Graphene quantum resistive sensing skin for the detection of alteration biomarkers

Tran Thanh TUNG[1], Mickael CASTRO[1], Tae Young KIM[2], Kwang S. SUH[3], Jean-François FELLER[1]*

[1] Smart Plastics Group, European University of Brittany, LIMAT[B]-UBS, Lorient, France.

[2] Electronic Materials & Device Research Centre, Korea Electronics Technology Institute, Gyeonggi-do, Korea.

[3] Department of Materials Science & Engineering, Korea University, Seoul, Korea.

Supporting Information

I.1 Materials

I.1.1 Synthesis of graphene oxide

Graphene oxide (GO) powder was prepared from graphite flakes using modified Hummers method [1-2]. Briefly, 5 g of graphite (Sigma-Aldrich, cat # 332461, ~ 150 µm) and 3.75 g of $NaNO_3$ were placed in a flask. Then, 375 cm^3 of H_2SO_4 was added while stirring in an ice-water bath, and 25 g of $KMnO_4$ were slowly added for 1 h. Stirring was continued for 2 h in the ice-water bath, the ice bath was then removed and the mixture was stirred at room temperature until it became pasty brownish and then diluted with slowly addition of 250 cm^3 deionized water. The reaction temperature was rapid increased to 98°C, and the colour changed to brown colour after 2 hours. Finally, 15 cm^3 of 30 wt% aqueous solution of H_2O_2 was added to complete oxidation. The ions of oxidant and other inorganic impurity were removed by repeating cycle of centrifugation, removal of the supernatant liquid, and redispersing the solid using 3 wt% HCl aqueous solution. After filtration, the solid was dispersed again in water using ultrasonication for 2 h and centrifuged at 6000 rpm for 30 min to remove the multilayered species.

PIL of poly(1-vinyl-3-ethylimidazolium) salts bearing the bis(trifluoromethylsulfonyl)amide anion (NTf_2^- or CF_3SO_2-N-SO_2CF_3) was synthesized according to a previously reported procedure [3, 4].

I.1.2 Synthesis of poly(ionic liquid)

The poly(1-vinyl-3-ethylimidazolium bromide) (PIL(Br^-)) with an average molecular weight (M_w) of ~ 170000 was synthesized in our laboratory according to literature method [5].

a) Step 1: synthesis of ionic liquids (IL)

Monomers 1-vinyl-3-ethyllimidazolium bromides ($ViEtIm^+Br^-$) were prepared by the following procedure. 30 cm^3 alkyl-bromides were added dropwise to 20 cm^3 of 1-vinylimidazole in a 250 cm^3, one-necked round bottom flask under vigorous stirring at room temperature. After 24 hours, white solid monomers are formed, and then they were washed several times with ethyl acetate. The product was filtered and dried in a vacuum oven for 24 hours to get the constant weight of $ViEtIm^+Br^-$.

b) Step 2: synthesis of PIL

10 grams (49.3 mmol) of $ViEtm^+Br^-$ monomer was dissolved in 50 cm^3 of ethanol in a 250 cm^3, round-bottom flask. Then, 0.09 g (0.493 mmol) of azobis(2-methylpropionitrile) (AIBN) as radical initiator was added to the mixture. The solution was heated under N_2 atmosphere for 5 hours at 60 °C. After polymerization, the excess amount of acetone was poured into the formed solution to

precipitate the polymeric ionic liquids. The precipitates were filtered and washed several times with acetone; then, it was dried in vacuum oven at 30 ºC for 24 hours.

c) NMR analysis

In **Error! Reference source not found.**SI (a) ViEtIm$^+$Br$^-$: ^{1}H NMR (400MHz, $CDCl_3$, δ_H, ppm): 10.93 (s, 1H, NC*H*N), 7.83 (s, 1H, NC*H*C), 7.66 (s, 1H, CC*H*N), 7.45 (t, J = 9 Hz, 1H, CH_2C*H*N), 6.02 (d, J = 3 Hz, 1H, *H*CHCHN), 5.41 (d, J = 3 Hz, 1H, HC*H*CHN), 4.50 (m, 2H, NC*H*$_2$$CH_3$), 1.63 (t, J = 6 Hz, 3H, CH_2*C*H$_3$).

