Supplementary Information

Highly Responsive Methanol Sensor based on Graphene Oxide/Polyindole Composites

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Characterization of rGO



Figure S1 Characterization of cm-GO, thermally reduced GO (T-rGO), and chemically reduced GO (C-rGO): (a) FT-IR; (b) XRD; and (c) wide scan XPS.

GO reduction was prepared by two methods: thermal and chemical reductions. T-rGO was obtained by the thermal reduction of cm-GO in a mild thermal annealing at 120 °C, while C-rGO was obtained from the chemical reduction of cm-GO with ascorbic acid or vitamin C. In **Figure S1(a)**, the FT-IR spectrum of cm-GO shows dominant peaks consisting of the O-H stretching, C=O stretching, C=C stretching, O-H deformation of hydroxyl or carboxyl groups, and the C-O-C stretching located at 3388, 1723, 1621,1226, and 1053 cm⁻¹, respectively [1, 2]. The FT-IR spectra of T-rGO and C-rGO distinctly show the C-H stretching at 2899 cm⁻¹; especially in C-rGO, the peak intensity of oxygen functional groups is prone to a larger decrease relative to T-rGO probably because the C-rGO provides a better reduction efficiency. This was further verified by XPS and electrical conductivity testing.

X-ray diffraction spectra of cm-GO, T-rGO, and C-rGO, as shown in **Figure S1(b)**, exhibit different XRD characteristics. The cm-GO shows three diffraction peaks at $2\Theta = 10.43^{\circ}$, 22.71°, and 42.71 indicating the (001), (002), and (100) diffraction patterns, respectively. T-rGO and C-rGO spectra show the dominant (002) diffraction peaks observed at $2\Theta \sim 23.04$ and 24.02, respectively [3, 4]. Moreover, the interlayer spacing (d-spacing) between GO layers decreased from 8.44 Å to 3.90 Å by the thermal reduction and to 3.70 Å by the chemical reduction, in which the interlayer spacings of GO and rGOs were evaluated from the (001) diffraction peak and (002) diffraction peak, respectively. The decrement of the interlayer spacing of rGO is associated with the elimination of unstable oxygen species and moisture trapped between GO layers via the reduction processes [5, 6].

The wide scan XPS spectra are shown in Figure S1(c). For cm-GO, the wide scan XPS spectrum consists of C 1s, O 1s, and S 2p in which the amounts are equal to 67.12, 31.31, and 1.57 atom %, respectively. The presence of S 2p is due to the contamination from H₂SO₄ traces used in the oxidation process of the Hummers method [7]. T-rGO consists of the same elements as cm-GO in which the amount of C 1s, O 1s, and S 2p are 77.05, 21.34, and 1.61 atom %, respectively. But C-rGO composes of C 1s and O 1s at 80.94 and 19.06 atom %, respectively, excluding S 2p. The disappearance of S 2p possibly is a result of the rinsing process during the C-rGO preparation that removed the H₂SO₄ traces. The XPS results clearly show that the amount of oxygen atoms decreased because the unstable oxygen species and moisture trapped between GO layers were eliminated via the reduction processes, while the amount of carbon atom increased involving in the recovery of sp² carbon after the reduction of GO. The reduction ability can be evaluated from the C/O atomic ratio on the carbon skeleton of rGO [8]. The C/O ratio of C-rGO (4.24) is higher than that of T-rGO (3.61), and this suggests that the chemical reduction by ascorbic acid herein provides a better reduction ability than the thermal mild reduction at 120 °C, as observed from the lower residue oxygen moieties on the carbon structure. From the FT-IR and XPS results, they verify that the thermal and chemical reductions were partially completed because the remaining oxygen still remained.

