

Electronic Supplementary Information (ESI)

A Paper Indicator for Triple-Modality Sensing of Nitrite Based on Colorimetric Assay, Raman Spectroscopy, and Electron Paramagnetic Resonance Spectroscopy

Zhibin Wang,^a Jingfang Wang,^b Zhiwei Xiao,^c Junfei Xia,^a Peipei Zhang,^a Tao Liu,^c Jingjiao Guan^{a,d,*}

a. Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Florida State University, Tallahassee, Florida 32310

b. Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306

c. Department of Industrial and Manufacturing Engineering, FAMU-FSU College of Engineering, Florida State University, Tallahassee, Florida 32310

d. Integrative NanoScience Institute, Florida State University, Tallahassee, Florida 32306

Email: guan@eng.fsu.edu

Materials

Poly(4-aminosytrene) (PAS, Mw>150,000) was purchased from Polysciences, Inc. (Warrington, PA). 2-naphthol, sodium nitrite (99.999% trace metals basis), and sodium dodecylbenzene-sulfonate (SDBS) were purchased from Sigma-Aldrich. Filter paper (Grade 413, Qualitative) was purchased from VWR.

As-grown high-pressure catalytic decomposition of carbon monoxide (HiPco) single walled carbon nanotubes (SWCNTs) were purchased from Unidym Inc. (Sunnyvale, CA, batch #: R0544). Preparation and characterization of SWCNT dispersions are described in references 1 and 2 of this file. Briefly, 16 mg of SWCNTs were sonicated in 100 mL of 0.7 wt % SDBS/water solution by a horn sonicator (Misonix sonicator 3000, Frequency 20 kHz) in an ice bath. The sonication was operated at a pulse operation mode (on 10 sec, off 30 sec) with the power level set at 45 W for 4 hr. To eliminate SWCNT bundles and aggregates, the as-sonicated SWCNT dispersions were subject to ultracentrifugation at 200,000 g-force for 3 hr with a MLS-50

swinging bucket rotor using an OptimaTM MAX-XP Ultracentrifuge (Beckman Coulter). Supernatants were collected and used for preparing the paper indicators.

Methods

1. Preparation of paper indicators

The procedure for preparing the paper indicators impregnated with all three component materials is as follows: (1) A filter paper was cut into 1 cm × 0.7 cm rectangular or 0.7 cm-diameter circular pieces. (2) A piece of the paper was immersed in the SWCNT dispersion, kept for 1 hr, removed from the solution, rinsed with deionized (DI) water, and dried in air. (3) The piece of the paper was immersed in 1 wt% PAS aqueous solution (pH=1), kept for 5 min, removed from the solution, and dried in a 65°C oven. (4) The piece of paper was immersed in 15 wt% 2-naphthol in ethanol, kept for 2 hr, removed from the solution, and dried in the 65°C oven.

To prepare paper indicators impregnated with one component material, the corresponding step described above for the material was adopted. Two of the steps were combined to prepare the paper indicators containing two component materials.

2. Nitrite sensing

50 mL acidified nitrite solution was prepared by mixing 45 mL aqueous solution of sodium nitrite at specified concentrations with 5 mL 0.5 M HCl solution. The solution was added into a 50 mL plastic centrifuge tube (VWR). A piece of paper indicator was taped onto the internal face of the cap of the tube. The cap was snapped on the tube and held upright for a specified period of time at the room temperature (~20 °C) before the paper indicator was removed for characterization. The distance between the paper indicator and the surface of solution was ~9 mm.

1.5 mL acidified nitrite solution was prepared by mixing 1.3 mL aqueous solution of sodium nitrite at a specified concentration with 0.2 mL 0.5 M HCl solution in a 1.7 mL centrifuge tube (VWR). A piece of circular paper indicator with a diameter of 0.7 cm was taped to the internal face of the cap of the tube. The cap was then snapped on the tube and held upright for 20 min at the room temperature (~20 °C) before the paper indicator was removed for characterization. The distance between the paper indicator and the surface of the solution was ~6 mm.

