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Synthesis of defect graphene and its application for room temperature humidity sensing

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ABSTRACT

Defect graphene was reported by adding sugar through solvothermal method. The characterization results of XRD, IR, Raman, and XPS showed that the samples have tunable mount of oxygenated group, which plays a role as adsorption site to detecting humidity gas molecule. The sample from sucrose has the highest mount of functional oxygenated groups and shows the best humidity property.

1. Introduction

Graphene nanosheet is a potential gas sensing materials with extremely sensitivity [1]. Recent studies have demonstrated that the detecting molecules adsorb only weakly on pristine graphene [1], but more strongly on doped, decorated [2], or defective graphene [3] (i.e., graphene that contains oxygenated group). For defective graphene containing oxygenated group [3], the detected gases include reducing and oxidizing kinds, such as H_2, NH_3, and NO_2. The reported defective graphene containing oxygenated group was obtained by treating graphene oxide (GO) [3]. The sensitivity was mainly attributed to the electron transfer between the reduced GO and adsorbed gaseous molecules.

Herein, we present defect graphene with tunable mount of oxygenated group by adding carbohydrate sugar based on Stride's reports [4]. The selected sugar can increase oxygenated group on graphene. Also, the obtained samples show tunable mount of oxygenated groups and excellent room temperature humidity sensing property.

2. Experimental

Typically, sodium (5 g, >99.7 wt.% pure) and carbohydrate sugar (5 g) with ethanol (50 mL) as solvent was reacted in a sealed Teflon-lined reactor vessel (Parr Instr. Cor. 4843)at 220 °C for 72 h. The selected sugar was fructose and sucrose. The precursor was then rapidly pyrolysed at 600 °C for 2 h, and washed with deionized water and methanol, and then vacuum filtered and dried. For comparison, the sample without adding sugar was also prepared.

The samples were characterized by X-ray diffraction (XRD, Philips X'Pert Pro), infrared spectroscopy (IR, Bruker VERTEX 70), Raman spectroscopy (Horiba Jobin Yvon, LabRAM HR800), X-ray photoelectron spectroscopy (XPS, VG Multilab 2000), and scanning electron microscopy (SEM, FEI Sirion 200 FE-SEM). The gas sensing performance testing was partially based on our previously reported work [5]. Alumina thin flat (6×8 mm), with preprinted Au interdigital electrode, was selected as sensor substrate. The graphene sample methanol solution was gently released to the substrate by a dropper and dry for 5 h to evaporate the solvent. The device was vacuum annealed at 180 °C for 2 h to improve the contact. Finally, the Au electrode was connected with the Au pedestal by a Gold Wire Bonder. The device was located in a steel-made chamber and flowed a mixture of water vapor gas and dry air controlled by mass flow controllers at atmospheric pressure and room temperature. The variation of sensor conductance was measured by using a computer-controlled data collecting card (6008, National Instruments Cor.). The gas-sensing properties were assessed through sensor response, which is evaluated as the conductance ratio of (Gg–Ga)/Ga, where Gg and Ga stand for the electrical conductance in the target gas and in atmospheric air, respectively.

3. Results and discussion

The XRD patterns of the samples are demonstrated in Fig. 1(a). The d_{002} value of samples from fructose, sucrose, and without sugar

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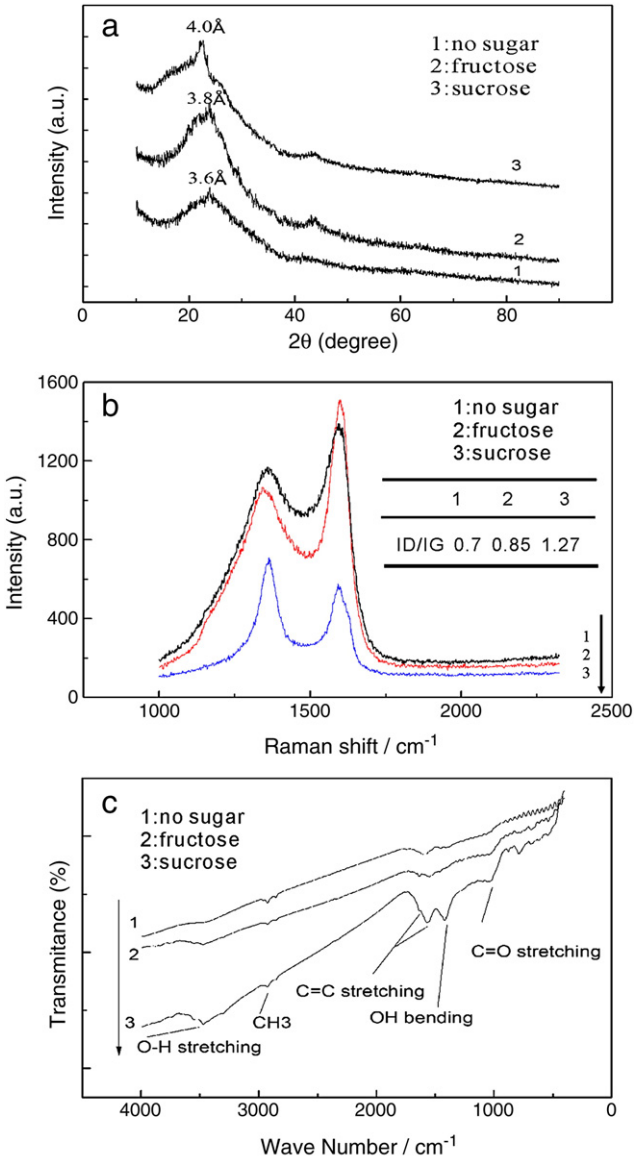


