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Chinese Science Bulletin

SPECIAL ISSUE: Graphene

August 2012 Vol.57 No.23: 3026–3029
doi: 10.1007/s11434-012-5252-6

Graphene-templated approach to ultrathin silica nanosheets

KAN LanYan, ZHENG BingNa & GAO Chao*

Key Laboratory of Macromolecular Synthesis and Functionalization (Ministry of Education), Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Received November 2, 2011; accepted March 30, 2012; published online June 15, 2012

Graphene, a perfect two-dimensional (2D) nanostructure, is an ideal template for 2D material design. We developed a graphene-templated method to synthesize 2D silica nanosheets through the crosslinking of poly(3-methacryloxypropyl trimethoxysilane)-grafted graphene oxide (GO-g-PMPS), followed by pyrolysis at 700°C for 10 h.

graphene oxide (GO), poly(3-methacryloxypropyl trimethoxysilane) (PMPS), 2D silica nanosheets

Citation: Kan L Y, Zheng B N, Gao C. Graphene-templated approach to ultrathin silica nanosheets. Chin Sci Bull, 2012, 57: 3026–3029, doi: 10.1007/s11434-012-5252-6

Two-dimensional (2D) nanostructures have attracted increasing interests since the rise of graphene in 2004 [1,2], and a number of 2D nanomaterials such as BN, MoS_2 and Bi_2Te_3 [3–5] have been obtained by either exfoliation of natural mineral or chemical method. As a perfect 2D model, graphene or chemically modified graphene could be used as template due to its large-scale availability to fabricate other 2D nanomaterials [6]. Despite the big progress made in the field of 2D nanomaterials, 2D silica nanosheets have rarely been reported. Silica nanostructures have been widely researched in recent years for their unique size-dependent properties which lead to potential utilization in both fundamental science and industrial research [7–9]. Consequently, 1D silica nanostructures (e.g. nanowires [9], nanotubes [10,11] and nanorods [12]) as well as 3D silica nanostructures (e.g. nanoparticles [13,14] and nanocubes [15]) have been widely investigated. Recently, graphene-supported large area silica nanosheets have been reported by our group [16]. Wang et al. [17] and Lee et al. [18] have also reported the graphene-templated methods of mesoporous silica fabrication [19]. However, simple and reliable preparation of 2D silica nanosheets still remains a challenge to be solved.

Here, we report a graphene oxide (GO)-templated methodology to synthesize silica nanosheets. Three steps are included in this method, as shown in Scheme 1: (1) silicon-contained vinyl polymer grafting on GO, (2) chemical crosslinking of the polymer layers on GO sheets, (3) pyrolysis at 700°C in air.

