

# Functioned RGO with PolySchiff base: Multi-Chemical Sensor for TNT, Acidochromic and Electrochromic Properties

Lina Ma<sup>1</sup>, Ping Zhao<sup>2</sup>, Wenjun Wu<sup>2</sup>, Haijun Niu<sup>1\*</sup>, Jiwei Cai<sup>1</sup>, Yongfu Lian<sup>1</sup>, Xuduo Bai<sup>1</sup>, Wen  
Wang<sup>3</sup>

<sup>1</sup>Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, Department of Macromolecular Materials and Engineering, *School of Chemistry and Chemical Engineering*, Heilongjiang University, Harbin 150086, P R China. Tel: 086-0451-86608616, E-mail: haijunniu@hotmail.com (Haijun Niu)

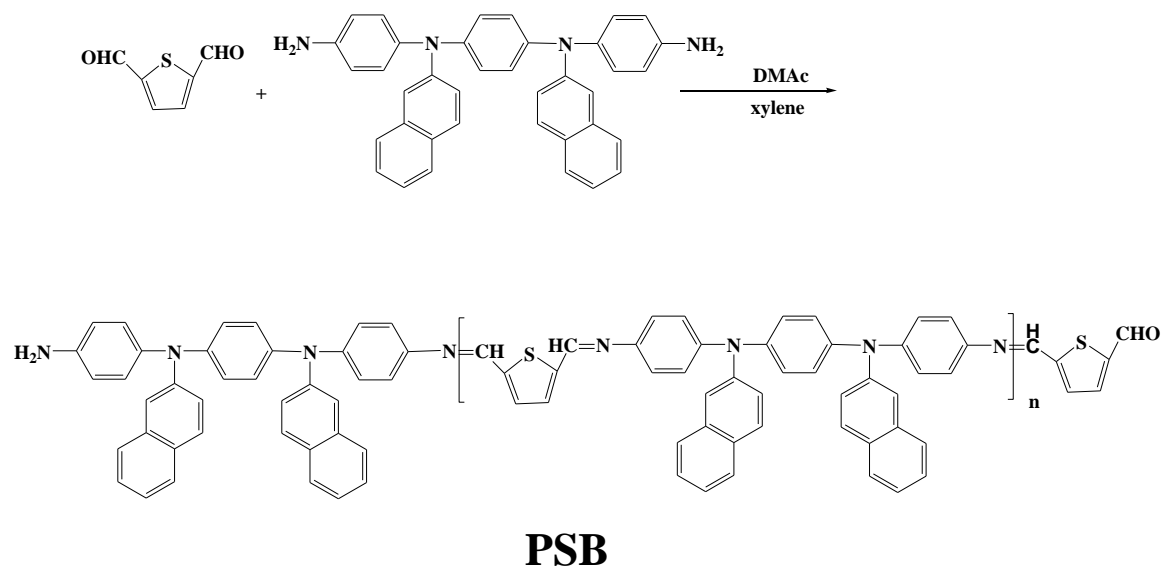
<sup>2</sup>Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, PR China

<sup>3</sup>School of Material Science and Engineering, Harbin Institute of Technology, Harbin 150080, P R China

\* Author to whom correspondence should be addressed

## Synthesis of PSB

Scheme S1 Synthesis routes of PSB



To a three necked 50 ml glass reactor fitted with a magnetic stirrer, Dean-stark trap and

reflux condenser was charged with 0.5420 g ( $1 \times 10^{-3}$  mol) N,N'-bis(4-aminophenyl)-N,N'-di-2-naphthalenyl-1,4-benzene diamine (compound 3), and 10 ml DMAc, 3 ml of toluene. To the stirred solution was added 0.1404 g ( $1 \times 10^{-3}$  mol) 2,5-thiophenedialdehyde three times every 20 minutes, and the solution was heated at 160 °C for 12 h to remove water under Nitrogen reflux. After the reaction, the obtained polymer solution was poured slowly into 50 ml of ice frozen methanol. The precipitate was collected by filtration, washed thoroughly with hot methanol in a Soxhlet apparatus for 48 h, then was dried under vacuum at 70 °C overnight. Reprecipitations of the polymer by NMP / methanol were carried out twice for further purification. Yield: 0.3691 g, 54.28 %, deep red.

