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A novel nanoporous graphitic composite

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A novel nanoporous composite containing micrographitic carbon layers is synthesized by preliminarily expanding the interlayer of an oxidized product of graphite using surfactant, followed by Si bridging/pillaring, and carbonization.

Graphite is a layered material having the thinnest atomic layer of all layered materials.[1] A nanoporous material with thin graphitic layers has been sought for the purposes of high efficiency adsorption and gas storage applications.[2] Because of the neutral properties of the graphite walls, there is no driving force strong enough for a rigid species to expand and prop the graphitic layers to form an open pore system using ordinary soft chemical methods. Although the weak van der Waals-type bonding between the graphitic layers allows the formation of graphite intercalation compounds (GIC) for electrochemical/tribological application, these materials are chemically unstable in air and seem to have only small surface areas due to the "stuffing" sandwich structures.[3] On the other hand, oxidation of graphite by strong oxidants leads to a layered graphite oxide (GO), which shows excellent swelling/exfoliation properties similar to clay minerals.[3a,4] A nanoporous material can generally be synthesized from a two-dimensional precursor by a soft chemical method such as pillaring/templating methods.[5] Thus, it may be possible to form a nanoporous material with thin carbon walls by treating the interlayer of GO using a soft chemical method, followed by an appropriate post-treatment such as carbonization. Fig. 1 shows our synthetic approach for obtaining this type of nanoporous material. We found that a novel nanoporous graphitic composite (NPGC) with a specific surface area greater than 1000 m^2 g^{-1} can be formed by a preliminary expansion and hydrophobic treatment of the GO interlayer, followed by introducing a bridging/pillaring species (Si) and subsequent carbonization.

We used natural graphite (G) as the precursor. G was oxidized with a mixture of concentrated sulfuric acid, fumed nitric acid, and potassium chloride using the Staudenmaier's method.[6] Elemental analysis shows the chemical formula of the GO to be $C_8O_{3.7}H_{1.8}$. After being dispersed in 0.05 M aq. NaOH by ultrasonic vibration for 15 min, 1.84×10^{-3} M aq. hexadecyltrimethyl anmmonium (C16TMA) bromide was added dropwise to the GO colloidal solution. The precipitates were filtered off, thoroughly washed with water, and dried overnight at 323 K in air to obtain the hydrophobic C16TMA-intercalated GO (GOC16). GOC16 was then treated in tetraethoxylsilane (TEOS) for one week and the product (GOC16S) was centrifuged, washed with ethanol, and dried at 323 K overnight. The final product (GOC16S-823) was obtained by slowly carbonizing GOC16S at 823 K under vacuum for 2–4 h. For comparison, a second product (GOS) was obtained by directly treating GO with TEOS, followed by the same carbonizing procedure. The surfactant and silicon contents in each sample were determined by weight difference before and after intercalation or elemental (N) analysis, and the weight of residual SiO_2 after burning-off in air above 1073 K. X-Ray diffraction patterns (XRD), N_2 adsorption at 77 K, and transmission electron microscopy (TEM) were measured with a Rigaku 1200 system, a Japan Bellsorp Co.-made volumetric apparatus, and a JEOL JEM 3010 apparatus, respectively.

Fig. 2 shows the XRD patterns of the samples. After oxidation, the graphitic (002) diffraction peak completely disappears and, instead, is replaced by a sharp peak at a lower diffraction angle ($2\theta = 10.2°$). The interlayer distance of GO (d_l = 0.865 nm) is in the range of the reported values (0.6–1.1 nm);[4] the weak peaks at $2\theta = 20.6°$ (d_l = 0.432 nm) indicate the existence of some stacking structures. The layered structure of GO becomes less ordered following the hydrophobic treatment with surfactant, probably due to the thorough water washing. However, three diffraction peaks with d_l = 4.02, 2.04 and 1.38 nm are still evident. These are probably due to a stacking structure of double C16TMA ion layers intercalated with a tilting angle of 65°, if the surfactant chain length of 2.15 nm is considered.[5a] Treatment in TEOS and the subsequent carbonization lead to products with completely disordered structures, having only a broad peak at $2\theta \sim 23.6°$. Fig. 3(a) shows the N_2 adsorption isotherms at 77 K on GOC16S-823, whose shape seems to be a mixture of type I (an initial steep rise

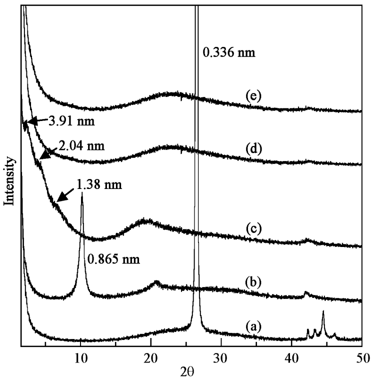

Fig. 2 XRD patterns of (a) G, (b) GO, (c) GOC16, (d) GOC16S and (e) GOC16S-823.