In **Error! Reference source not found.**SI (b) PIL: H^{1}NMR [400 MHz, H_2O, δ_H, ppm]: 7.37 (t, J = 9 Hz, 3H, Im), 4.65 (s, 1H, -CH_2C*H*N), 3.98 (m, 2H, NC*H*$_2$$CH_3$), 2.37 (s, 2H, -C*H*$_2$CH-), 1.31 (t, J = 6 Hz, 3H, CH_2*C*H$_3$).

References

1. W. S. Hummers, R. E. Offeman, Preparation of graphitic oxide, **J. Am. Chem. Soc.** 80 (1958) 1339-1339.
2. Y. Liang, D. Wu, X. Feng, K. Mullen, Dispersion of graphene sheets in organic solvent supported by ionic interactions, **Adv. Mater.** 21 (2009) 1679-1683.
3. T. Y. Kim, T. T. Tung, T. H. Lee, J. E. Kim, K. S. Suh, Poly(ionic liquid)-mediated hybridization of single-walled carbon nanotubes and conducting polymers, **Chem. Asian J.** 5 (2010) 256-260.
4. R. Marcilla, E. Ochoteco, C. Pozo-Gonzalo, H. Grande, J. A. Pomposo, D. Mecerreyes, New organic dispersions of conducting polymers using polymeric ionic liquids as stabilizers, **Macromol. Rapid Com.** 26 (2005) 1122-1126.
5. T. Y. Kim, T. H. Lee, J. E. Kim, R. M. Kasi, C. S. P. Sung, K. S. Suh, Organic solvent dispersion of poly(3,4-ethylenedioxythiophene) with the use of polymeric ionic liquid, **J. Polym. Sci. A: Chem.** 46 (2008) 6872-6879.

Figures

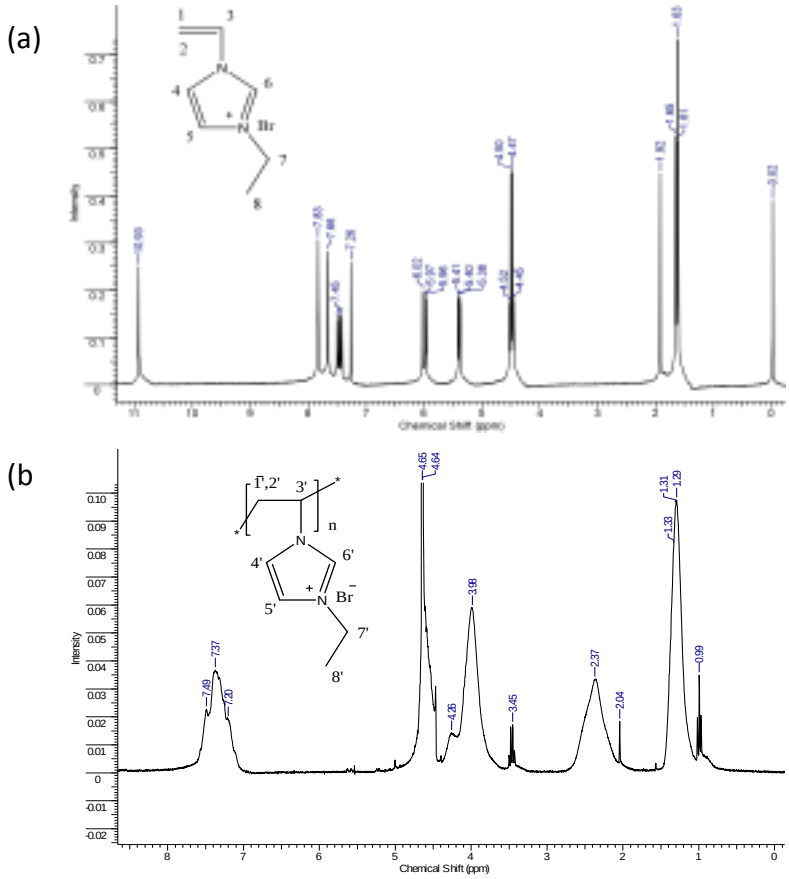
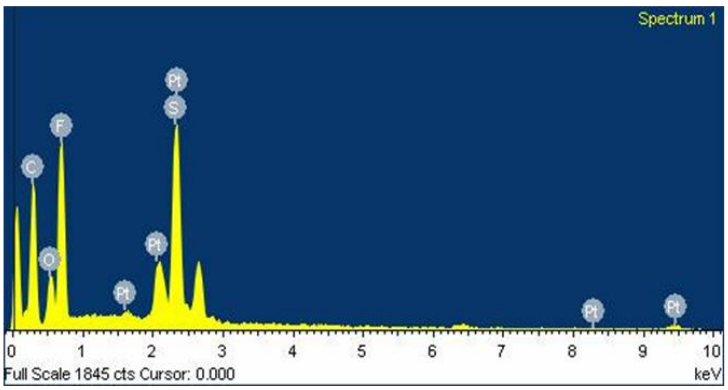
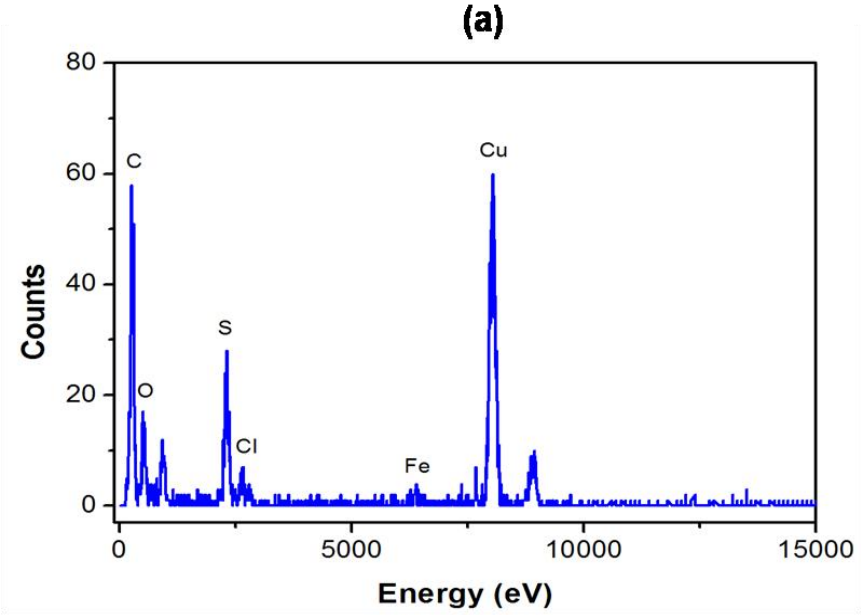


