Synthesis of three-dimensional nanoporous graphene for use as surface-enhanced Raman scattering substrate

Zhiqiang Tu [a], Shangfei Wu [b], Fan Yang [a], Yongfeng Li [a,*], Liqiang Zhang [a], Hongwen Liu [b,*], Hong Ding [b,c], Pierre Richard [b,c]

[a] State Key Laboratory of Heavy oil Processing, China University of Petroleum, Beijing 102249, China
[b] Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
[c] Collaborative Innovation Center of Quantum Matter, Beijing, China

ABSTRACT

We synthesized 3D nanoporous graphene by a chemical vapour deposition method with nanoporous copper as a catalytic substrate, and we show that the resulting nanoporous graphene has the same average pore size and the same morphology as the underlying copper substrate. Our surface-enhanced Raman scattering (SERS) investigation indicates that the nanoporosity of graphene significantly improves the SERS efficiency of graphene as a substrate, which is better than that of planar single-layer graphene substrates.

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1. Introduction

Surface-enhanced Raman scattering (SERS), which consists in the enhancement of inelastic light scattering of molecules adsorbed on a surface, is an attractive analytical method able to provide quantitative structural information for analytes. Although this effect is most often generated by the strong local electromagnetic confinement resulting from rough metallic surfaces or nanostructures such as colloidal silver or gold nanoparticles [1,2], large SERS effect has been observed recently in dealloyed nanoporous metallic films [3,4]. Interestingly, three-dimensional (3D) architectures of graphene have also been synthesized recently [5], including continuous 3D-foam-like graphene with pore sizes of several hundred micrometres obtained by the metal-catalysed chemical vapour deposition (CVD) method using Ni substrates [6,7]. This is an encouraging development since graphene has many advantages over metal substrates, such as lower cost and better biocompatibility. In principle though, graphene as substrate does not support the electromagnetic mechanism (EM) for SERS because the surface plasmons on graphene are in the terahertz range rather than in the visible range [8]. However, SERS can also arise from a charge transfer between the adsorbed molecules and a substrate with proper chemical affinity with these molecules, and SERS has been reported for two-dimensional single-layer graphene [9–11]. Unfortunately, whether properly controlled nanoporosity can improve the SERS properties of graphene is unknown. Here we present a study of SERS enhancement for nanoporous graphene (NG) with a 3D network of nanometre pore sizes. Our results indicate a significant SERS enhancement as compared to planar graphene and nanoporous copper (NC).

2. Experimental

The 3D NG used in this study has been synthesized by a CVD method with NC as catalytic substrate. In order to synthesize 3D NG, NC substrates with different pore size distributions are fabricated by dealloying 0.14 mm-thick $Cu_{30}Mn_{70}$ alloys synthesized by a melt spinning method [12–14]. The pore size of NC is adjusted by changing the dealloying time of the erosion aqueous solution consisting of $(NH_4)_2SO_4 \cdot H_2O$ (1 M L^{-1}) and $MnSO_4 \cdot H_2O$ (0.01 M L^{-1}). Then, NC substrates are used to synthesize NG films by a CVD process using a mixture of gases with a composition of CH_4: Ar: H_2=8: 200: 20 sccm min^{-1}. Owing to the high activity of NC, the growth temperature is lowered to 600–900 °C. Finally, to investigate the SERS effect from 3D NG itself without the influence of the NC substrate, the 3D NG is released by etching graphene/NC stacks in aqueous $FeCl_3$ solution, then rinsed in deionized water and finally transferred to a Si substrate.

3. Results and discussion

Fig. 1 shows the scanning electron microscopy (SEM) images of NCs with average pore sizes ranging from 23 to 40 nm, which can also be observed in a cross sectional SEM image of NC (Fig. S1).