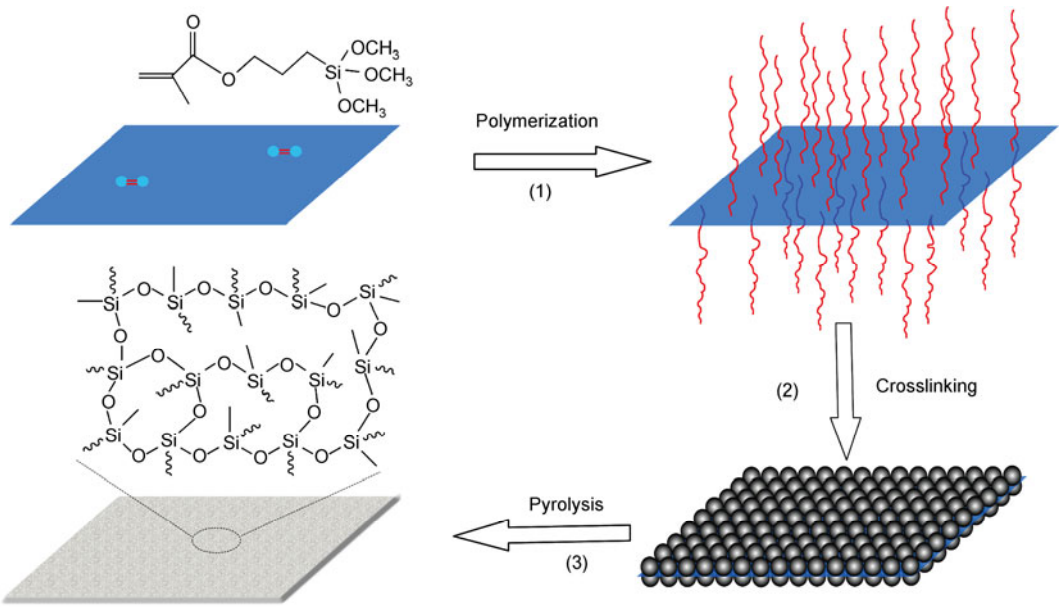
1 Experimental

Poly(3-methacryloxypropyl trimethoxysilane) (PMPS) was covalently grafted on GO sheets by *in situ* free radical polymerization approach presented previously by our group [20], affording PMPS-grafted GO brushes (Sample 1). The resulting Sample 1 were crosslinked in aqueous ammonia solution for 24 h [21]. Then, the crosslinked GO-g-PMPS (Sample 2) was collected and dispersed in water and freeze-dried. Finally, the dried powder of Samples 1 and 2 were both treated with pyrolysis at 700°C in air for 10 h. After the decomposition of graphene template and other carbon units, Sample 1 gave rise to small pieces of silica clusters (Sample 3) and Sample 2 gave rise to silica nanosheets (Sample 4). The resultant products were characterized by thermal gravimetric analysis (TGA), atomic force microscopy (AFM), scanning electron microscope (SEM), transmission electron microscope (TEM), Raman spectroscopy and so on.

2 Results and discussion

AFM is considered to be the most effective equipment for

*Corresponding author (email: chaogao@zju.edu.cn)



Scheme 1 (Color online) The synthesis protocol for two-dimensional silica nanosheets. Conditions: (1) In DMF, at 65°C for 24–36 h; (2) 25% aqueous ammonia solution at room temperature for 24 h; (3) pyrolysis in air at 700°C for 10 h.

the visualization of graphene and its hybrid structures [5,22–25]. Figure 1(a) shows the AFM images of Sample 1 at different synthesis stages. Various protuberances, tufts of polymeric hairs, are evenly distributed on GO sheet after PMPS grafting. The height of Sample 1 reached to 5 nm, much higher than pristine GO sheet (~0.8 nm) [26], indicating the successful grafting of PMPS on GO sheet. Uniform and continuous sandwich-like layer without obvious cleavages was obtained after the crosslinking of grafted PMPS (Sample 2, Figure 1(b)). Obviously, independent polymer protuberances crosslink with each other and develop into a continuous network through the chemical crosslinking. A pyrolysis process at 700°C in air for 10 h was employed to generate template-free 2D nanosheets. The sample without crosslinking decomposed into small pieces after pyrolysis (Sample 3, Figure 1(c)), while the crosslinked sample treated with pyrolysis still maintains a continuous form revealing the integrity of the silica nanosheets (Sample 4, Figure 1(d)). This is due to the continuous network forms from chemical crosslinking of grafted PMPS, which can serve as the backbone of silica nanosheets after the pyrolysis. Without the backbone and GO template, Sample 3 cannot maintain the morphology and naturally decomposed into pieces. From FT-IR spectra, intensive peaks at 660 and 1090 cm^{-1} which ascribe to stretching vibration of Si–C and asymmetric vibration of Si–O–Si were shown in Samples 1 and 2 while no such peaks can be detected for pristine GO. This is another evidence of successful grafting of PMPS to GO.

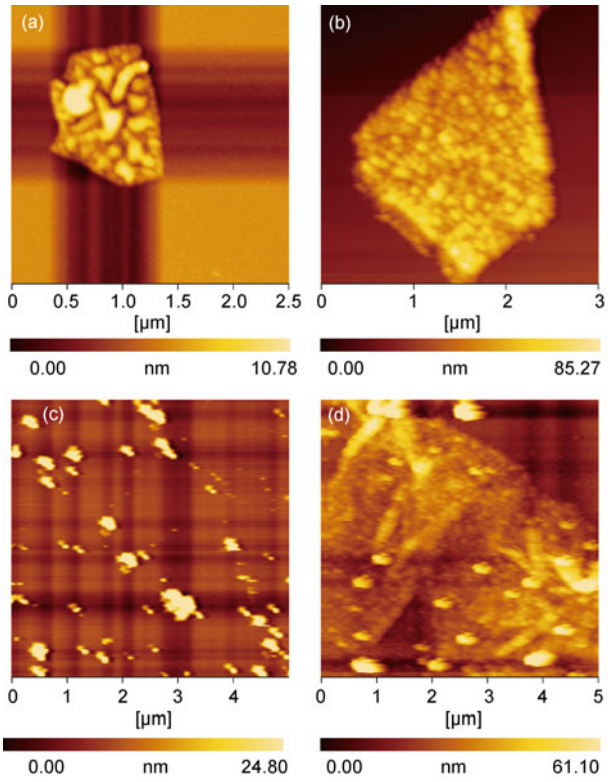


Figure 1 (Color online) AFM images of GO-g-PMPS after different treatments. (a) As-prepared Sample 1; (b) Sample 2; (c) Sample 3; (d) Sample 4.

