

3-D nanorod arrays of metal-organic KTCNQ semiconductor on textile for flexible organic electronics

Rajesh Ramanathan,^a Ahmad Esmailzadeh Kandajani,^a Sumeet Walia,^b Sivacarendran Balendhran,^b
Suresh K. Bhargava,^c Kourosch Kalantar-zadeh^b and Vipul Bansal^{a,*}

^aNanoBiotechnology Research Laboratory (NBRL), ^cCentre for Advanced Materials and Industrial
Chemistry, School of Applied Sciences, and ^bSchool of Electrical and Computer Engineering, RMIT
University, GPO Box 2476V, Melbourne VIC 3001, Australia

Fax: +61 3 9925 3747; Tel: +61 3 9925 2121 ; *E-mail: vipul.bansal@rmit.edu.au

Electronic Supplementary Information

Experimental Details

Materials. Cotton fabric was purchased locally. 7,7,8,8-Tetracyanoquinodimethane (TCNQ), potassium hydroxide (KOH) and acetonitrile were obtained from Fluka, Sigma and Ajax, respectively. All chemicals were used as received.

Textile-templated KTCNQ substrate synthesis. In a typical synthesis of KTCNQ substrates, a piece of textile ($1 \times 2 \text{ cm}^2$) was initially immersed in 1 mL of 1 M KOH solution in water for 1 hour. The textile was then removed and dried in an oven ($100 \text{ }^\circ\text{C}$) for one minute following which it was immobilized on a glass surface for chemical vapor deposition (CVD) process. For CVD, TCNQ powder was loaded into a ceramic boat and the textile immobilized on the glass surface was placed on the top of the ceramic boat with the textile side facing down. The boat with the substrates was placed into a 2" quartz tube inserted into a tube furnace. The reaction time and temperature were accurately controlled. The temperature was first increased to $140 \text{ }^\circ\text{C}$ and then held for 2 h for CVD. At the end of the reaction, the tube was allowed to cool down to room temperature. The CVD process was carried out under argon gas environment with a flow rate of 50-80 standard cubic centimeters per minute. Following the completion of the CVD process, the surface of the textile was observed to turn reddish/purplish, indicating the formation of KTCNQ. These KTCNQ textile substrates were further utilized for all characterisation and electrical measurements.

Characterisation. The nanostructured surfaces of pristine and KTCNQ textile were studied by scanning electron microscopy (SEM) using FEI Quanta 200 ESEM instrument operated at an accelerating voltage of 20 kV. Raman spectroscopy measurements were carried out using Perkin-Elmer Raman Station 200F utilizing an excitation wavelength of 785 nm, 100 μm spot size, 1 sec exposure time and an average of 20 acquisitions. The Raman spectra were background corrected using an in-house developed wavelet transform/signal removal algorithm (Kandjani, A. E. *et al.* **2013**, 44, 608). FTIR measurements were carried out using Perkin-Elmer D100 spectrophotometer in attenuated total reflectance (ATR) mode with a resolution of 4 cm^{-1} . X-ray photoemission spectroscopy (XPS)

measurements were carried out using Thermo K-Alpha XPS instrument at a pressure better than 1×10^{-9} Torr ($1 \text{ Torr} = 1.333 \times 10^2 \text{ Pa}$). The general scan, C 1s, N 1s, O 1s, and K 2p core level spectra for the samples were recorded with un-monochromatized Mg K α radiation (photon energy of 1253.6 eV) at a pass energy of 20 eV and electron take off angle of 90°. The overall resolution was 0.1 eV for XPS measurements. The core level spectra were background corrected using Shirley algorithm and chemically distinct species were resolved using a nonlinear least squares fitting procedure. The core level binding energies (BE) were aligned with adventitious carbon BE of 285 eV.

