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Development of Graphene Doped TiO_2 Nanotube Array based MIM Structured Sensors and its Application for Methanol Sensing at Room Temperature †

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Abstract: This work concerns with the development of good quality graphene doped TiO_2 nanotube array sensor for efficient detection of methanol. Pure and graphene doped TiO_2 nanotube array was synthesized by electrochemical anodization method. Morphological, structural and optical characterizations were performed to study the samples. Both the nanotube samples were fabricated in Au/TiO_2 nanotube/Ti type MIM structured devices. Pure and graphene doped TiO_2 nanotubes offered a response magnitude of 20 % and 28 % to 100 ppm of methanol at room temperature respectively. Response/Recovery time was fast in case of graphene doped TiO_2 nanotube array (34 s/40 s) as compared to pure TiO_2 nanotube array (116 s/576 s) at room temperature. This study confirmed the notable enhancement in methanol sensing due to the formation of local heterojunctions between graphene and TiO_2 in the hybrid sample.

Keywords: methanol sensing; graphene doping; electrochemical anodization

1. Introduction

Methanol is one of the essential organic solvent which has numerous applications in fabrication of dyes, drugs, perfumes and colors. Moreover, it is extensively utilized in automobile fuel, waste water denitrification and electricity generation [1]. Methanol is extremely toxic VOC which is disastrous to human health. Repeated exposure to methanol vapors causes many problems to human beings like blindness, acidosis, headaches, blurredness, shortness of breath and dizziness. Skin contact with methanol results in dermatitis or scaling and eye contact results in vision destruction [2]. With all these concerns, there is a high demand for the development of methanol sensors which are reliable, stable, sensitive and can perform at low temperatures.

Different materials like metal oxide semiconductors, polymers, carbon nanostructures, metal nanoparticles, nanocomposites have been extensively utilized by different researchers for chemical sensing. Solid state sensors based on semiconducting metal oxides have achieved a lot in the field of chemical sensing due to their exceptional properties [3]. TiO_2 is an efficient semiconducting metal oxide which can be synthesized in different nanoforms (nanotubes, nanorods, nanoparticles and nanosphere etc.) for different applications like photocatalysis [4], chemical sensing [5], waste water purification [6]. 1D-TiO_2 nanotubes performs very well in the field of vapor sensing due to its magnificent properties like uniformity, stability and one dimensional electron flow [7]. Different researchers have applied different techniques such as formation of TiO_2 based hybrid to improvise the performance of TiO_2 based sensors.

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2-dimensional graphene offers advanced opportunities to develop hybrids with amazing electronic catalytic behavior. The flat monolayer of graphene offers unique properties like high surface to volume ratio, excessive mobility and good electrical conductivity [8]. These properties make graphene an ideal candidate to support or form hybrid with metal oxide semiconductors having high catalytic properties [9]. Some reports have been published depicting the sensing performance of graphene-TiO_2 based hybrid. Fan and group demonstrated the fabrication of TiO_2-graphene nanocomposite by hydrothermal method. They depicted electrochemical sensing of dopamine [10]. Ye and co-workers reported room temperature ammonia sensing by rGO-TiO_2 hybrid. They fabricated the hybrid by simple hydrothermal method [11]. Galstyan and group reported the fabrication of rGO-TiO_2 nanotube hybrid for hydrogen sensing. They depicted the impact of GO concentration on the response of TiO_2 nanotubes.

In this current work, a highly aligned and uniform graphene doped TiO_2 nanotubes array was synthesized by electrochemical anodization route for efficient detection of methanol vapors. Pure TiO_2 nanotube array and graphene doped TiO_2 nanotube array were fabricated by electrochemical anodization route. Both the samples were examined and analyzed through various characterization techniques which confirmed the presence of graphene in graphene doped TiO_2 nanotube array. Metal insulator Metal (MIM) structured sensors were fabricated by using both pure and graphene doped TiO_2 nanotubes. Graphene doped TiO_2 nanotubes depicted a sensitivity of 28% with quite a fast response and recovery time of 34s and 40s towards 100 ppm of methanol. On the other hand, pure TiO_2 nanotubes array depicted a sensitivity of 20% with relatively slow response/recovery time (116 s/576 s) in the same conditions.