* Corresponding authors.
E-mail addresses: yfli@cup.edu.cn (Y. Li), hliu@iphy.ac.cn (H. Liu).
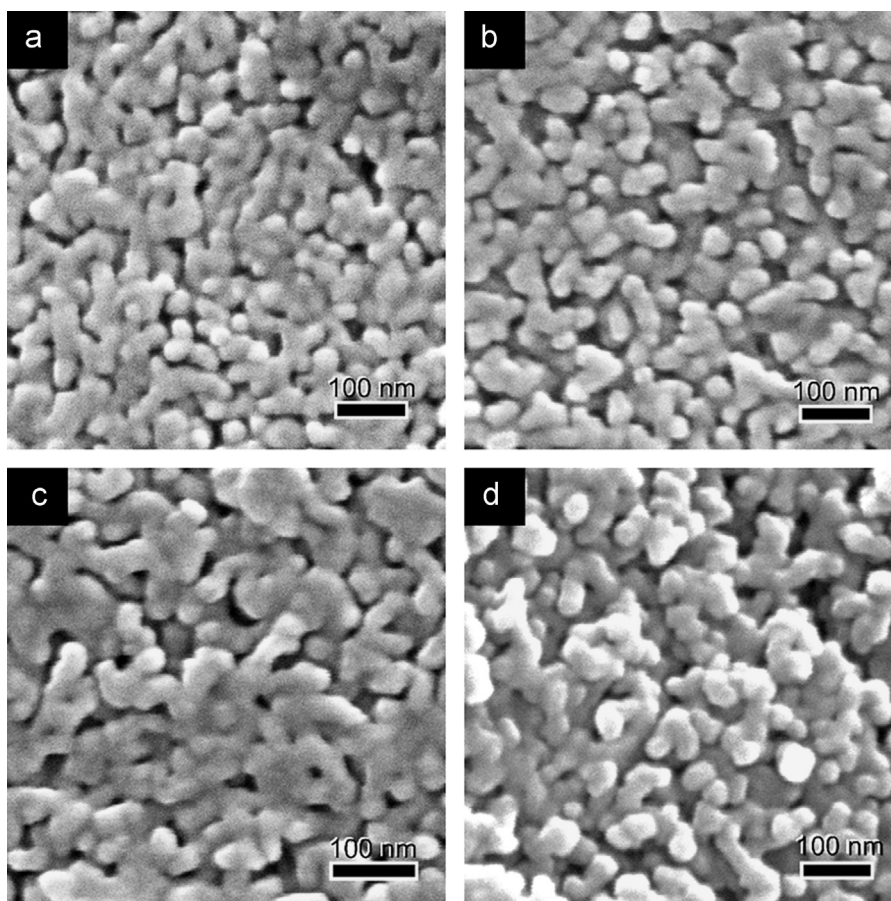
Fig. 1. SEM images of nanoporous coppers with different pore sizes: (a) 23 nm, (b) 28 nm, (c) 33 nm and (d) 40 nm.

Fig. 2a shows the cross-sectional SEM image of NG obtained after etching NC. The porous morphology of NG is shown in Fig. 2b. Our transmission electron microscopy (TEM) characterization of NG indicates that it consists of continuous 3D porous graphene (Fig. 2c), which is only one layer at the edge, as shown in Fig. S2. The selected area electron diffraction image displayed in Fig. 2d exhibits hexagonal spots in one circle, implying that the NG sample has a single crystal structure. From these experiments we conclude that the NG films grown on the NC surfaces have similar nanoporous structure as the underlying NC templates.

We further study the NG films using a Horiba JY-T64000 Raman spectrometer. In Fig. 3a we show the Raman spectra of NG films synthesized at different temperatures via NC substrates with 33 nm pore size. All G peaks, associated with the degree of graphitization, are found around 1590 cm^{-1}. Strong and broad D and 2D modes are observed, which can be understood in terms of high disorder induced from edges and nanoclusters [15–17]. A downshift of the D peak from 1364 to 1347 cm^{-1} is observed with the synthesis temperature increasing. Samples obtained at 600 and 700 °C show poor crystal structure (Fig. S3), whereas 800 °C is suitable to obtain NG with good quality, as displayed in Fig. 2c and d. Raman spectra of NG samples synthesized on NC substrates with different pore sizes at the optimized synthesis temperature of 800 °C are shown in Fig. 3b. Because of some melting of NC substrates (as shown in Fig. S4) with different pore sizes, NG samples eventually show very similar structures (as shown in Fig. 2a and b) without obvious differences in the Raman spectra.