The chemical reduction mechanism by ascorbic acid is still an issue, as J. Gao *et al.*, 2010 proposed that it was arisen from the two-step of bimolecular nucleophilic substitution ($S_N 2$) and then the one step thermal elimination. Because ascorbic acid is nucleophile, it can attack the reactive oxygen species such as the epoxide and hydroxyl groups of GO by the $S_N 2$ reaction, then the H₂O elimination by a thermal process, then rGO and dehydroascorbic acid (the oxidized form of ascorbic acid) are obtained. Finally the dehydroascorbic acid is eliminated by a thermal heating to obtain only the rGO [9]. The thermal reduction mechanism as reported by M. Acik *et al.* in 2011 consists of 3 steps: (i) the hydrolysis by heat in which moisture trapped in GO layers is dissociated

by heat to form H[•] and HO[•] radicals; (ii) the propagation relating to the attack on hydroxyls as well as the ring-opening of epoxide groups by H[•] and HO[•] radicals; and (iii) the termination by forming benzyl/phenyl radicals with CO_2/CO production generated into the spaces between GO layers during the thermal annealing [10].

The electrical conductivity of rGOs was also investigated, the electrical conductivity of C-rGO (1143.11 \pm 3.09 S/cm) is greater than that of T-rGO (684.57 \pm 25.36 S/cm) resulting from the higher reduction ability as confirmed by the greater C/O atomic ratio from XPS. The electrical conductivity values of both rGOs are much higher than that of cm-GO (1.23 \pm 0.38 S/cm), owing to the recovery of sp² hybridized carbon or conjugation network via the reduction process resulting in the increase of electron transfer [11].

The surface morphology of rGOs was also characterized by SEM, shown as Supplementary **Figure S2.** The SEM images showed that C-rGO possessed a more wrinkle surface than T-rGO; the wrinkle was created by the decomposition of oxygen content which eradicated carbon atoms from carbon planes during the GO reduction resulting in a carbon plane distortion afterward [11].



Figure S2 Surface morphologies at 10,000x magnification of (a) GO; (b) T-rGO; and (c) C-rGO.



Characterization of the synthesized GO (OIHM-GO)



The synthesized GO was achieved by the chemical oxidation of graphite powder by the optimized improved Hummers method, it was named OIHM-GO. **Figure S3(a)** illustrates the FT-IR spectra of graphite and OIHM-GO. The characteristic IR absorption peaks of graphite are at 3339, 2896, 1648, and 1053 cm⁻¹ which can be assigned to the O-H stretching, C-H stretching, the C=C stretching of sp² carbon, and C-O stretching in the graphite skeletal, respectively. The presences of the O-H and C-O stretchings in the graphite result from the chemisorption and physisorption of moisture, CO₂ or O₂[12]. The IR characteristic absorption of OIHM-GO shows the dominant peaks at 3178, 1730, 1607, 1403, 1227, and 1052 cm⁻¹ which can be assigned to the O-H stretching, C=O stretching, C=C stretching, O-H deformation of C-OH or carboxyl group, C-O stretching, and C-O-C stretching, respectively [2, 13]. The existence of various oxygen functional groups confirms that the chemical oxidation of graphite was successful.

X-ray diffraction spectra of graphite and OIHM-GO are shown in **Figure S3(b)**, where the XRD diffractogram of graphite shows the remarkably sharp intensity (002) diffraction peak at $2\Theta =$

26.6° indicating the high order of the graphene crystal [14]. The interlayer spacing or distance between the adjacent planes of graphite evaluated from the (002) diffraction peak is 3.34 Å. The XRD pattern of OIHM-GO is similar to the XRD pattern of cm-GO, with the main (001) diffraction peak at $2\Theta = 10.26^{\circ}$ and the low intensity (002) and (100) diffraction peaks at $2\Theta = 20.24^{\circ}$ and 42.44° , respectively. However, the low intensity (001) diffraction peaks and the existing (002) diffraction peak of OIHM-GO suggest the low degree of oxidation [15]. The interlayer spacing of OIHM-GO as evaluated by the (001) diffraction peak is 8.61 Å. The increase in interlayer spacing of OIHM-GO, relative to graphite, results from the existence of oxygen species and water molecules trapped onto the interlayer planes of GO structure after the oxidation process [16, 17].