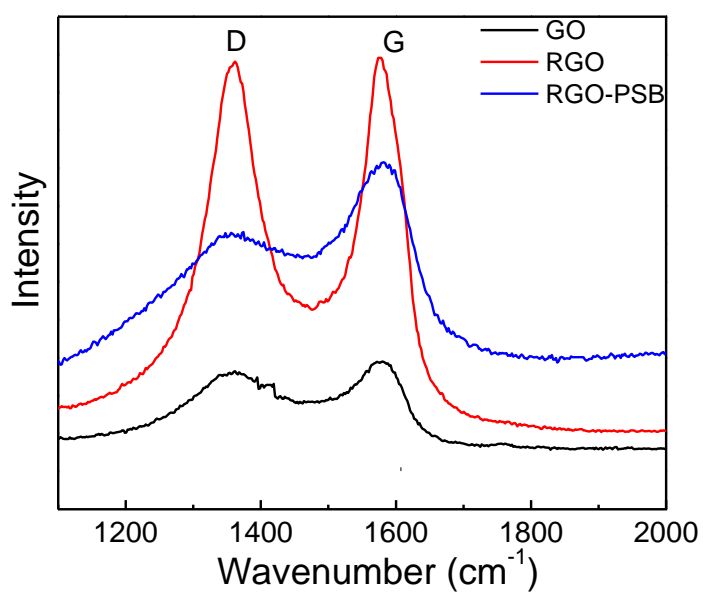
### Measurements and Characterization

The obtained compounds and composites were characterized by the following techniques. Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer in the range of 4000-400  $\text{cm}^{-1}$  at a resolution of 2  $\text{cm}^{-1}$  and for an accumulated 32 scans. Samples were analyzed in a film as pellet in potassium bromide. Raman spectra excited by the second harmonic light of a Nd:YVO<sub>4</sub> laser (532 nm), were recorded on a micro-Raman spectrometer (T64000 Jobin Yvon). Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 6 TGA. Experiments were carried out on approximately 6-8 mg powder samples heated in flowing nitrogen (flow rate = 20  $\text{cm}^3 / \text{min}$ ) at a heating rate of 10 °C / min. UV-vis absorption spectra were recorded using a SHIMADZU UV-3600 spectrophotometer whereas the photoluminescence solution spectra were registered on a Jasco FP-6200 spectrometer with 450 W xenon lamp as the light

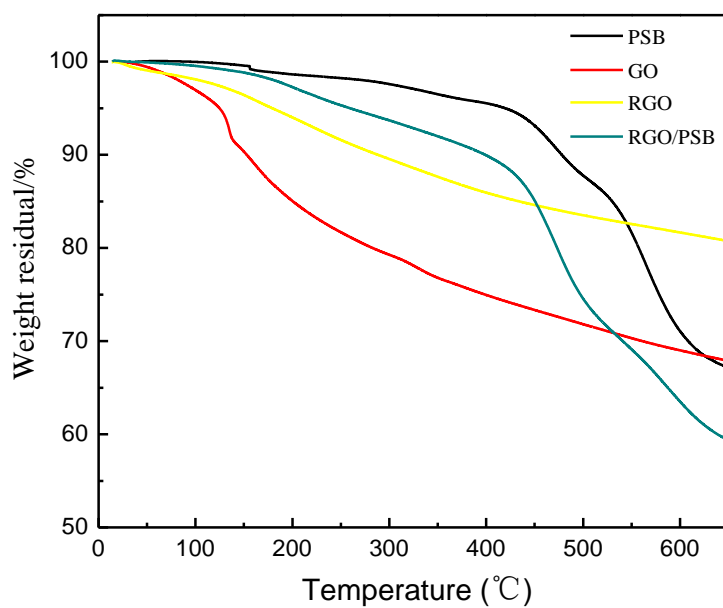
source. The emission spectra of composite were taken at  $\lambda_{\text{exc}}$  being equal to about the wavelength of the absorption maximum. SEM measurement was carried out on a S-4800 instrument with an accelerating voltage of 2 KV, and the samples were sputtered with Pt prior to observation. XPS (X-ray photoelectron spectroscopy) analysis was performed on a VG ESCALABMK II with a Mg K $\alpha$  (1253.6 eV) achromatic X-ray source. Transmission electron microscopy (TEM): JEM-2100) with an acceleration voltage of 200 kV. Carbon-coated copper grids were used as sample holders for TEM analysis. AFM images were recorded on a VECCO. with a Nanonavi Probe Station in tapping mode (dynamic force mode). Commercially available Si cantilevers with a force constant of 20 N/m were used as substrate.

Cyclic voltammetry (CV) measurements were conducted on a CH Instruments 660A electrochemical analyzer at a scan rate of 50 mV s<sup>-1</sup> with a 0.1 M solution of LiClO<sub>4</sub> as an electrolyte under nitrogen atmosphere in dry CH<sub>3</sub>CN. The oxidation and reduction potentials of polymer film coated on an ITO disk were measured using a Pt wire and an Ag / AgCl electrode as a counter electrode and a quasi reference electrode, respectively. Under these conditions, the onset of oxidation and reduction potentials of the polymers thin films against the Ag/AgCl quasi reference electrode were measured and calibrated against the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple.

