Plasma etching of polystyrene latex particles for the preparation of graphene oxide nanowalls

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Abstract: Graphene oxide nanowalls were prepared by casting an aqueous dispersion of polystyrene latex particles onto a graphene oxide film followed by tetrafluoromethane plasma etching. Mild plasma etching conditions allowed the oxygen functional groups on the graphene oxide nanowalls to be retained. It was found that exposure to a xenon light source of such graphene oxide nanowalls coated with a gold thin film results in an increase in the electrical conductivity.

Keywords: nanostructures; etching; electrical properties characterization; electrical conductivity.

INTRODUCTION

The optoelectronic properties of graphene have attracted substantial interest because graphene can absorb light and turn it into a photocurrent over a wide range of the electromagnetic spectrum, from the UV to the visible and infrared regimes.[1] A photocurrent response at graphene–metal contacts was reported by various groups, and the origin of such a photocurrent generation was discussed.[2] Graphene oxide (GO), namely a layered material produced by the oxidation of graphite, has been widely exploited but graphene oxide is electrically insulating and requires further reduction steps to generate a photocurrent signal.[3]

One possible way of overcoming these restrictions is to utilize metallic nanostructures placed at the metal/carbon interfaces. Light absorbed by such metal nanostructures is converted into surface plasmon resonances that cause a local increase in the temperature inducing a reduction of the GO.[4–6] Instead of producing metallic nanostructures by expensive and time-consuming electron-beam lithographic technique, a cheap and fast method relies on the possibility to utilize polymer nanoparticles deposited onto the graphene oxide surface as mask for the

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localized etching of GO layer and then to use such carbon nanowalls for the deposition of a conformal thin metal film.

The fabrication of graphene nanoribbons by utilizing nanosphere lithography in combination with oxygen plasma etching was recently reported.[7] This technique takes advantage of the use of ordered arrays of latex nanospheres as lithographic masks. Instead of the results found by Liu *et al.*[7], when we used polymer nanoparticles for tetrafluoromethane-assisted plasma etching of graphene oxide sheets, it was surprisingly found that this method was capable of fabricating carbon nanowalls.

The polymer nanoparticles served here as a ''sacrificial'' template, protecting the covered graphene oxide from ablation by the plasma. The choice of polymer nanoparticles was motivated by their low cost and the advantage of self-assembled, ordered arrays of nanospheres as lithographic masks, which has long been known to be a low-cost nanofabrication strategy.

In this communication, a novel method consisting of plasma etching of a polystyrene-coated GO surface for the preparation of graphene oxide nanowalls is reported. The effects of the processing on the resulting morphology together with the chemical composition were employed to characterize the graphene structure. In addition, it was found how a simple device consisting of a thin gold film deposited onto such GO nanowalls induces an increase in the electrical current when exposed to light.

EXPERIMENTAL

Graphene oxide was purchased from Cheaptubes (GO; thickness 0.7–1.2 nm estimated by AFM). An aqueous GO solution (1 mg ml^{-1}) was prepared and tip sonicated (750 W, 60 % amplitude) for 1 h to yield a yellow suspension. The solution was transferred to a vial and centrifuged for 30 min at 9000 rpm. The supernatant of the dispersion was carefully extracted and separated from the residual visible at the bottom of the vial. The graphene nanowalls device was prepared as reported in Scheme 1. Al electrodes (1 mm×5 mm) were deposited on a glass substrate by vacuum evaporation with a thickness of 60 nm and space of 0.5 mm. The aqueous GO solution was drop cast onto the Al electrodes. Polystyrene latex particles (Agar Scientific, 10 wt. % dispersion in water with surface-bound sulphate groups as stabilizer, average particle diameter 125 nm) were spin-cast at 500 rpm. The plasma treatment of the samples was realized in a CF$_4$ plasma with a gas flow rate of 20 sccm min^{-1}. The vacuum of the chamber was set at 0.133 Pa and a 13.56 MHz radiofrequency source with power fixed at 35 W was used to create the plasma on top of the sample. The plasma treatments were performed for 5 and 10 min, keeping the substrate temperature at 25 °C. The surface morphology of the films was investigated by field emission scanning electron microscopy (FE–SEM). Infrared spectroscopy in the 500–4000 cm^{-1} range, in the transmission mode was used to investigate the chemical composition.