2. Experimental Details

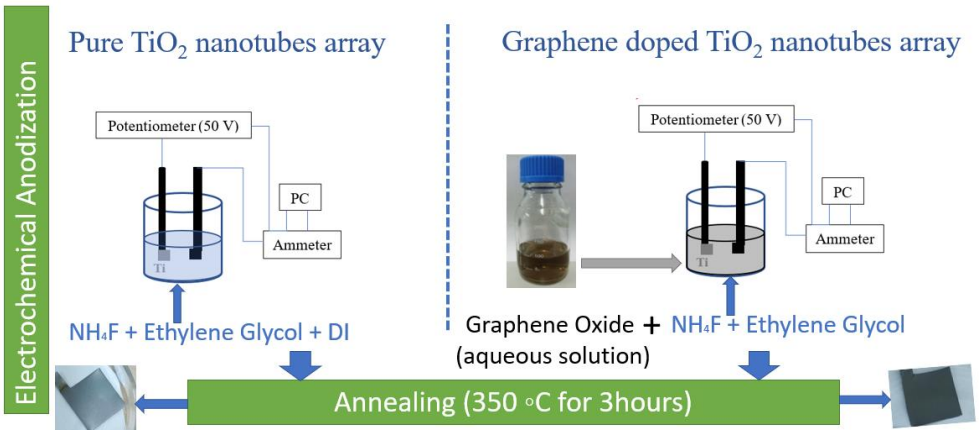

Figure 1. Flow chart describing the synthesis procedure of pure TiO_2 nanotube array and graphene doped TiO_2 nanotubes array were synthesized.

A highly ordered and oriented pure TiO_2 nanotube array and graphene doped TiO_2 nanotubes array were synthesized by electrochemical anodization route. Two electrodes anodic oxidation was performed for 120 min under 40 V potential where Ti foil was used as the anode and graphite was used as the cathode. The electrolyte was made up of 0.5 wt% of NH_4F, 10% vol of DI water and ethylene glycol. The method to synthesize the TiO_2 nanotube array has been described in detail in our previous reports [13].

High purity graphene oxide suspension was used to prepare from 0.2 wt% graphene oxide (GO) aqueous solution. Then an electrolyte was prepared with 0.5 wt% NH_4F, 10 vol% of GO aqueous solution and ethylene glycol for the preparation of graphene doped TiO_2 nanotubes array. Again, the anodization was performed for 120 min by applying a constant voltage of 40 V. Due to the constant availability of GO in the electrolyte, graphene

was doped uniformly in the TiO_2 nanotubes. Both the pure TiO_2 nanotube array and graphene doped TiO_2 nanotubes array were annealed for 3 hours at 450 °C in air ambient. Annealing made the nanotubes more robust and stable and hence more reliable to use. The flow chart describing the steps for the synthesis of pure TiO_2 nanotube array and graphene doped TiO_2 nanotubes array is represented in Figure 1.

The morphology of the fabricated samples was analysed by FESEM. The crystallographic structure of both the samples was examined via X-ray diffraction spectroscopy. Raman spectroscopy was performed for both samples which confirmed the doping of graphene in graphene doped TiO_2 nanotube array (GO-TiO_2).

To fabricate the MIM structure for the sensors, Au was deposited on the top of TiO_2 nanotube/Ti and GO-TiO_2 nanotube/Ti samples by electron beam evaporation technique. 100 nm thick deposited Au was considered as the top electrode and Ti was considered as the bottom electrode. Both samples were enveloped in Cu mask to ensure 1*1mm^2 Au top electrode. A part from the corner of the TiO_2 nanotubes was etched with hydro fluoric acid to induce Ti as the bottom electrode.

