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Sensing of ammonia at room temperature by polypyrrole-tin oxide nanostructures: Investigation by Kelvin probe force microscopy

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ABSTRACT

The present investigations focus on gas sensing response of nanowires of pure polypyrrole (PPy) and polypyrrole-tinoxide nano-composites (PPy-SnO_2). These composites comprise of polypyrrole nanotubes enveloped around tin oxide nanoparticles. The sensing response of these nanowires towards ammonia gas has been estimated by measuring changes in the surface resistance of the samples in ammonia with respect to air. At room temperature, at 100 ppm of ammonia, the sensitivity of pure PPy nanowires is about 18%, whereas no response has been observed in the SnO_2 particles upto 250 °C. However, it is intriguing that the sensitivity (~26%) of the composite sample is greater than the pure PPy sample at room temperature. Also, the sensitivity increases with an increase in ppm level of ammonia. To probe this sensing behavior, we have employed Kelvin probe force microscopy (KPFM) system for imaging the potential changes on the surface of the sample. Ammonia gas was introduced in a specially designed cell. With the help of our KPFM investigations, it has been proposed that the faster and greater response of sample PPy-SnO_2 towards ammonia can be attributed to the presence of large number of charge compensating sites/diode interfaces which are absent in pure PPy sample.

1. Introduction

The ability to test small amount of gas molecules in the surroundings plays a very vital role in life saving situations. Various sensing devices help in perceiving presence of toxic gases and volatile vapors. In sensor technology, metal oxides have been of great interest. Metal oxides like tin oxide (SnO_2) have exceptionally good sensitivity, selectivity, and stability and hence find wide range of applications in sensing devices. But these conventional inorganic sensors exhibit a complex assembly process because of their higher operating temperatures (150–400 °C).They require round the time working of the heating element, causing degradation of material and vulnerability of heating element [1–5].

For sensing devices, conducting polymers have come up as a better alternative to inorganic sensors. The oxidation level of conducting polymers is readily affected by chemical or electrochemical doping/dedoping (oxidation/reduction) mechanisms, causing a sensitive and rapid response [5–9] to a variety of chemicals. This interaction between a conducting polymer and gas analyte is pretty strong at room temperature and is generally measured as a change in the surface resistance of the sample when exposed to the analyte. Therefore, the sensors based on conducting polymers can give significant response [6–9], while those based on inorganic metal oxide nearly have no sensitivity at room temperature. Moreover, the sensors based on conducting polymers have lower energy consumption and simple device configuration [7–10]. However, these materials still have stability issues under ambient conditions. Therefore, ideal device operations can be anticipated by preparing composites, where, polymer governs the room temperature applicability and metal oxide provides stability and selectivity. Several research groups have shown the effectiveness of an organic/inorganic hybrid system for gas sensing applications [11–15]. Furthermore, the mechanism of interactions of metal oxide with PPy needs better understanding for full device optimization. For example, the interaction between p-type polymers like polypyrrole with n-type oxide like tin oxide in presence of an electron donor or acceptor gas still requires thorough investigations. We have attempted to answer these issues by Kelvin-probe force microscopy (KPFM) investigations of our samples. The KPFM technique has been used to quantify the change in contact potential difference in the presence of analyte gas.

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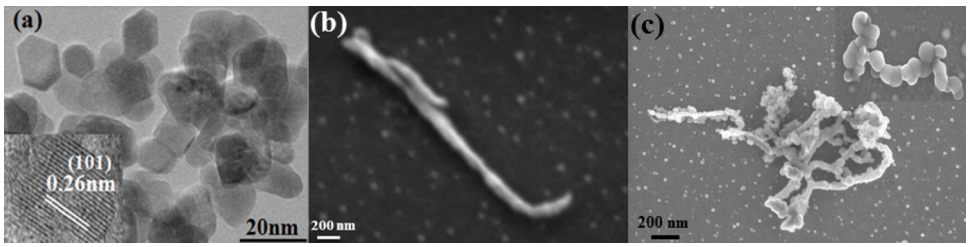

Fig. 1. (a) HRTEM image of SnO_2 nanocrystals; SEM micrographs of (b) PPy nanowires (c) PPy-SnO_2 nanostructures.