We now discuss the SERS properties of NG using rhodamine 6G (R6G) as a probed molecule. First, the NG films have been transferred from the NC substrates onto SiO$_2$/Si substrates. Then, R6G molecules are deposited on a NG substrate by soaking them in

R6G solutions for 30 min. After soaking, the samples are dried naturally. The setup for Raman detection of R6G on a plain 3D NG substrate is schematically drawn in Fig. 4a.

We show in Fig. 4b the Raman spectra of 10^{-5} M R6G obtained on NG, NC, multi-layer graphene (MLG, 10 layers, CVD method) and single-layer graphene (SLG, CVD method) substrates. The fabrication method of MLG and SLG is discussed in detail in our previous work [18]. According to our findings, the SERS enhancement follows the sequence: NG > SLG ⩾ NC ⩾ MLG. This phenomenon is attributed to the strong interaction between NG and R6G through the photo-induced charge transfer and π–π interactions. Fig. 4b clearly indicates that the SERS intensity of NG is higher than that of SLG substrates. It has been reported that the excitation of intrinsic graphene plasmons are tuneable and strengthened by natural nanoscale inhomogeneities, such as wrinkles [19,20]. Most likely, the better SERS efficiency of NG than SLG suggests that enhancement of the local electromagnetic field due to porosity and surface roughness plays an important role in tuning the plasmonic properties of these materials [21].

4. Conclusions

3D-foam-like graphene films with nanopore sizes have been synthesized by a CVD method with NC as substrates, and the resulting nanoporous graphene has a similar porous structure as the underlying NC substrates. The Raman enhancement effect has been investigated by using R6G molecules. Our results indicate that NG has a great potential as SERS substrate that is better than those of NC, MLG and even SLG.
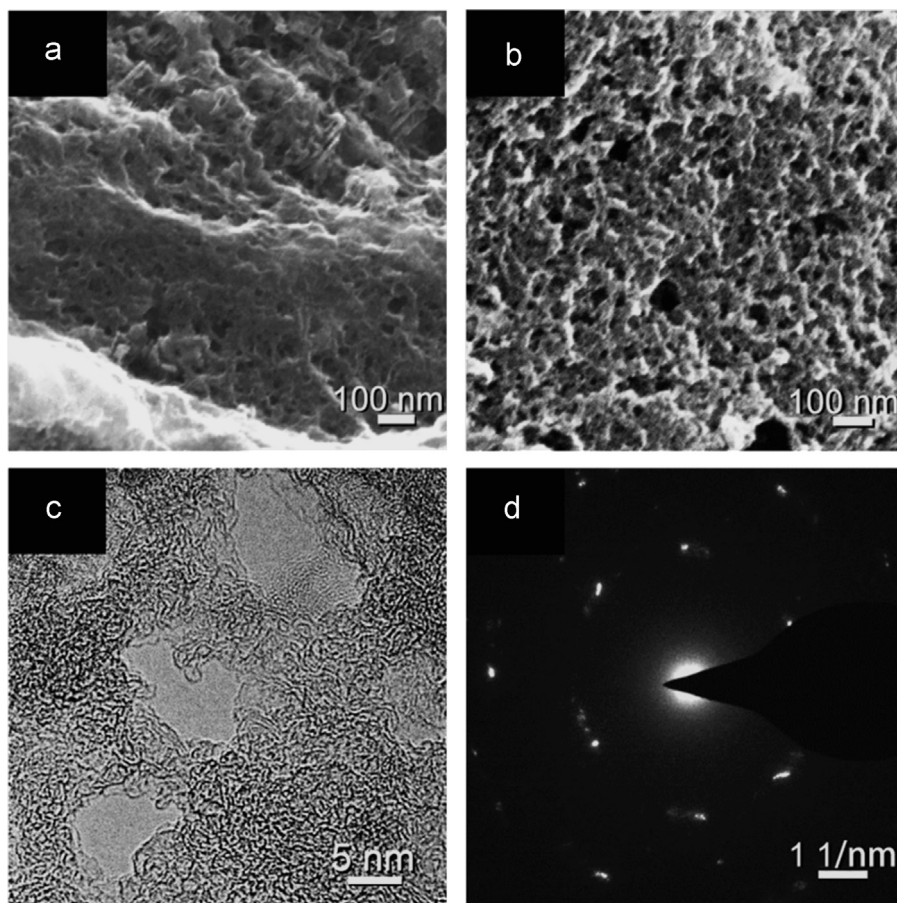
Fig. 2. SEM images of NG with (a) a side view and (b) a top view, (c) a typical TEM image, and (d) a SAED image of NG synthesized on a 33 nm NC under 800 °C.
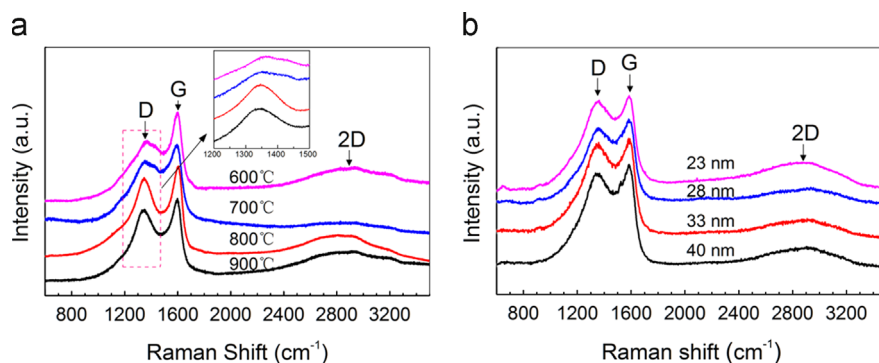

