloids and KOH activation produce the sp^3 carbon linkages between the nanographene units. The simple heating treatment of the highly porous graphene monoliths at high temperature cannot induce uniform and smooth migration of component atoms with preservation of the nanoscale graphene-based pore structure. However, the present Raman spectroscopic study shows that nanoscale graphene layers grow continuously with the heating temperature, while the X-ray diffraction study shows the growth of graphitic structure accompanying with mismatching in the ordered stacking of nanographene sheets and segregation of the disordered sp^3 carbon frames by the heat treatment. Accordingly suppression of segregation of sp^3 carbon frames should be promising to produce highly porous and crystalline graphene monolith, expanding the application of high surface area graphenes.

4. Conclusions

In this work, highly porous graphene monolith (PGM) produced from reduction and KOH activation of graphene oxides was heat-treated in Ar up to 3073 K. The structure of PGM doesn't show significant change up to 1373 K of heating temperature. Heat treatment from 1373 K to 1873 K gives remarkable decrease of both microporosity and mesoporosity due to the stacking of graphene layers and segregation of sp^3 carbons, while the crystallization cannot be observed by Raman and XRD studies; this indicates that the stacking of the nanographene layers has a lower activation energy than the crystallite growth. Heat treatment from 1873 K to 2473 K leads to the further decrease of porosity and growth of the graphitic structure, which is caused by the coalescence of the nanographenes. Graphitic crystallites with 3-dimensional ordering can be obtained at heating temperature above 2673 K. The electrical conductivity measurements indicate that PGM treated at high temperature have a semimetallic nature; their semimetallic property is not perfect due to presence of many crystallite boundaries. The cyclic voltammogram data of PGM-T samples indicate that the supermicropores whose pore size is in the range of 0.7 nm to 2 nm efficiently contribute to the specific capacitance with 2 M KCl aqueous solution as an electrolyte. These results are not so different from changes of properties and structure of other porous carbons with high temperature treatment. However, segregation of disordered sp^3 carbon frames is explicitly shown in the porous graphene monoliths, being a hint for future route to prepare highly porous graphene monoliths of high crystallinity. We need to embed thermally stable sp^3 linkage centers at the edges of well-crystalline nanographenes in advance to get the target carbon in future.

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Reference

- [1] Berger C, Song Z, Li X, Wu X, Brown N, Naud C, et al. Electronic confinement and coherence in patterned epitaxial graphene. *Science* 2006, 312: 1191–1196.
- [2] Heersche HB, Jarillo-Herrero P, Oostinga JB, Vandersypen LMK, Morpurgo AF. Bipolar supercurrent in graphene. *Nature* 2006, 446: 56–59.
- [3] Qiao Z, Jung J, Niu Q, MacDonald AH. Electronic highways in bilayer graphene. *Nano Lett* 2011, 11(8): 3453–3459.
- [4] Avouris P. Graphene: electronic and photonic properties and devices. *Nano Lett* 2010, 10(11): 4285–4294.
- [5] Kim JY, Lee JH, Grossman JC. Thermal transport in functionalized graphene. *ACS Nano* 2012, 6(10): 9050–9057.
- [6] Malekpour H, Chang KH, Chen JC, Lu CY, Nika DL, Novoselov KS, Balandin AA. Thermal conductivity of graphene laminate. *Nano Lett* 2014, 14(9): 5155–5161.
- [7] Titov AV, Král P, Pearson R. Sandwiched graphene–membrane superstructures. *ACS Nano* 2010, 4(1): 229–234.
- [8] Boukhvalov DW, Katsnelson MI, Son YW. Origin of anomalous water permeation through graphene oxide membrane. *Nano Lett* 2013, 13(8): 3930–3935.
- [9] Williams G, Seger B, Kamat PV. TiO₂-graphene nanocomposites. UV-assisted photocatalytic reduction of graphene oxide. *ACS Nano* 2008, 2(7): 1487–1491.