3. Characterization

Colorimetric assay: The paper indicators were scanned with an Epson Perfection® V200 Photo scanner into images. Image J program (U.S. National Institutes of Health) was used to read the red and green intensities of the scanned images. Data were collected from six sets of paper indicators.

Raman spectroscopy: All Raman spectra were obtained using a Jobin-Yvon Horiba LabRAM HR800 800 mm focal length microRaman spectrograph. The spectrometer was equipped with a 50× objective (Leica, NA=0.80) for precise focal positioning and a 600 gr/mm holographic grating. Excitation for a normal Raman studies was provided by a 785 nm laser (TOptica DL100 Diode laser). Signals were detected by a 1024×256 element CCD detector (Wright, Open electrode). All samples were analyzed in the spectral range of 100-1700 cm^{-1} at room temperature. Each spectrum was the result of three 20 sec exposures which were ensemble averaged. Six sets of paper indicators were measured with three points on each paper indicator being randomly chosen for the measurement.

EPR spectroscopy: EPR samples were prepared by cutting the paper indicators into several small rectangular pieces of $\sim 2 \text{ mm} \times \sim 3 \text{ mm}$ in dimensions. The small pieces were loaded into a quartz tube, which was then inserted into a Bruker Elexsys-500 X-band spectrometer. Continuous-wave EPR measurements were carried out at room temperature with power of 1 mW, modulation frequency of 60 kHz, and modulation amplitude of 2 Gauss. Every EPR spectrum was normalized by dividing its amplitude by the weight of the sample.

Supplementary results

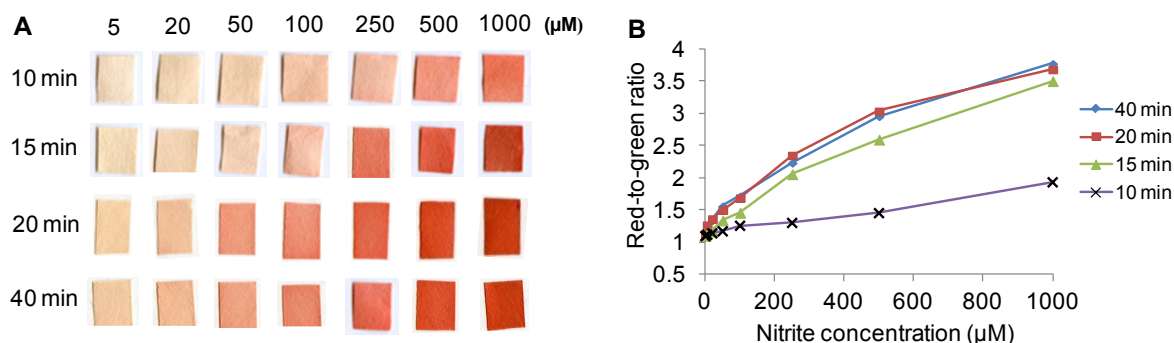


Fig. S1. Effect of exposure time on nitrite detection by colorimetric assay. (A) Scanned images of the paper indicators exposed to vapour generated from acidified nitrite solutions with a series of concentrations for different exposure times. (B) Quantification of colour changes of the paper indicators. The 10 min exposure generated red colour with different intensities, but the range of the colour intensity and the range of the red-to-green ratios were smaller than those generated by the longer exposure times. 10 min exposure time is thus undesirable for achieving the highest possible resolution of the technique. The 15 min exposure generated larger ranges of red colour and red-to-green ratio than those produced by the 10 min exposure. However, the colours at 5, 20 and 50 μM nitrite were too similar to differentiate. So 15 min exposure time was not desirable either. Both 20 and 40 min exposure times generated wide ranges of colours and red-to-green ratios. The colours and ratios were also differentiable over all nitrite concentrations. For the envisioned sensing application, the shorter exposure time (20 min) is obviously superior to the longer time (40 min).