Gold was sputtered onto the plasma treated GO films for 40 s; the average thickness of the gold films as measured by atomic force microscopy was 12 nm. Electrical characterization was performed using a computer-controlled Keithley 4200 source measure unit. Photocurrent

generation was investigated under exposure of the samples to a solar simulator AM1.5D with an output power of 100 mW cm^{-2}.
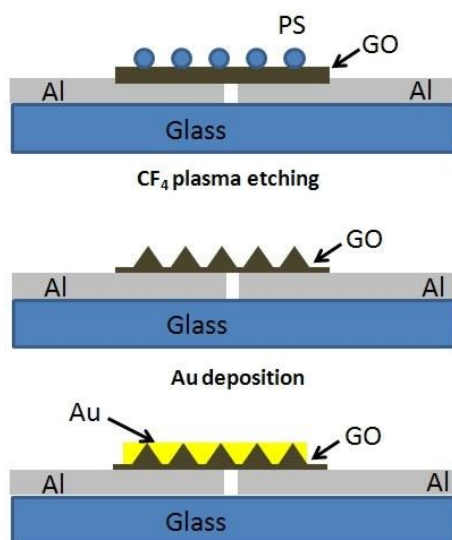
Scheme 1. Schematic presentation of the preparation of GO nanowall devices.

RESULTS AND DISCUSSION

By proper adjustment of the plasma process parameters, a precision control of the obtained nanostructures was achieved; the FE–SEM characterization performed on flat GO (Fig. 1a) and PS latex-coated GO (Fig. 1b) samples showed that after plasma treatment for 5 min, the flat GO morphology was in the form of columnar walls, mainly vertically oriented to the surface of the substrate with the edge having the same dimension of the diameter of the PS latex particles (Figs. 1b and 1c). From Fig. 1c, no trace of residual PS latex particles was found. It was interesting to note that the deposition of gold onto the GO nanowalls did not fill the columnar walls but was conformal to the GO nanowalls (Fig. 1d).

The formation of the GO nanowalls under the nanoparticle masks is due to the anisotropic etching process that has been related to the anisotropic distribution of the plasma ions deflected into the interspacing of the masking nanospheres, as illustrated in Scheme 1. It is expected that the anisotropic etching process plays a role in the anisotropic chemical reactivity of graphene oxide sheet in the reactive plasma etching process.

The most characteristic features in the FTIR spectrum of the GO sample (Fig. 2) are the adsorption bands corresponding to C=O stretching at 1720 cm^{-1} and the sp^2-hybridized C=C in plane stretching at 1629 cm^{-1}.[3] The bands at 3432 and 1390 cm^{-1} are associated, respectively, with the stretching and deformation vibrations of the O−H bond of CO−H; while the band at 1059 cm^{-1} is due to C−O−C in an epoxide group and the signal at about 1246 cm^{-1} could be attri-