Electrical measurements and sensing. For electrical and NO₂ gas sensing experiments, KTCNQ textile devices were fabricated by placing a $0.5 \times 1.5 \text{ cm}^2$ piece of KTCNQ textile on a quartz substrate and placing 1 mm^2 contacts on either side of the long axis of the fabrics using silver paste. These devices were placed in a temperature-controlled closed quartz chamber fitted with microelectrodes in a two electrode configuration. The resistance variation as a function of time of the textile-templated KTCNQ substrates was measured using a Keithley 2001 multimeter equipped with a data acquisition system. The sensor cell and electronics were enclosed in a temperature-controlled chamber (Linkam Scientific Systems) and exposed to H₂ (1.0% hydrogen zero air balance) and NO₂ (10 ppm in ambient air) gases. The gas exposure was maintained at 200 sccm using a MKS mass flow controller. The measurements were carried out at different operating temperatures in the range of 30–180 °C. For solar light exposure, an ABET Technologies LS-150 series 150 W Xe arc lamp source that simulates solar light under equator conditions was used, producing 1.5 sun, with the device placed in the quartz chamber at 8 cm distance from the source.

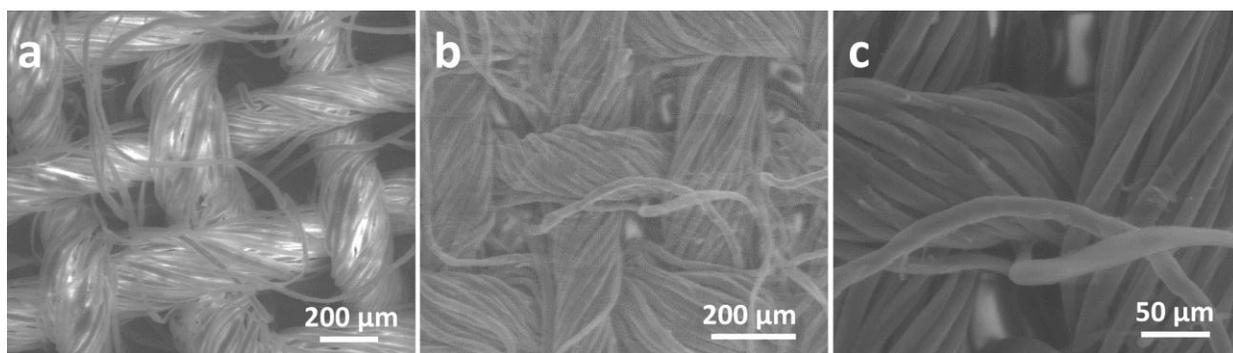


Figure S1. SEM images of (a) pristine untreated textile and (b and c) KOH-treated textile.

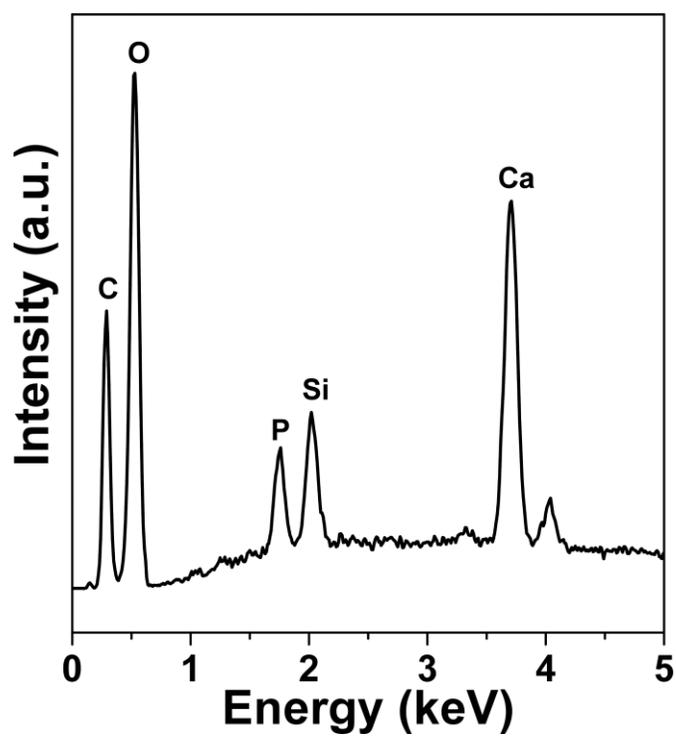


Figure S2. EDX spectrum of pristine untreated textile.