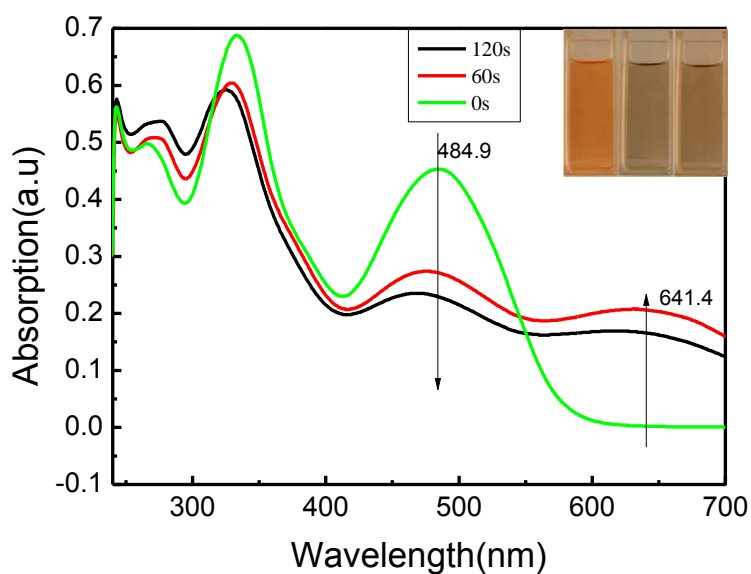
The work function of the PSB and RGO/PSB were obtained by KPFM measurements. The sample solution was cast onto an FTO-coated glass substrate, KPFM studies were performed on KP Technology, SKP-5050 system, using a platinum (Pt)-coated silicon cantilever.



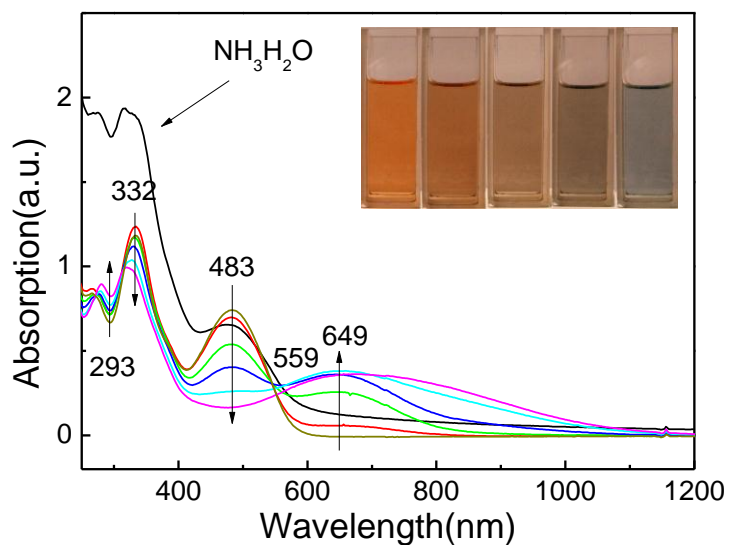
**Fig. S1** Raman spectra of GO, RGO and RGO /PSB



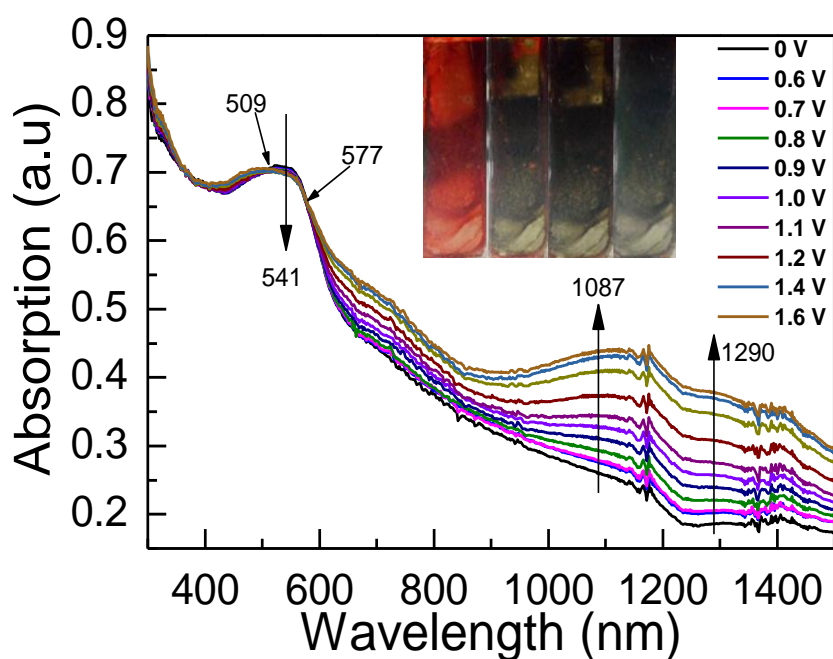
**Fig. S2** Thermogravimetric analysis (TGA) profiles of the samples measured in  $\text{N}_2$ . Heating rate:  
10  $^{\circ}\text{C}/\text{min}$ .