The fabricated sensors were tested against the methanol vapours. The sensors were examined at room temperature. The sensor setup with their properties has been discussed previously [14]. The resistance in the air ambient (R_a) and in exposure of the reducing vapours (R_g) – methanol was observed. The response magnitude is calculated as [(R_a-R_g)/R_a] *100. The response time and recovery time for both sensors is defined as the 90 % of maximum change of the resistance when exposed to methanol vapours and exposed to synthetic air for the removal of vapors respectively.

3. Results and Discussion Section (Heading 1)

3.1. Material Characterization

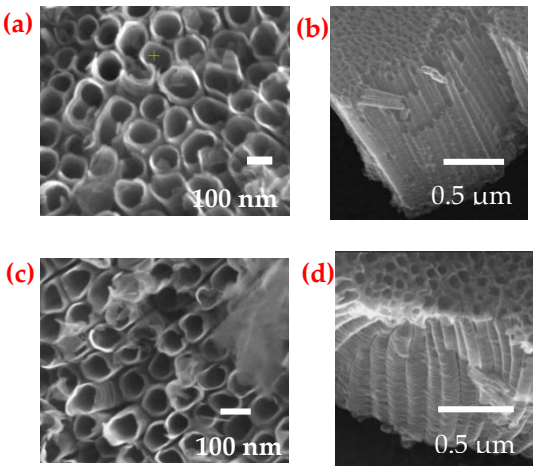

Figure 2. FESEM Image of Pure TiO_2 nanotube array (**a**) Top view, (**b**) Side view and Graphene doped TiO_2 nanotube array (**a**) Top view, (**b**) Side view.

FESEM confirmed the formation of highly ordered and uniform nanotubes in both the samples (Figure 2). Highly aligned nanotubes were formed with approximate average outer diameter of 110 nm and length of 1 µm in both the pure TiO_2 nanotube array and graphene doped TiO_2 nanotubes array. Graphene does not hamper the original morphology of TiO_2 nanotubes (Figure 2c and d). As graphene was uniformly doped inside the nanotubes, it was hard to observe the graphene with scanning electron microscopy.

The sharp intensity peak at 25.3° in both the samples attributes to the anatase crystallinity of TiO_2 nanotubes (Figure 3a). A low intensity peak at 52° corresponding to the anatase crystallinity A(105) in both the samples. A small peak at 54.1° present only in pure TiO_2 nanotube array corresponds to A (201) and clearly states the presence of more anatase in pure TiO_2 nanotube array. The peaks labelled as T are originated due to the use of

Titanium substrate in both the samples. T peaks intensity is high in pure TiO_2 nanotube array and less in graphene doped TiO_2 nanotube array in comparison to A(101) peak.

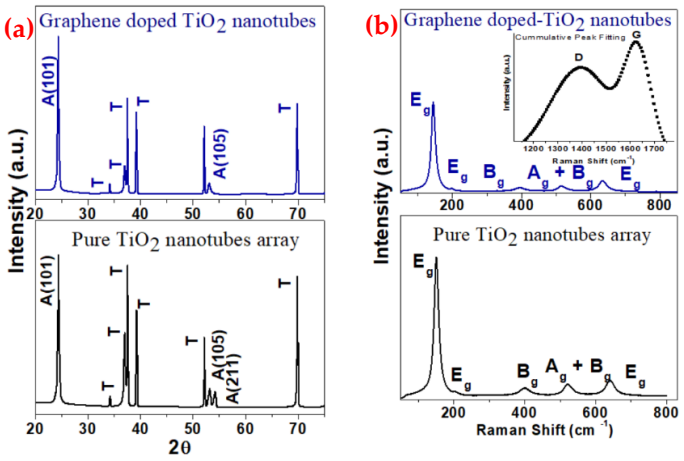

Figure 3. Pure TiO_2 nanotube array and Graphene doped TiO_2 nanotube array (**a**) XRD Spectra, (**b**) Raman spectra.