- [10] Burress JW, Gadipelli S, Ford J, Simmons JM, Zhou W, Yildirim T. Graphene oxide framework materials: theoretical predictions and experimental results. *Angew Chem Int Ed* 2010, 49(47): 8902–8904.
- [11] Liu M, Zhao H, Chen S, Yu H, Quan X. Interface engineering catalytic graphene for smart colorimetric biosensing. *ACS Nano* 2012, 6(4): 3142–3151.
- [12] Wen Z, Wang X, Mao S, Bo Z, Kim H, Cui S, et al. Crumpled nitrogen-doped graphene nanosheets with ultrahigh pore volume for high-performance supercapacitor. *Adv Mater* 2012, 24(41): 5610–5616.
- [13] Dai L. Functionalization of graphene for efficient energy conversion and storage. *Acc Chem Res* 2013, 46(1): 31–42.
- [14] Zhu Y, Murali S, Stoller MD, Ganesh KJ, Cai W, et al. Carbon-based supercapacitors produced by activation of graphene. *Science* 2011, 332: 1537–1541.
- [15] Wang S, Tristan F, Minami D, Fujimori T, Cruz-Silva R, Kaneko K, et al. Activation routes for high surface area graphene monoliths from graphene oxide colloids. *Carbon* 2014, 76: 220–231.
- [16] Zheng G-B, Sano H, Uchiyama Y. New structure of carbon nanofibers after high-temperature heat-treatment. *Carbon* 2003, 41(4): 853–856.
- [17] Vázquez-Santos MB, Geissler E, László K, Rouzaud J-N, Martínez-Alonso A, and Tascón JMD. Comparative XRD, Raman, and TEM study on graphitization of PBO-derived carbon fibers. *J Phys Chem C* 2012, 116 (1): 257–268.
- [18] Song L, Khoerunnisa F, Gao W, Dou W, Hayashi T, Kaneko K, Endo M, Ajaya PM. Effect of high-temperature thermal treatment on the structure and adsorption properties of reduced graphene oxide. *Carbon* 2013, 52: 608–612.

- [19] Ohkubo T, Yang C-M, Raymundo-Piñero E, Solano L, Kaneko K. High-temperature treatment effect of microporous carbon on ordered structure of confined SO₂. *Chem Phys Lett* 2000, 329(1–2): 71–75.
- [20] Bougrine A, Dupont-Pavlovsky N, Naji A, Ghanbaja J, XMarêché JF, Billaud D. Influence of high temperature treatments on single-walled carbon nanotubes structure, morphology and surface properties. *Carbon* 2001, 39(5): 685–695.
- [21] Neimark AV, Lin Y, Ravikovitch PI, Thommes M. Quenched solid density functional theory and pore size analysis of micro-mesoporous carbons. *Carbon* 2009, 47(7): 1617–1628.
- [22] Marcano DC, Kosynkin DV, Berlin JM, Sinitskii A, Sun Z, Slesarev A, et al. Improved synthesis of graphene oxide. *ACS Nano* 2010, 4(8): 4806–4814.
- [23] Zhang N, Qiu H, Si Y, Wang W, Gao J. Fabrication of highly porous biodegradable monoliths strengthened by graphene oxide and their adsorption of metal ions. *Carbon* 2011, 49(3): 827–837.
- [24] Wen P, Gao J, Zhang Y, Liu Y. Fabrication of chitosan scaffolds with tunable porous orientation structure for tissue engineering. *J Biomater Sci, Polym Ed* 2011, 22(1-3): 19–40.
- [25] Mukai SR, Nishihara H, Hajime T. Formation of monolithic silica gel microhoneycombs (SMHs) using pseudosteady state growth of microstructural ice crystals. *Chem Commun* 2004, 874–875.
- [26] Kaneko K, Ishii C, Ruike M, Kuwabara H. Origin of superhigh surface area and microcrystalline graphitic structures of activated carbons. *Carbon* 1992, 30(7): 1075–1088.
- [27] Setoyama N, Suzuki T, Kaneko K. Simulation study on the relationship between a high resolution α_s -plot and the pore size distribution for activated carbon. *Carbon* 1998, 36(10): 1459–1467.

- [28] Dubinin MM. Fundamentals of the theory of adsorption in micropores of carbon adsorbents: characteristics of their adsorption properties and microporous structures. *Carbon* 1989, 27(3): 457–467.
- [29] Endo M, Furuta T, Minoura F, Kim C, Oshida K, Dresselhaus G, Dresselhaus MS. Visualized observation of pores in activated carbon fibers by HRTEM and combined image processor. *Supramolecular Sci* 1998, 5(3-4): 261–266.
- [30] Harris PJF, Liu Z, Suenaga K. Imaging the atomic structure of activated carbon. *J Phys: Condens Matter* 2008, 20(36): 362201–362205.
- [31] Wang H, Gao Q, Hu J. High hydrogen storage capacity of porous carbons prepared by using activated carbon. *J Am Chem Soc* 2009, 131(20): 7016–7022.
- [32] Shimada T, Sugai T, Fantini C, Souza M, Cançado LG, Jorio A, et al. Origin of the 2450 cm^{-1} Raman bands in HOPG, single-wall and double-wall carbon nanotubes carbon. *Carbon* 2005, 43(5): 1049–1054.
- [33] Dresselhaus MS, Jorio A, Hofmann M, Dresselhaus G, Saito R. Perspectives on carbon nanotubes and graphene Raman spectroscopy. *Nano Lett* 2010, 10(3): 751–758.
- [34] Malard LM, Pimenta MA, Dresselhaus G, Dresselhaus MS. Raman spectroscopy in graphene. *Phys Rep* 2009, 473(5–6): 51–87.
- [35] Tuinstra F, Koenig JL. Raman spectrum of graphite. *J Chem Phys* 1970, 53(3): 1126–1130.
- [36] Mattia D, Rossi MP, Kim BM, Korneva G, Bau HH, Gogotsi Y. Effect of graphitization on the wettability and electrical conductivity of CVD-carbon nanotubes and films. *J Phys Chem B* 2006, 110(20): 9850–9855.
- [37] Matthews MJ, Pimenta MA, Dresselhaus G, Dresselhaus MS, Endo M. Origin of dispersive effects of the Raman D band in carbon materials. *Phys Rev B* 1999, 59(10): R6585–R6588.