Fig. 3. (a) Raman spectra of 3D NG samples synthesized at different temperatures on 33 nm NC substrates. (b) Raman spectra of NG samples on different NC substrates prepared at 800 °C. The laser power is 30 mw.
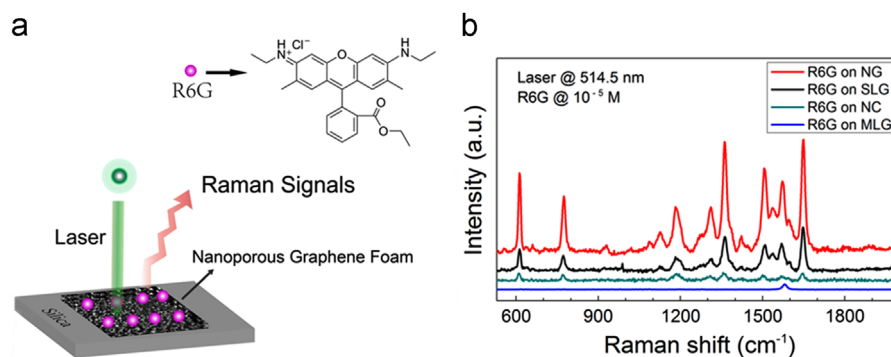

Fig. 4. (a) Scheme of Raman detection of R6G on a plain 3D NG substrate. Raman signals of R6G on different substrates (b). The laser power is 30 mw. The fluorescence background of R6G in (b) has been removed from the spectra.

Acknowledgements

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2015.03.131.