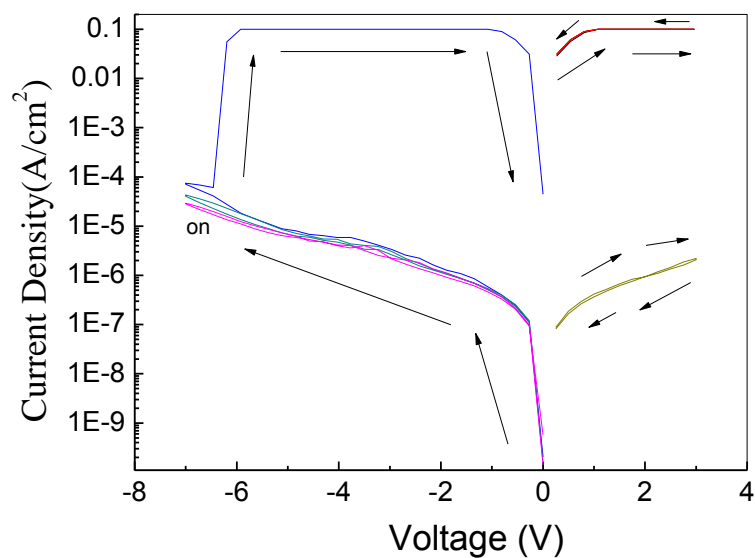
**Fig. S3** UV- visible spectra of RGO /PSB in  $\text{CHCl}_3$  in photochromic process under UV at 365 nm during different time at room temperature .



**Fig. S4** UV-visible absorption spectra of pure PSB in  $\text{CHCl}_3$  solution as it were protonated by HCl vapor in steps, where the concentration PSB was  $0.05 \text{ mg L}^{-1}$ . Spectra proceeded with HCl doping time increasing, and the colour of the solutions changed from yellow to blue, further exposure of the solutions to ammonia vapor reversed the color to the initial state. Inset photographs indicated the color evolved in the process of doping HCl vapor.



**Fig. S5** Electronic absorption spectra of PSB in the process of electrochemical p-type doping between 0.0 and 1.6 V with 0.05 V potential intervals ( insets are the pictures of doped PSB).



**Fig. S6** Current density-voltage (J-V) characteristics of the Au / RGO/PSB / Pt device  
The electrically controlled bidirectional electron transfer between RGO noncovalently functionalized by PSB was observed from the characteristic J-V curves of the Au / RGO-PSB / Pt device (Fig. 1) under ambient conditions. The J-V curves

clearly displayed electrical bistable memory behaviors. The voltage applied to the device was varied in a cycle from  $0 \rightarrow -7 \rightarrow 0 \rightarrow 3$  V. Starting with the OFF state (low-conductivity state) in the as-fabricated device, the current increases slowly with the applied negative voltage sweep ( $0 \rightarrow -7$ ). At the switch-on voltage of about -5.9 V, the current density increases abruptly from  $10^{-4}$  to  $10^{-1}$  A/cm<sup>2</sup>, indicating device transition (writing process) from the OFF state to the ON state (high-conductivity state). After removing the power supply, the device is still in the ON state. These results indicated that “OFF” and “ON” can be encoded from the corresponding low-conductivity state (before writing) and high-conductivity state (after writing), with an applied voltage (read voltage) in the range of 0 to -5.9 V. The OFF state of the device can be read and reprogrammed to the ON state again in the subsequent negative sweep. Such a cycle is a typical “write-read” process for a nonvolatile rewritable memory device. The devices based on RGO /PSB show nonvolatile resistive switching behavior with a good ON /OFF ratio. These results provide a new strategy for controlling the electronic properties of RGO /PSB for high performance memory device applications. The further efforts including the application of RGO /PSB in memory effect are currently underway in our lab.