- [38] Franklin RE. Crystalline growth in graphitizing and non-graphitizing carbons. *Proc R Soc Lon Ser A* 1951, 209: 196–218.
- [39] Li ZQ, Lu CJ, Xia ZP, Zhou Y, Luo Z. X-ray diffraction patterns of graphite and turbostratic carbon. *Carbon* 2007, 45(8): 1686–1695.
- [40] Takagi H, Maruyama K, Yoshizawa N, Yamada Y, Sato Y. XRD analysis of carbon stacking structure in coal during heat treatment. *Fuel* 2004, 83(17–18): 2427–2433.
- [41] Patterson A. The Scherrer formula for X-Ray particle size determination. *Phys Rev* 1939, 56(10): 978–982.
- [42] Inagaki M, Kang F. Carbon materials science and engineering. Beijing: Tsinghua University Press. 2006: 160–164.
- [43] Sing KSW, Everett DH, Haul RAW, Moscou L, Pierotti RA, Rouquerol J, Siemieniewska T. Reporting physisorption data for Gas/solid systems with special reference to the determination of surface area and porosity. *Pure & Appl Chem* 1985, 57(4): 603–619.
- [44] Rouquerol J, Avnir D, Fairbridge CW, Everett DH, Haynes JM, Pernicone N, et al. Recommendations for the characterization of porous solids. *Pure & Appl Chem* 1994, 66(8): 1739–1758.
- [45] Larher Y. “Phase transitions” between dense monolayers of atoms and simple molecules on the cleavage face of graphite, with particular emphasis on the transition of nitrogen from a fluid to a registered monolayer. *J Chem Phys* 1978, 68(5): 2257–2263.
- [46] Grillet Y, Rouquerol F, Rouquerol J. Two-dimensional freezing of nitrogen or argon on differently graphitized carbons. *J Colloid Interface Sci* 1979, 70(2): 239–244.
- [47] Steele WA, Vernov AV, Tildesley DJ. Studies of the adsorption of N₂ on the graphite basal plane by computer simulation. *Carbon* 1987, 25(1): 7–17.

- [48] Wang S, Minami D, Kaneko K. Comparative pore structure analysis of highly porous graphene monoliths treated at different temperatures with adsorption of N₂ at 77.4 K and of Ar at 87.3 K and 77.4 K. *Micropor Mesopor Mat* 2015, 209: 72–78.
- [49] Oberlin A. Carbonization and graphitization. *Carbon* 1984, 22(6): 521–541.
- [50] Emmerich FG. Evolution with heat treatment of crystallinity in carbons. *Carbon* 1995, 33(12): 1709–1715.
- [51] Pedraza DF, Klemens PG. Effective conductivity of polycrystalline graphite. *Carbon* 1993, 31(6): 951–956.
- [52] Spain, IL. Electronic transport-properties of graphite, carbons, and related materials. *Chem Phys Carbon* 1981, 16: 119–304.
- [53] Conway BE. In *electrochemical supercapacitor: scientific fundamentals and technological applications*. New York: Kluwer. 1999: 186–193.
- [54] Frackowiak E, Béguin F. Carbon materials for the electrochemical storage of energy in capacitors. *Carbon* 2001, 39(6): 937–950.
- [55] Shi H. Activated carbons and double layer capacitance. *Electrochim Acta* 1996, 41(10): 1633–1639.
- [56] Chmiola J, Yushin G, Dash R, Gogotsi Y. Effect of pore size and surface area of carbide derived carbons on specific capacitance. *J Power Sources* 2006 158 (1): 765–772.