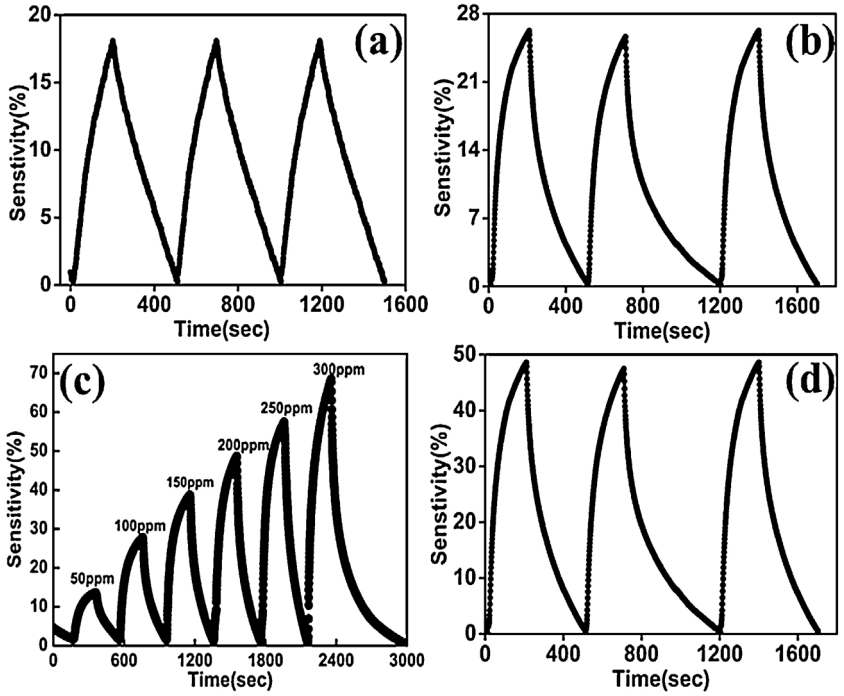

Fig. 2. Sensing response at °C for 100 ppm of ammonia (a) PPy nanowires (b) PPy-SnO_2 nanostructures; Sensing response by PPy-SnO_2 nanostructures (c) at various ppm levels of ammonia at 27 °C (d) at 100 ppm level of ammonia at °C.

2. Experimental

For the synthesis of PPy/SnO_2, separately prepared SnO_2 nanoparticles were added (5% by weight) to the 15 mM cationic surfactant (CTAB) solution and ultrasonicated for 45 min, followed by magnetic stirring to ensure homogeneous mixing of SnO_2 nanoparticles. The oxidant, ammonium peroxy sulfonate (APS) solution was mixed with above solution and the white precipitates of $CTA^+S_2O_8^-$ crystals were observed immediately after. Distilled pyrrole monomer was added drop-wise to the above prepared micro emulsion solution and with the addition of monomer, the black precipitates of PPy appeared within 10 s. The reaction was carried out for 12 h for completion and terminated by pouring excess amount of methanol. The prepared nanocomposite powder was separated with the help of centrifuge (8000 rpm) and washed several times with distilled water and methanol, alternately. The prepared dark green powder was dried in the oven at 50 °C. The experiments utilized KPFM system VEECO, FE-SEM Philips and HRTEM FEI, Tecnai G2 F30- STWIN.

3. Results and discussion

The estimated size of prepared SnO_2 nanoparticles from HR-TEM images (Fig. 1a) is about 15 nm. The well visualized lattice planes (inset of Fig. 1a) in this image further support the crystalline nature of the synthesized samples. The interplaner spacing for SnO_2 nanocrystals is about 0.26 nm which corresponds to (1 0 1) plane [16,17] of the rutile SnO_2. Moreover, the crystallites, distributed into the samples have different orientations which indicate the polycrystalline nature of SnO_2 nanoparticles. PPy nanotubes are formed as shown in SEM micrograph (Fig. 1b). The composite samples show bead type structures in a tube. It seems that SnO_2 nanoparticles are wrapped by PPy nanotubes (Fig. 1c).

To investigate the sensing behavior of PPy on doping with SnO_2, the gas sensitivity of the nanocomposite, pure polypyrrole sample and pure SnO_2 was separately tested in ammonia environment. The gas sensitivity was calculated by measuring change in surface resistance of the sample in presence of ammonia per unit its original surface resistance in air $((\Delta R/R) \times 100)\%$. The alternate cycles of exposure to ammonia (200 s) and recovery from ammonia (300 s) were repeated several times. Within the operating temperature range of the setup, the SnO_2 sample did not give any sensing response upto 250 °C, which further shows its higher operating temperature. It is observed that the electrical resistance of PPy and its composite increases in ammonia environment which is obvious behavior of pure PPy. At 100 ppm of ammonia the sensitivity of pure PPy nanowires is about 18%. It is interesting to observe, rather worth exploring, that the sensitivity of the composite sam-