Wide scan XPS spectra of graphite and OIHM-GO are illustrated in Figure S3(c), where the graphite possesses C 1s and O 1s at 93.49 and 6.51 atomic %, respectively, while OIHM-GO exhibits C 1s, O 1s, and S 2p at 66.62, 31.77, and 1.61 atomic %, in which S 2p indicates a residual H₂SO₄ used in the oxidation process of graphite [7]. The amount of oxygen content in the OIHM-GO (31.77 atomic %) is almost equal to cm-GO (31.31 atomic %). The O/C ratio of OIHM-GO is equal to 47.69 % associated with the band gap energy of approximately 2.87 eV, as estimated by the O/C ratio vs band gap energy graph as reported by V. Gupta et al. in 2017 [18]. The band gap of OIHM-GO is larger than that of graphite (ideal band gap energy of graphite is zero [18]), and thus this confirms the oxidation of graphite. The oxygen species generated by the graphite oxidation can be identified by the high resolution scan C 1s XPS spectra as shown in Figure S3(d). Graphite possesses the high sp² hybridized carbon at approximately 284.59 eV, indicating a conjugation structure with a small quantity of sp³ hybridized carbon at 285.83 eV. Moreover, low amounts of C-O-C and C-OH appear at 287.55eV and 286.69 eV, respectively, as a result of the chemisorption and physisorption of moisture, CO_2 , or O_2 [19]. After the graphite oxidation, a variety of oxygen species such as C=O(OH), C=O, C-O-C, and C-OH groups are observed at the binding energies of 289.75, 288.60, 287.30, and 286.70 eV, respectively. The presences of lower sp² and higher sp³ hybridized carbons are observed at the binding energies of 285.03, and 284.45 eV, respectively, corresponding to the GO structure consisting of a mixture of the sp³ hybridized carbon and the short range sp² hybridized carbon. The conversion of sp² to sp³ hybridization of carbon is due to the creation of free pi-electron in the excited state; it was bonded with oxygen atoms during the graphite oxidation and formed C-O bonds in the graphite layer, resulting in the decrease in the electrical conductivity by several orders of magnitude [18].

The electrical conductivity of OIHM-GO was investigated by the 2-point probe technique. The electrical conductivity of OIHM-GO $(1.45 \pm 0.02 \text{ S/cm})$ was ~ 4 orders of magnitude lower than that of graphite $(17826.36 \pm 5012.23 \text{ S/cm})$; this result is due to the hybridization of sp² carbon changing to the hybridization sp³ carbon after the oxidation resulting in the decrease in the conjugation structure.

Surface morphologies of graphite and OIHM-GO are shown by SEM images in **Figures S3(e) and S3(f)**, respectively. It is apparent that the surface morphologies of these two materials are rather different; the graphite surface is smooth and many graphite layers are observed, while the OIHM-GO shows a rough surface, an agglomeration, and a few GO layers as a result of the oxidation process. Lavin-Lopez, 2016 reported that the GO synthesized by this method had a larger surface area when compared to graphite because the graphite layer expanded after the oxidation process [20].

Characterization of graphene based materials/PIn composites

Peak Assignments	Wavenumber (cm ⁻¹)				
	cm-G/dPIn	cm-GO/dPIn	OIHM-GO/dPIn	C-rGO/dPIn	T-rGO/dPIn
O-H stretching	-	3354	3354	-	-
N-H stretching	3145	3212	3212	3149	3146
C-H stretching	2961, 2925	-	-	-	-
C=O stretching	1704	1686	1685	1702	1701
C=C stretching in aromatic	1612	1617	1617	1612	1611
N-H deformation	1570	1576	1577	1570	1571
C-N stretching	1451	1451	1451	1451	1451
C=N stretching	1379	1381	1381	1379	1379
Cl-O stretching	1144, 1088	1144, 1088	1144, 1088	1144, 1088	1144, 1088
Out of plane deformation of C-H	746	742	742	746	744

 Table S1 Summary of peak assignments of FTIR spectra of the composites

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