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Supporting Information

Synthesis of three-dimensional nanoporous graphene and its surface-enhanced Raman scattering as a substrate

Zhiqiang Tu [a], Shangfei Wu [b], Fan Yang [a], Yongfeng Li [a,*], Liqiang Zhang [a], Hongwen Liu [b,*], Hong Ding [b,c], Pierre Richard [b,c]

[a] State Key Laboratory of Heavy oil Processing, China University of Petroleum, Beijing, 102249, China

[b] Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, China

[c] Collaborative Innovation Center of Quantum Matter, Beijing, China

E-mail addresses: yfli@cup.edu.cn (Y. Li); hliu@iphy.ac.cn (H. Liu)
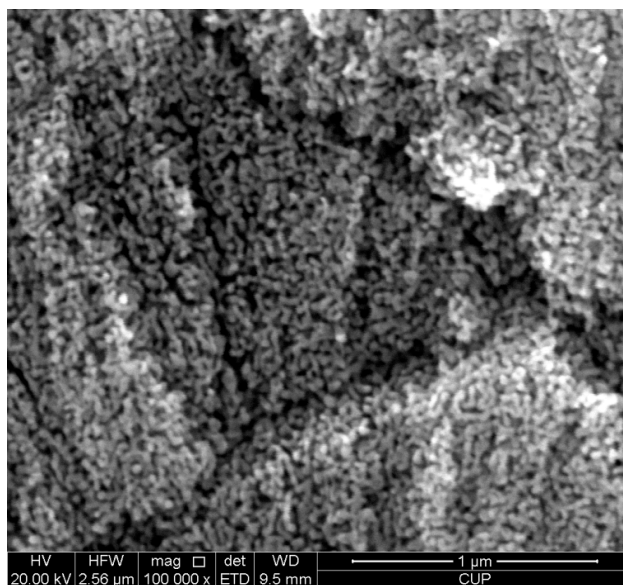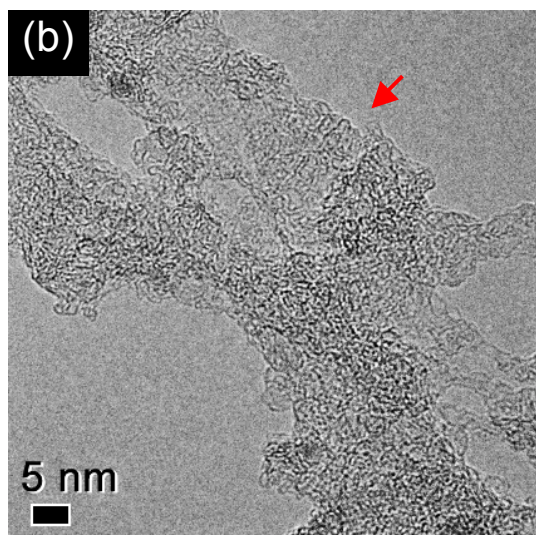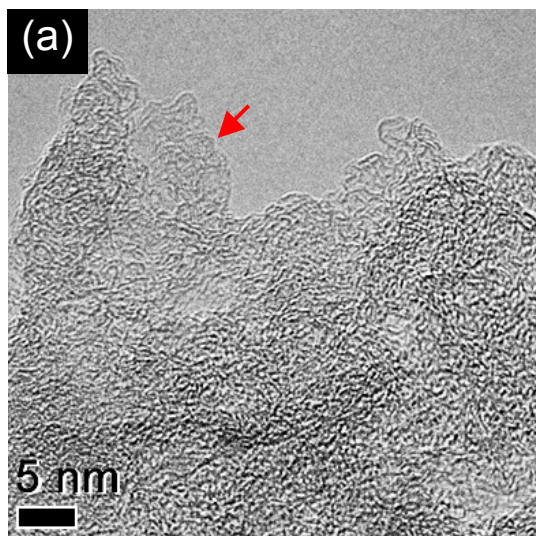
Fig. S1 A cross-sectional SEM picture of 33 nm NC
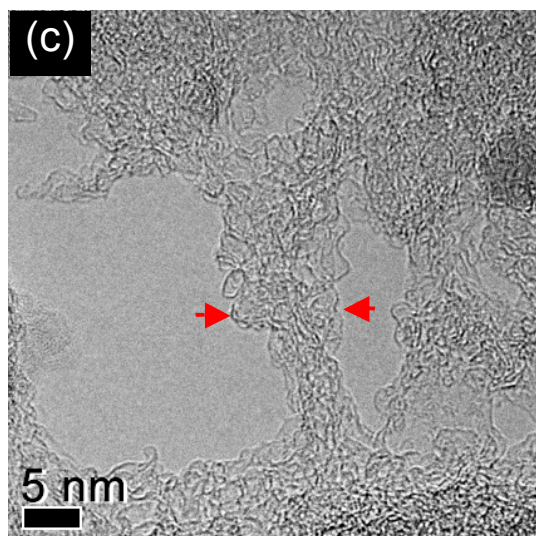
Fig. S2 High solution TEM images of NG. The arrows show that single layer graphene exists in the samples.