The Raman spectra of pure TiO_2 nanotube array and graphene doped TiO_2 nanotube array is represented in Figure 3b. The presence of pure anatase is determined by six active modes E_g (144 cm^{-1}), E_g(197 cm^{-1}), B_g (399 cm^{-1}) A_g+B_g (516 cm^{-1}) and E_g (639 cm^{-1}) present in both the samples [13]. The sharp intensity peak at 144 cm^{-1} determines the formation of Ti-O in the anatase phase of TiO_2. The presence of graphene is authenticated by the sharp peaks at 1348 cm^{-1} (D band) and 1596 cm^{-1} (G band) in graphene doped TiO_2 nanotube array [15]. The active modes of anatase TiO_2 nanotube and graphene were present at their corresponding positions even after the uniform doping of graphene.

3.2. Methanol Sensing

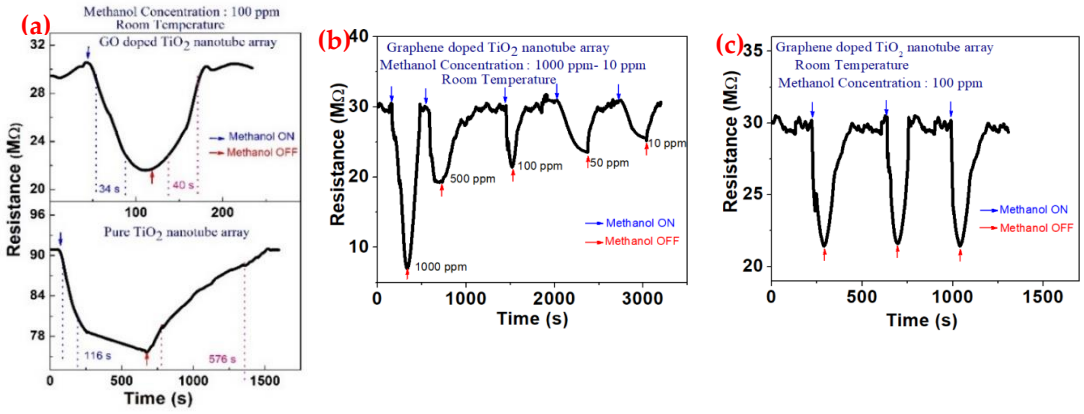

Figure 4. (**a**)Transient behavior of pure TiO_2 nanotube array sensor and graphene doped TiO_2 nanotube array sensor in 100 ppm methanol at RT with measured response time and recovery time; Graphene doped TiO_2 nanotube array sensor (**b**) Transient behavior from methanol concentration range - 1000 ppm to 10 ppm, (**c**) Repeated cycles in 100 ppm methanol at RT.

The two MIM structure based sensors were examined against the reducing vapours – methanol at room temperature. The resistance of pure TiO_2 nanotube array and graphene doped TiO_2 nanotube array was 90 MΩ and 30 MΩ respectively. The reduced resistance (increased conductance) of graphene doped TiO_2 nanotube array sensor clearly defines the incorporation of graphene inside TiO_2 nanotube. Both the sensors were subjected to 100 ppm of methanol at room temperature. The response magnitude of pure TiO_2 nanotube array and graphene doped TiO_2 nanotube array was 20 % and 28 % respectively.

Pure TiO_2 nanotube array has a response time and recovery time of 116 s and 576 s respectively. Moreover, there was the improvement in response time (34 s) and recovery time (40 s) in case of graphene doped TiO_2 nanotube array (Figure 4a).

A transient was measured within a concentration range of 1000 ppm to 10 ppm for graphene doped TiO_2 nanotube array sensor (Figure 4b). A good response magnitude was obtained in 1000 ppm methanol (77.7 %) and an average response magnitude was obtained in 10 ppm methanol (19 %) at room temperature. Graphene doped TiO_2 nanotube array sensor exhibited a stable baseline resistance with highly repeatable transient behavior at room temperature (Figure 4c). Graphene doped TiO_2 nanotube array sensor response was improvised with short response time and recovery time due to the incorporation of graphene inside TiO_2 nanotubes.