Figure 11SI: 400 MHz 1H NMR spectra of (a) 1-vinyl-3-ethyl-imidazolium bromide and (b) poly(1-vinyl-3-ethylimidazolium) bromide.



(a)



(b)

Figure 12SI: (a) The EDX spectra corresponding to the SEM image of RGO-PIL sample, and **(b)** EDX spectra corresponding to TEM image of RGO-PIL/PEDOT sample.

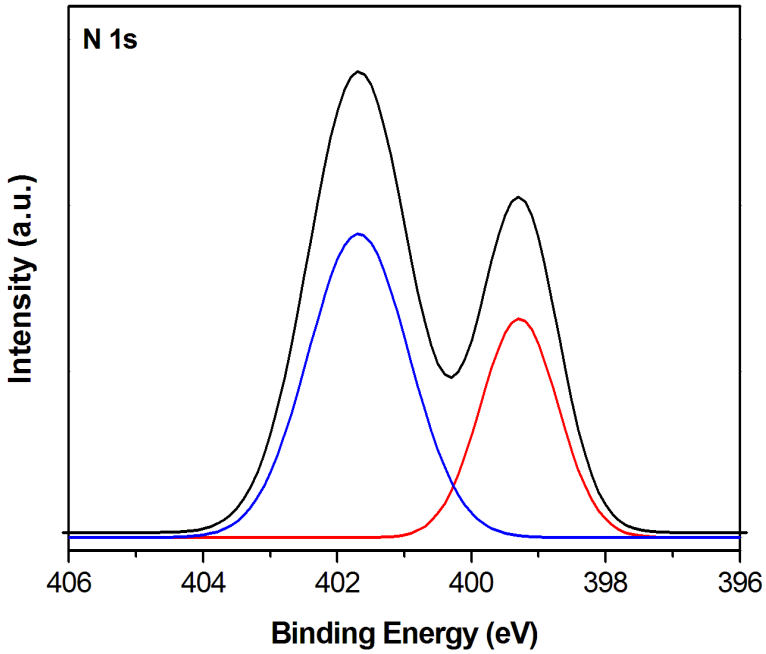


Figure 13SI: N 1s XPS spectrum.