buted to C–O epoxide groups.[3] After the plasma treatment, it was observed that the GO nanowalls had retained the same functional groups.
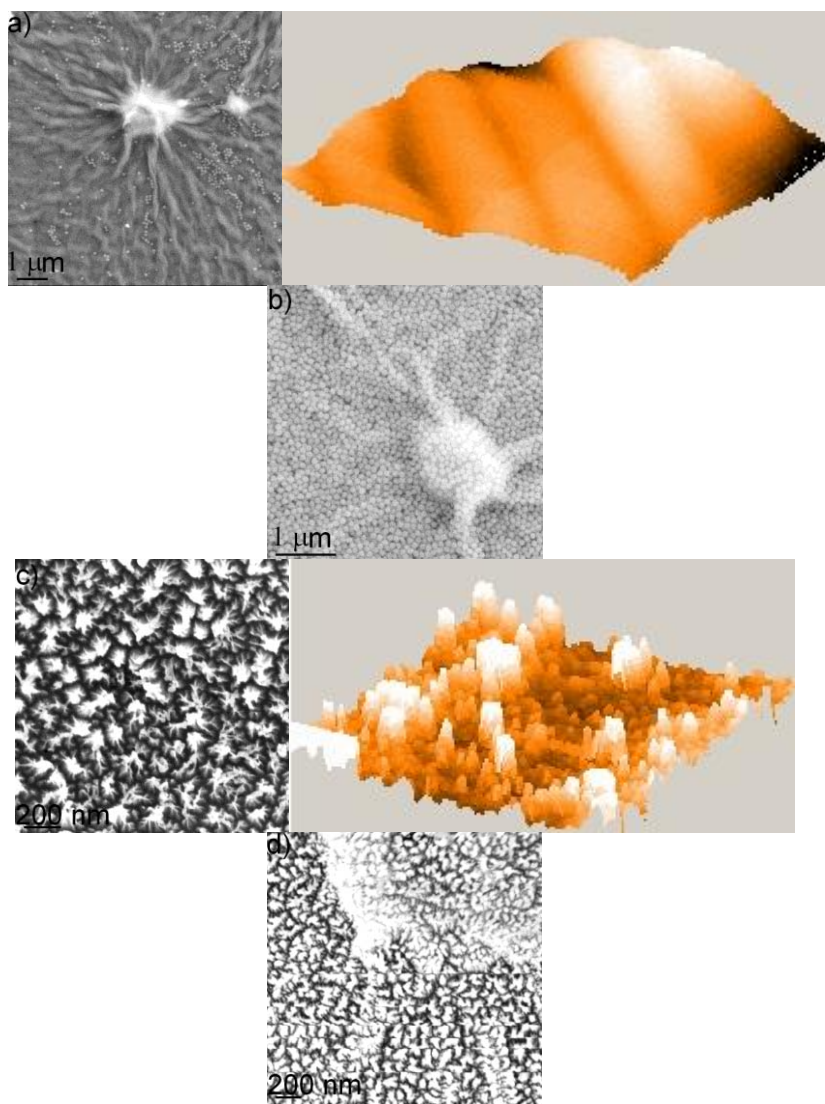

Fig. 1. a) FE–SEM and 3D AFM (500 nm×250 nm) images of GO; b) FE–SEM image of PS latex-coated GO film before plasma treatment and c) FE–SEM and 3D AFM (500 nm×250 nm) images of GO after plasma treatment. d) FE–SEM Image of gold coated GO nanowalls.

GO alone, due to the existence of oxygen-containing groups and its intrinsic high electrical resistance, could not generate a photocurrent signal. The Au film

is very thin and almost transparent to light (Fig. 3a) hence, it could be expected that the GO nanowalls under the gold film are reached by light irradiation, thus allowing the synergic effect of gold sputtered onto such carbon nanostructures to be studied. The current-voltage characteristic of GO nanowalls, as well as of gold coated GO nanowalls, was monitored under illumination. From Figs. 3b and 3c, an increase of the current of the gold-coated GO nanowalls during exposure to light illumination was observed. Uncoated GO nanowalls, as expected (Fig. 3b), did not show a well-defined photocurrent signal when the light was switched "on". Therefore, the photocurrent is attributed to the synergic effect of GO nano-walls and the Au film. The only way to explain these findings could be a deoxy-genation that could recover the GO conductivity to some extent.
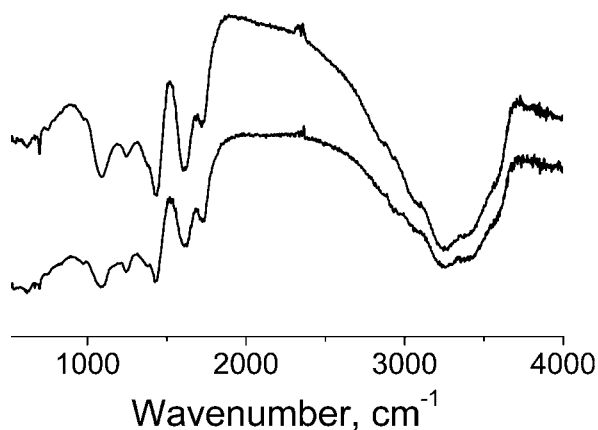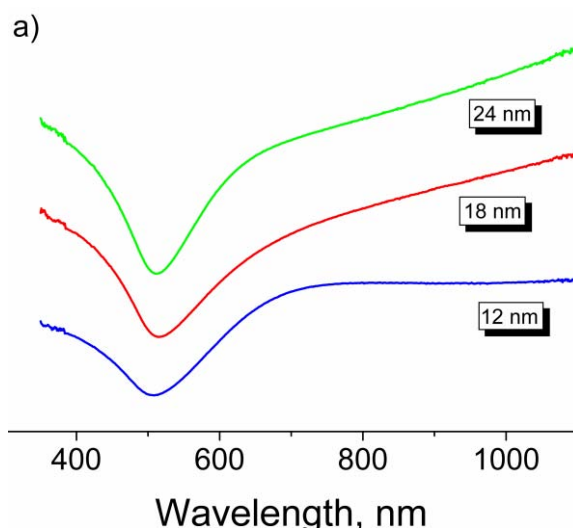