Figure 2(a) shows the TGA curves of GO and Sample 1, and the weight loss of Sample 1 is obviously higher than GO which is another evidence of the successful grafting of PMPS on GO sheet [27]. Raman spectroscopy is useful in probing sp^3 and sp^2 hybridized carbon atoms which was employed to trace the transformation from Sample 1 to Sample 4. In Figure 2(b), the two intensive peaks of GO at 1333 and 1592 cm^{-1} correspond to D band representing

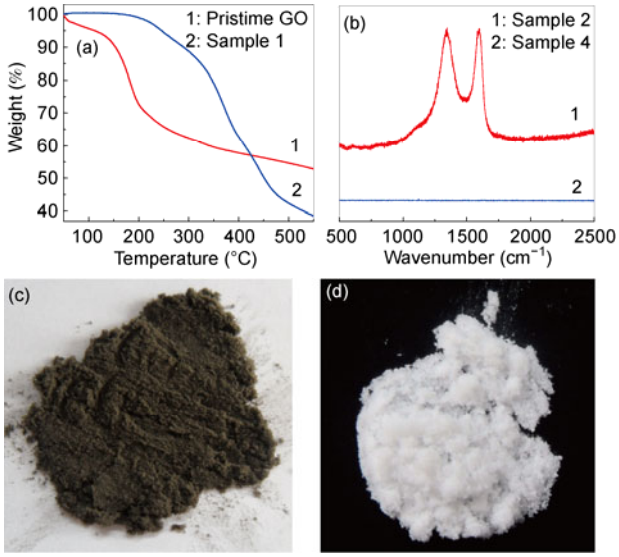


Figure 2 (Color online) (a) TGA curves of pristine GO and Sample 1; (b) Raman spectra of Sample 2 and Sample 4; powder of Sample 2 (c) and Sample 4 (d).

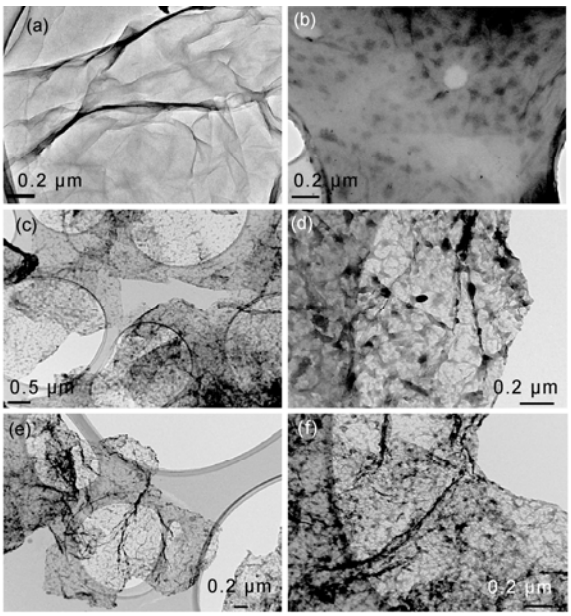


Figure 3 TEM images of GO (a), Sample 1 (b), Sample 2 (c), (d) and Sample 4 (e), (f).

disordered sp^3 carbon structure and G band of sp^2 ordered crystalline graphite-like structures, respectively [5,28–31]. On the contrary, Sample 4 showed no apparent peak in the whole testing range. The vanishment of D and G bands is a strong evidence that the sp^3 and sp^2 carbon structures of GO decomposed totally after the pyrolysis process. Figure 2(c) and (d) exhibit the color change from black gray (Figure 2(c)) to pure white (Figure 2(d)) after pyrolysis, giving the direct visualization that the carbon in GO and the grafted carbon sources were completely burned out. This further indicated that pure 2D silica nanosheets were obtained through our method.