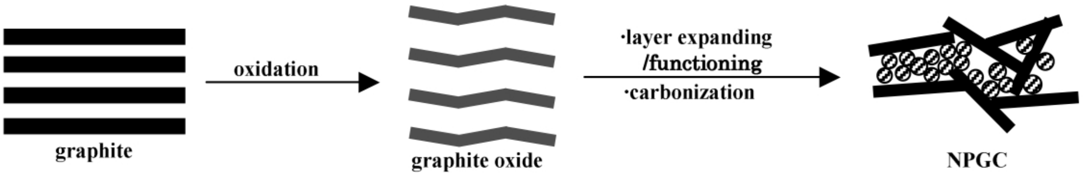

Fig. 1 Schematic of nanoporous graphitic composite (NPGC) synthesis.

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at $P/P_0 < 0.05$) and type IV (a gradual increase at $P/P_0 > 0.2$ with an evident desorption hysteresis closed at $P/P_0 = \sim 0.45$).[7] The shape of the desorption branch is of typical type H2, indicating that the sample's mesopores may be formed by aggregation of various plate particles of different sizes.[7c] A high-resolution α_s-plot[7d] and Dollimore–Heal analysis[7b] [Fig. 3(b)] show the average micropore and mesopore dimension to be 1.07 nm and ∼2 nm, respectively. Table 1 shows the surfactant and silicon contents and the Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}) of GOC16S-823 in comparison with G, GO, GOS-823 and GOC16-823. Except for GOC16S-823, all the samples have a S_{BET} value below 90 m^2 g^{-1}, indicating not only the expanding of the GO interlayer but also the introduction of a robust bridging/pillaring species are important for formation of the nanoporous structure. The intercalated surfactant used for preliminary expansion of GO layers serves as a intermediary material and is gradually replaced and lost by TEOS introduction and carbonization, resulting in a nanoporous composite having very high surface area (1100 m^2 g^{-1}) and containing carbon and silicon as the main components. Fig. 4 shows the TEM image of GOC16S-823 in which some clear but disordered layered structures having one, two or several stacking walls with intercalated powdered particles can be observed. The gallery height of one of these structures is estimated to be 1.1 nm, very similar to the average micropore size determined from N_2 adsorption. Raman spectra show absorption bands at 1600 and 1340 cm^{-1} due to the disordered graphitic structures, indicating that the sheet structures in this composite have partial graphene properties.[1a] Other XPS and NMR results confirm the powdered particles to be silica species even though they are formed under reductive carbonization conditions. A water adsorption measurement shows that the hydrophilicity of GOC16S-823 is between that of hydroxyl silica and porous carbonaceous materials. Therefore, this material is special in its carbonaceous walls compared with other pillared materials and could be suitable for applications which require both hydrophobic properties and the role of intercalated active species.

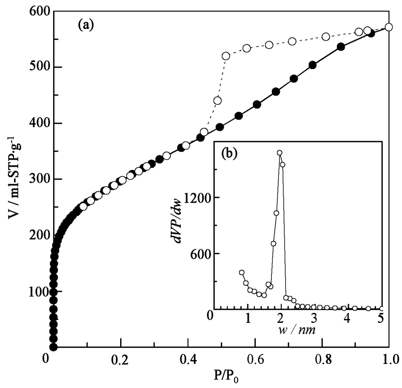

Fig. 3 (a) N_2 adsorption isotherm at 77 K on GOC16T-823 and (b) mesopore distribution curve calculated by the Dollimore–Heal method from the desorption branch. Adsorption and desorption branches are shown by filled and empty circles, respectively.

Table 1 Surfactant and silicon contents and BET specific surface areas of samples

Sample[a]	C16TMA/ mmol g^{-1}	Si/mmol g^{-1}	S_{BET}/m^2 g^{-1}
G	0	0	15
GO	0	0	25
GOS-823	0	1.2	81
GOC16-823	1.52[b]	0	84
GOC16S-823	0.69,[b] 0.13	7.9,[b] 10.2	1100

[a] Values after '-' are the carbonization temperatures. [b] Contents before carbonization.

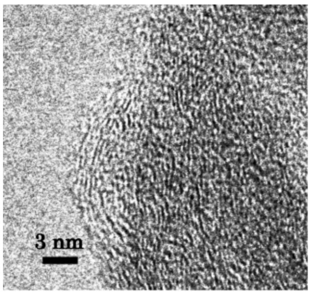

Fig. 4 TEM images of GOC16S-823.

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