3.2. Methanol Sensing Mechanism

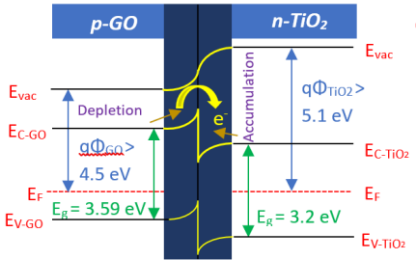

Figure 5. Heterojunction formed between *p*-type GO and n-TiO_2 nanotubes with electron depletion in GO and electron accumulation in TiO_2.

The large surface area and two dimensional structure of graphene enhanced the sensing performance of graphene doped TiO_2 nanotube array sensor. This increased conductance of graphene doped TiO_2 nanotube array sensor can be attributed to the large carrier mobility and high electrical conductance of graphene. The uniform doping of graphene inside the TiO_2 nanotubes improved the sensing parameters of graphene doped TiO_2 nanotube array and enabled room temperature sensing.

Energy band diagram of both junctions was sketched by considering the work function of GO $q\varphi_{GO}$~4.5 eV [16] and anatase n-TiO_2 $q\varphi_{TiO2}$~5.1 eV [17]. Energy band gap of 3.59 eV for pure GO and 3.2 eV for pure TiO_2 (S_0) were estimated from literature survey. On the formation of heteraojuntion between TiO_2 and GO, electrons are transferred to TiO_2 and gets accumulated on the TiO_2 surface.

$$O_2(gas) \rightarrow O_2(adsorbed) \quad (1)$$

$$O_2(adsrorbed) + e^- \rightarrow O_2^- (adsorbed) \quad (2)$$

$$O_2^- + e^- \rightarrow 2O^-(adsorbed) \quad (3)$$

Surface adsorption of oxygen groups (O_2^-, O^-, O^{2-}) reduces the electron concentration (Equations 1–3) and increases the width of the depletion region, resulting in the formation of built-in potential on the surface of the graphene doped TiO_2 nanotube array sensor as represented in Figure 5. Upon exposure to the methanol vapors, the trapped electrons oxygen groups are released back to the surface of graphene doped TiO_2 nanotube array sensor, lowering the built in potential.

$$CH_3OH + O^- \rightarrow HCOH + H_2O + e^- \quad (4)$$

$$CH_3OH + O_2^- \rightarrow HCOOH + H_2O + e^- \quad (5)$$

When methanol vapors reacts with the oxygen species it gets oxidised into formaldehyde and afterwards to formic acid and then releases electrons to conduction band, which

in turn reduces the resistance of the sensor in exposure to methanol vapors (Equations 4 and 5) [18].

Formation of depletion region across the TiO_2 and GO juntion plays an important role for improving the sensor response. Uniform doping of graphene on the TiO_2 surface is the main reason for enhancing the change of current in-between air and VOC ambient that eventually shows high sensitivity towards methanol by the graphene doped TiO_2 nanotube sensor at room temperature with quick response time and recovery time.

4. Conclusion

In this present work, electrochemical anodization technique was applied to develop pure TiO_2 nanotube array and graphene doped TiO_2 nanotube array. Graphene was doped in the TiO_2 nanotubes without hampering the original morphology of the nanotubes. Morphological characterization confirmed the formation of highly aligned and uniform nanotubes and structural characterization confirmed the anatase crystallinity of TiO_2 nanotubes in both the samples. The evidence of graphene in the in the hybrid nanotubes was authenticated by the D and G peak in the Raman spectra. Pure and graphene doped TiO_2 nanotube array sensor was fabricated in MIM structure where Au was considered as the top electrode and Ti was considered as the bottom electrode. Pure TiO_2 nanotube array depicted a response magnitude of 20% with slow response time (116 s) and recovery time (576 s) to 100 ppm methanol at room temperature. Graphene doped TiO_2 nanotube array depicted a better response magnitude of 28 % with quick response time (34 s) and recovery time (40 s) to 100 ppm of methanol at room temperature. Also, lower detection limit till 10 ppm with good response magnitude (19 %) towards methanol was achieved with graphene doped TiO_2 nanotube array sensor at room temperature. A significant improvement in methanol sensing was achieved by the formation of localized heterojunctions between graphene and TiO_2 in the hybrid sample.

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