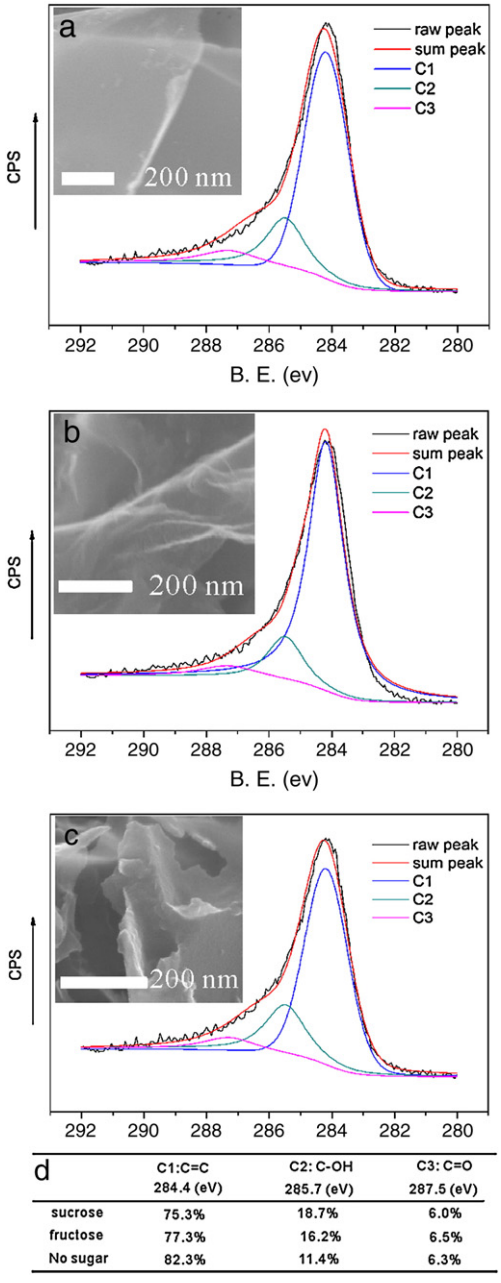
Fig. 1. XRD (a), Raman (b) and IR (c) spectra of graphene sheets. The inset in (b) is the intensity ratio of I_D/I_G.

is 3.8 Å, 4.0 Å, and 3.6 Å, respectively. For pristine graphene, the d_{002} value is 3.4 Å, which is lower than as-prepared samples. For the presence of oxygenated groups attached on both sides of the graphene sheet, graphene samples are expected to be thicker than pristine graphene. The increase means these samples are decorated with organic radicals to tunable extent [6] and the largest d_{002} value means, the sample from sucrose is decorated with densest radicals. Similar results [6,7] about varying d_{002} value were also reported.

For graphene, the intensity ratio of D and G bands (I_D/I_G) of Raman spectra is sensitive to structural changes [8]. As Fig. 1(b) shows the D and G band are situated at 1355 cm^{-1} and 1600 cm^{-1}. The I_D/I_G ratio was calculated to be ca. 0.7 for sample without sugar, and for fructose and sucrose, the value was ca. 0.85 and 1.27, respectively. The increasing of I_D/I_G ratio is due to large mount of defects and impurities caused by residual radicals. This phenomenon can be also attributed to significant decrease of the size of the in-plane sp^2 domains [7].

IR spectra were shown in Fig. 1(c) to further study the residual radicals. For sample from sucrose, strong and obvious absorption peaks were observed. The absorption at 3460 cm^{-1} and 1420 cm^{-1} are attributed to O-H stretching and bending vibration. The C=O stretching is observed at 1025 cm^{-1}. The peaks at 1638 cm^{-1} and 1568 cm^{-1} are attributed to the sp^2-bonded structure of C=C. The absorption at 2925 cm^{-1} is attributed to C—H vibration. The absorption of the other two samples for O—H and C=C vibration are much more weak. However, the skeletal graphene vibration at 1638 cm^{-1} and 1568 cm^{-1} remained the same. These results mean that the sample from sucrose remains the most mount of residual groups on the surface, such as epoxide and hydroxyl radicals.

The high-resolution C 1 s spectra of XPS are carried out to check carbon atoms and oxygen atoms configurations [9]. The complex band was fitted to three components based on IR results, including



d	C1:C=C 284.4 (eV)	C2: C-OH 285.7 (eV)	C3: C=O 287.5 (eV)
sucrose	75.3%	18.7%	6.0%
fructose	77.3%	16.2%	6.5%
No sugar	82.3%	11.4%	6.3%

Fig. 2. Deconvolution of XPS spectra of graphene, (a) with no sugar; (b) from fructose; (c) from sucrose; the inset in (a–c) is the corresponding SEM images; the deconvolution results of XPS (d).