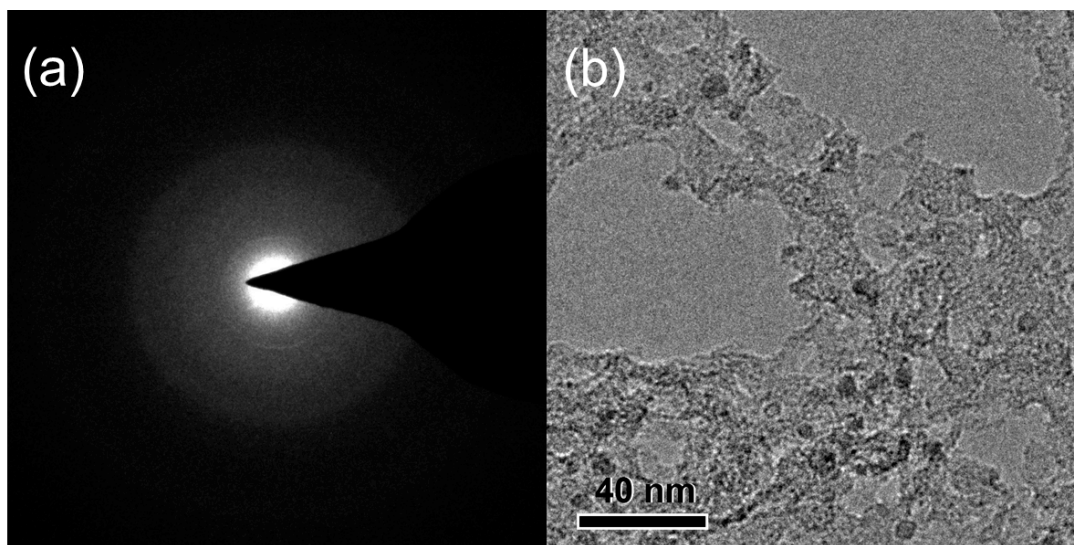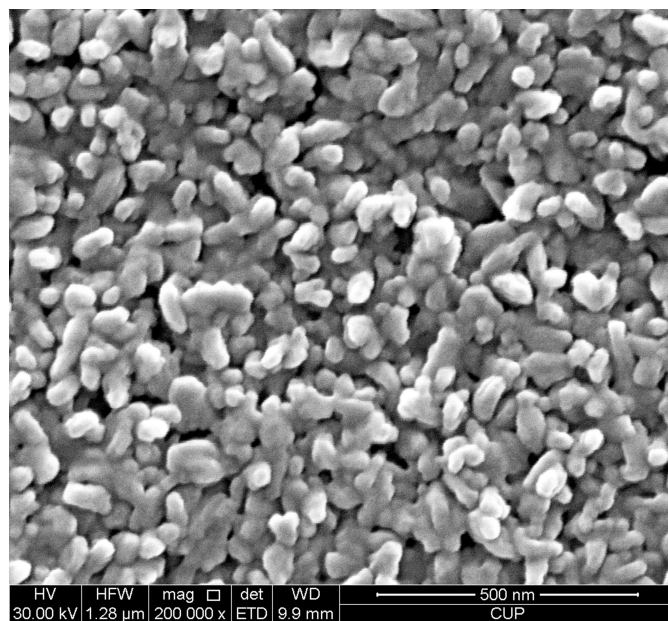Fig. S3 TEM and SAED images of NG obtained at 600 and 700 ^{o}C.

Fig. S4 A SEM of 33 nm NC with graphene grown on its surface