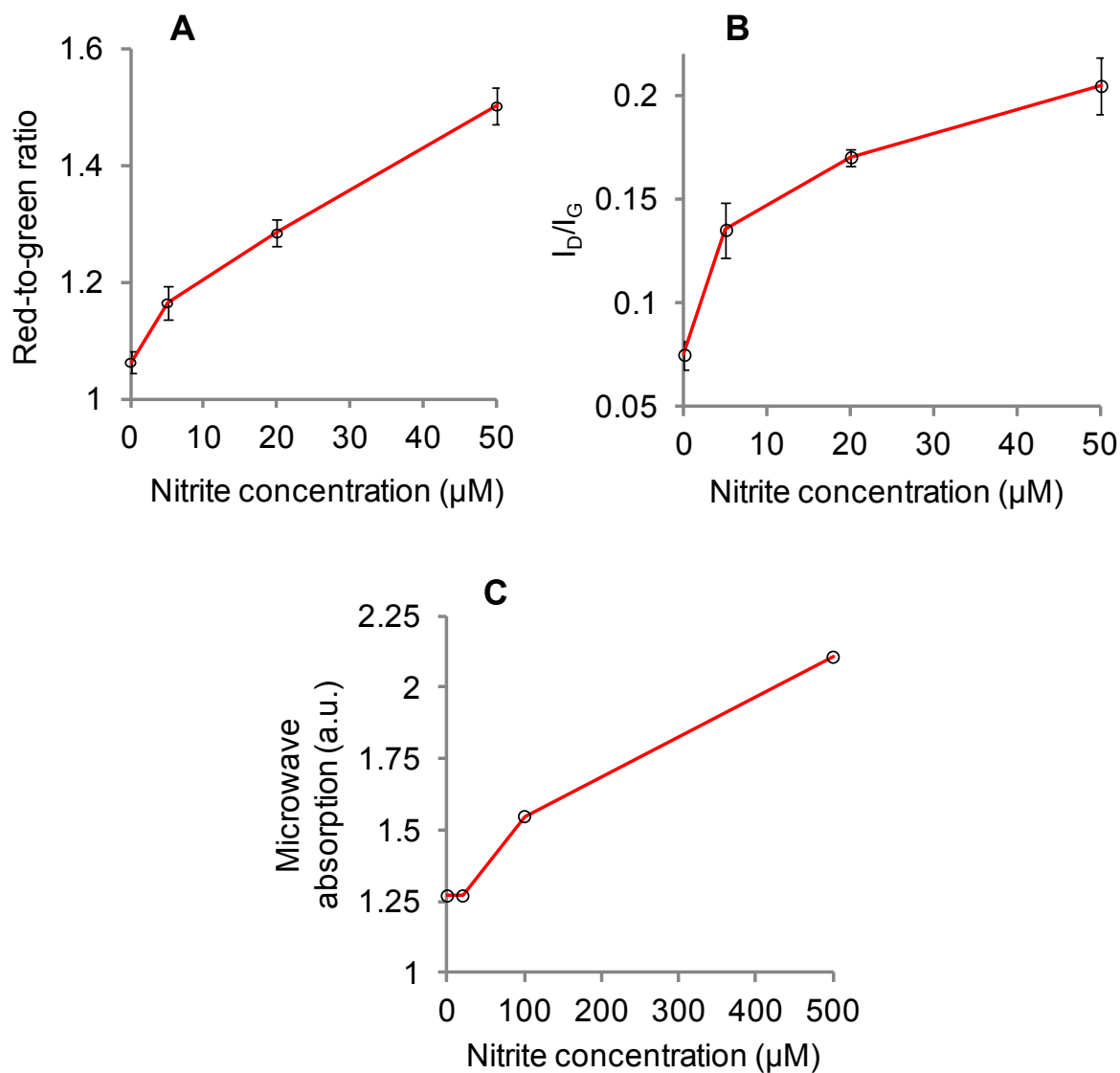


Fig. S2. (A) Plot of the first four data points of Fig. 3A2. The lower detection limit (LDL) was visually determined to be 5 μM . (B) Plot of the first four data points of Fig. 3B2. The LDL was visually determined to be 5 μM . (C) Plot of the first four data points of Fig. 3C2. The LDL was visually determined to be 100 μM .