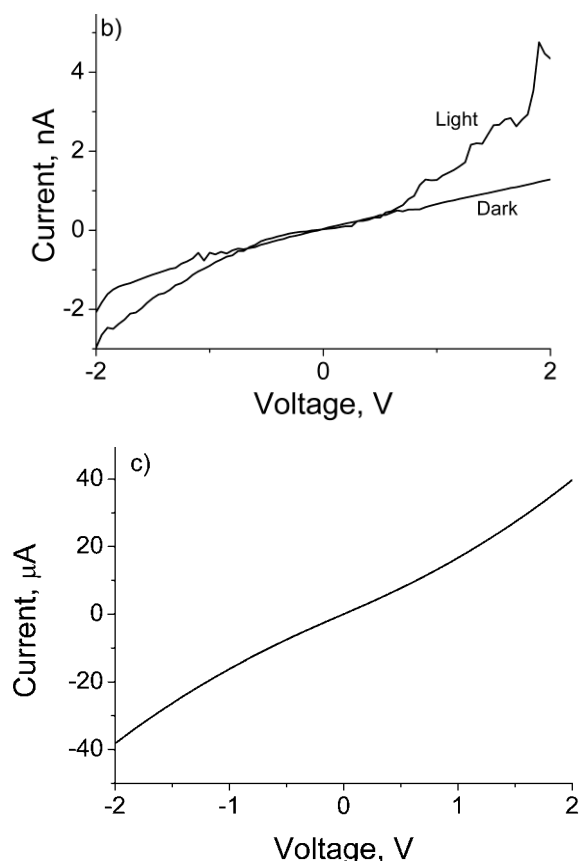Fig. 2. FTIR Spectra of GO (bottom) and GO nanowalls (top) samples.

Fig. 3. a) UV–Vis Transmission spectra of sputtered Au films of different thicknesses; b) *I–V* Curves of GO nanowalls under dark and light conditions; c) *I–V* Curve of gold-coated GO nanowalls under light condition.

Recently, the use of metal nanostructures to induce local heating at metal/carbon interfaces was exploited.[4] The surface plasmon resonances in response to the external electromagnetic radiation causes a local increase in the temperature of the metal nanostructures, which could increase the rate of photo-induced deoxygenation of GO. In this study, a photochemical reduction in which the oxygen functional groups of GO decompose by accepting a hot electron from the photo-excited gold is also suggested.[8]

CONCLUSIONS

A polystyrene latex-assisted plasma etching was used as a novel, fast and economical method for preparation of graphene oxide nanowalls. Mild plasma etching was found to leave the oxygen-based functional groups, but led to the formation of carbon nanostructures that when coated with a thin metallic film

become photoresponsive. Photoresponsive carbon–metal interconnect could be important in graphene-based applications.

И З В О Д

ПЛАЗМА-НАГРИЗАЊЕ ПОЛИСТИРЕНСКИХ ЛАТЕКС ЧЕСТИЦА ЗА ПРИПРЕМУ НАНОЗИДОВА ГРАФЕН-ОКСИДА

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Нанозидови (енгл. *nanowalls*) графен-оксида припремљени су наношењем водене дисперзије полистиренских латекс честица на филмове графен-оксида и накнадним нагризањем тетрафлуорометана у плазми. Благи услови нагризања у плазми омогућавају задржавање кисеоничних функционалних група на зидовима графен-оксида. Уочено је да након излагања зидова графен-оксида превучених танким филмом злата извору ксенонске светлости долази до повећања електричне проводљивости.

(Примљено 22. октобра 2012)

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