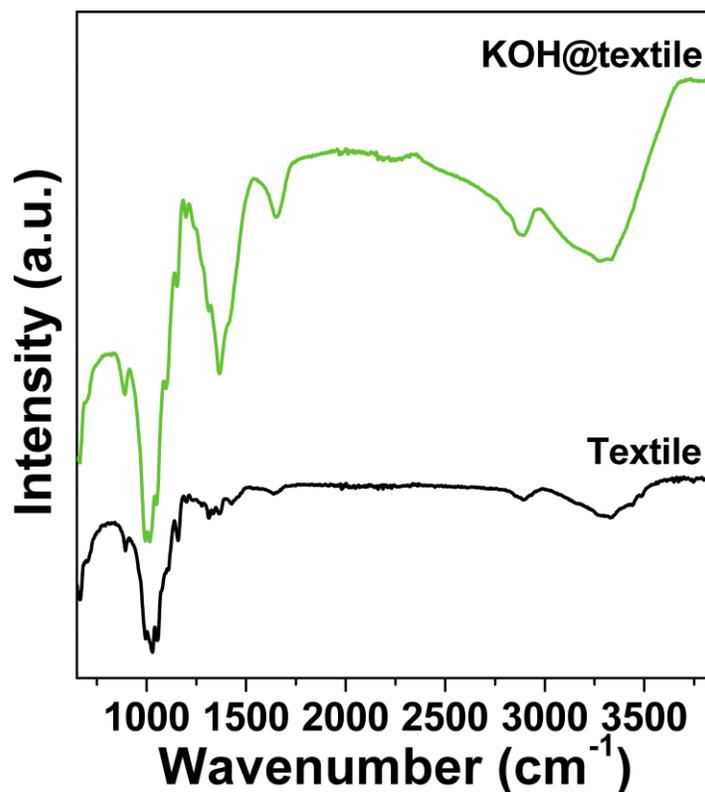


Figure S3. FTIR spectra of pristine untreated textile and KOH-treated textile. The pristine textile shows characteristic stretching vibrations arising from the cellulose component that typically includes the –OH stretching vibrations between 3600-3100 cm⁻¹, –CH stretching between 3000-2800 cm⁻¹, and bands at 1363, 1425 and 1640 cm⁻¹ due to –OH, symmetric –CH and H-O-H bending modes, while the ring C-O stretching is observed at 1061 and 1032 cm⁻¹. The KOH treated fabric also showed similar vibrations suggesting that there is no degradation of the cellulose components. Interestingly, the –OH vibrations at 1363, 1640 and 3100 cm⁻¹ were found stronger suggesting that the binding of KOH to the cellulosic components of the fabric.

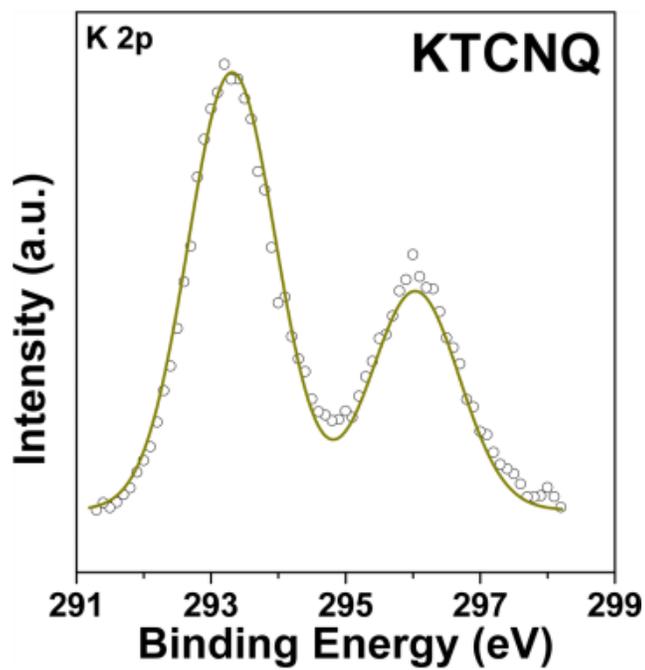


Figure S4. XPS analysis showing K 2p core level from the KTCNQ textile.