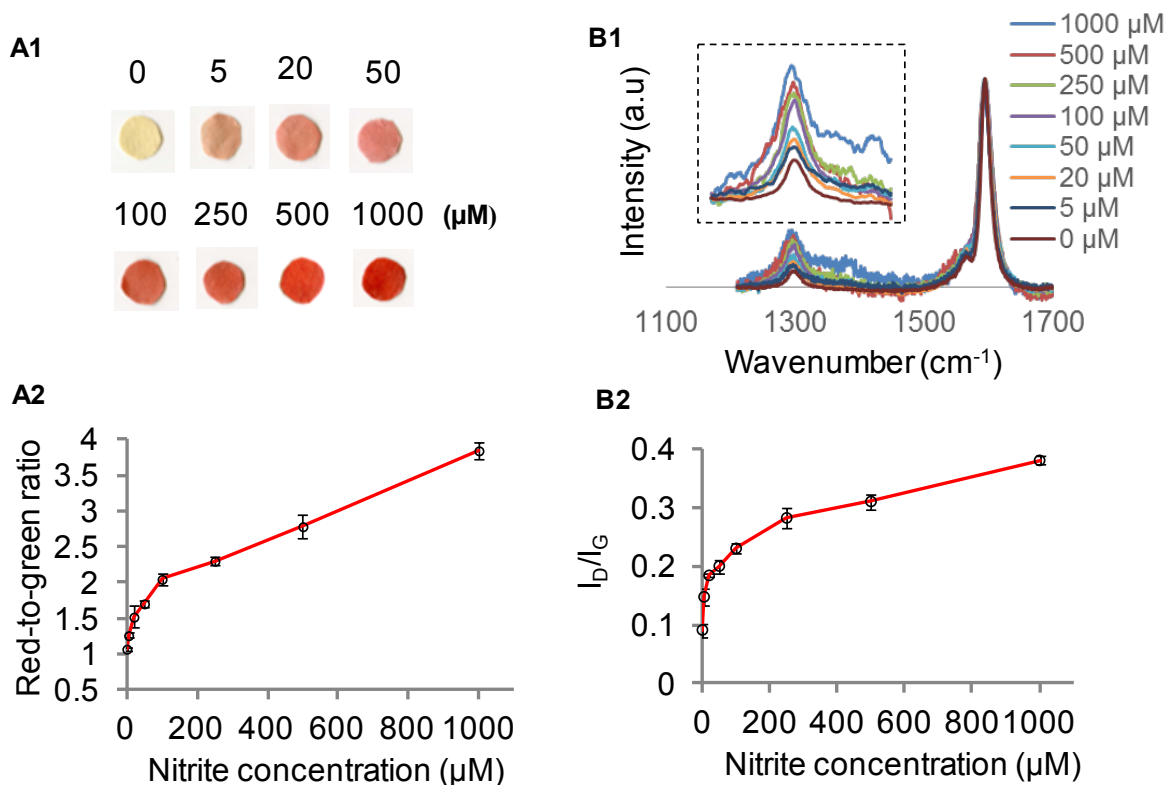


Fig. S3. Nitrite sensing by colorimetric assay and Raman spectroscopy using a 1.5 mL volume of the nitrite solution. (A1) Scanned images of the paper indicators exposed to vapour generated from acidified nitrite solutions with a series of concentrations. (A2) Quantification of colour change of the paper indicators. Points and bars represent averages and standard deviations respectively obtained from 3 sets of samples. (B1) Raman spectra of the paper indicators. Each spectrum was normalized against its G band. Inset shows enlarged D bands. (B2) I_D/I_G ratios plotted against nitrite concentration. Points and bars represent averages and standard deviations respectively obtained from 3 sets of samples.

References:

- 1 Tao Liu, Sida Luo , Zhiwei Xiao , Chuck Zhang and Ben Wang, Preparative Ultracentrifuge Method for Characterization of Carbon Nanotube Dispersions. *Journal of Physical Chemistry C*, 2008. 112(49): 19193-19202.
- 2 Tao Liu, Zhiwei Xiao, Ben Wang, The exfoliation of SWCNT bundles examined by simultaneous Raman scattering and photoluminescence spectroscopy. *Carbon*, 2009. 47(15): 3529-3537.