Representative TEM images are displayed in Figure 3 for further observation of the sample morphology. Comparing with smooth pristine GO (Figure 3(a)), various of protuberances are uniformly distributed on the nanosheet of Sample 1 (Figure 3(b)), which is in accordance with the result of AFM. In Figure 3(c), several evenly dispersed nanosheets of Sample 2 are observed and each sheet is attached with tufts of polymer protuberances. The corresponding magnified image (Figure 3(d)) shows that it is decorated with a thin and soft polymer layer resulting from the crosslinking of the grafted PMPS. Sample 4 in Figure 3(e) exhibit that several monolayer silica nanosheets which still maintain intact sheet morphology similar to the GO template are obtained. It indicates that the morphology of prepared silica nanosheets can be controlled through design of the templates. From the magnified image of silica nanosheet in Figure 3(f), we can find that rigid rough surface different from the soft polymer layer in Figure 3(d) are dispersed on its surface.

To investigate the original form of Sample 1 and silica nanosheets dispersed in water, freeze drying was adopted after crosslinking. As shown in Figure 2(d), the final sample is loose white powder. It is worth mentioning that Sample 1 is insoluble in water before crosslinking, whereas it can be dispersible in water after crosslinking. The final sample of silica nanosheets (Sample 4) is also dispersible in water, which lays the foundation of further functionalization and utilization.

Figure 4(a) shows the morphology of Sample 1, and it can be found that dispersed nanosheets are equipped with a shaggy surface differing from the smooth surface of pristine GO nanosheets [32]. One sheet with visible serried clusters densely coated on the flat surface is displayed in Figure 4(b). As for Sample 2, scattered nanosheets are still visible and each surface is developed into a uniform layer (Figure 4(d)) rather than a coating of serried clusters in Figure 4(b). From Figure 4(e), Sample 2 was turned into silica nanosheets (Sample 4) and could be dispersed in water with sheet morphology. Interestingly, almost all the nanosheets were continuous and intact except one hole indicating that grafted PMPS were not entirely coated on such sheet template in Figure 4(f). Consequently, the results obtained from TEM and SEM are consistent with each other, showing the flake morphology of the prepared 2D silica nanosheets through graphene oxide-templated method.

3 Conclusion

In summary, we developed a GO-templated method for facile, large-scale and shape controlled preparation of 2D silica nanosheets. By free radical polymerization, the silicon-contained vinyl polymer was effectively grafted onto GO nanosheets. Subsequently, water-dispersible 2D silica nano-

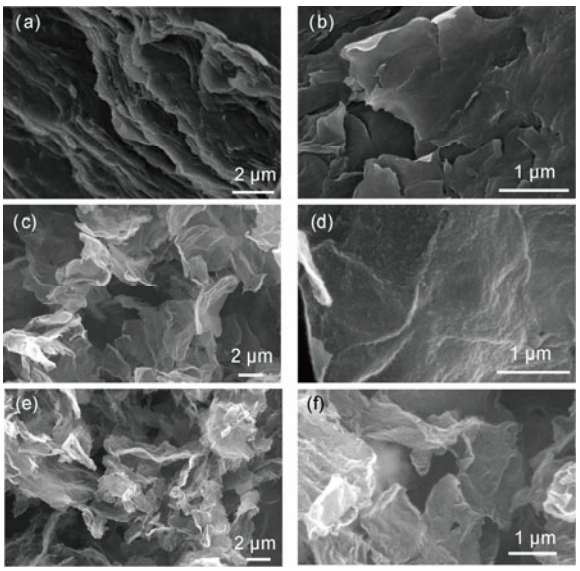


Figure 4 SEM images of GO-g-PMPS in different forms. (a), (b) Sample 1; (c), (d) Sample 2; (e), (f) Sample 4.

sheets were obtained after decomposition of GO template by treatments of crosslinking and pyrolysis. Owing to the large size and unique flat morphology, 2D silica nanosheets hold great promise in many applications.

This work was supported by the National Natural Science Foundation of China (*51173162 and 20974093*)*, Research Fund for the Doctoral Program of Higher Education of China* (*20100101110049*)*, the Fundamental Research Funds for the Central Universities* (*2011QNA4029*)*, Qianjiang Talent Foundation of Zhejiang Province* (*2010R10021*)*, and Zhejiang Provincial Natural Science Foundation of China* (*R4110175*).

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