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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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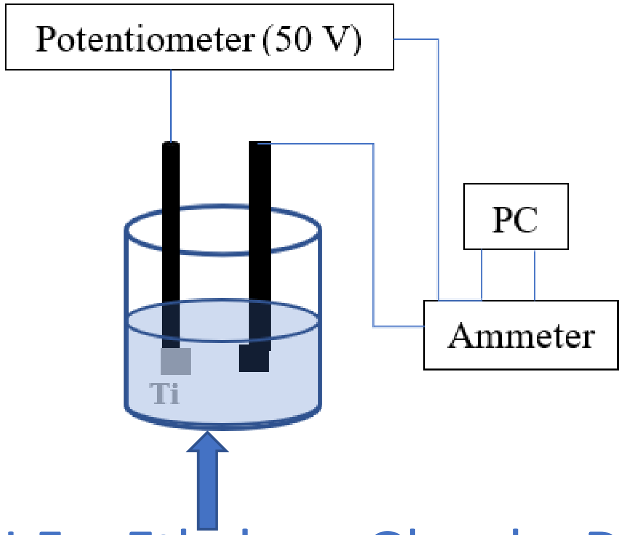
Introduction

- There is a high demand for the development of extremely toxic or harmful VOC – Methanol sensor which is reliable, sensitivity, stable and can perform at low temperatures.
- 1D-TiO_2 nanotubes posses good thermal stability, chemical inertness, one dimensional electron transport and various cost effect fabrication methods
- 2D graphene with unexceptional physical and chemical properties like high specific area, good electrical conductivity, the high mobility of charge carriers, fine mechanical strength have been extensively applied in vapor sensing.
- Graphene oxide, small band gap material is more active and sensitive due to the various functional groups attached.
- Motivated by the characteristics of 1D-TiO_2 nanotubes and 2D-graphene, we have fabricated GO-TiO_2 nanotube hybrid for methanol detection at room temperature.
- 2D-graphene and 1D- TiO_2 nanotubes act complementary to each other due to their outstanding properties.

Experimental Procedure

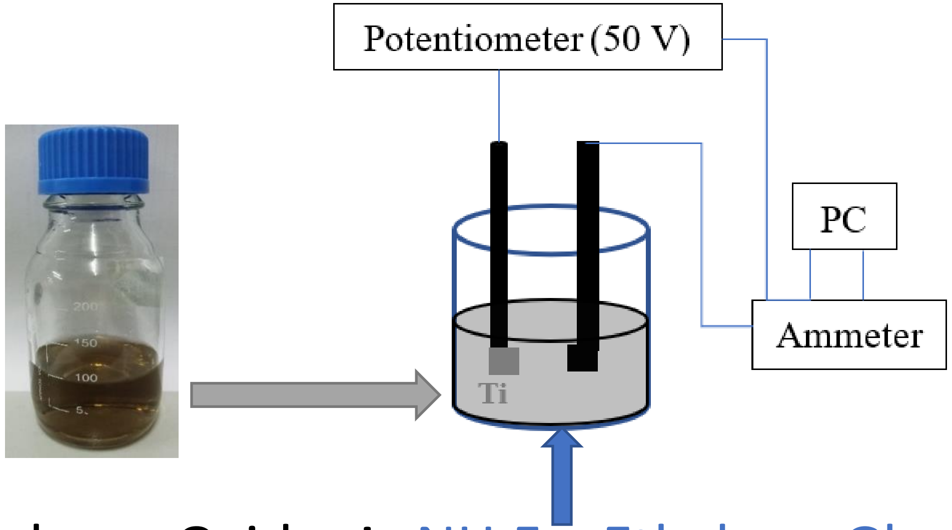
Electrochemical Anodization

Pure TiO_2 nanotubes array

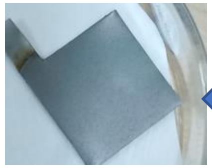


NH_4F + Ethylene Glycol + DI

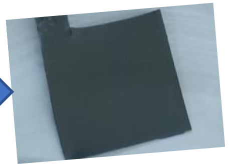
Graphene doped TiO_2 nanotubes array



Graphene Oxide (aqueous solution) + NH_4F + Ethylene Glycol



Annealing (350 °C for 3hours)



Morphological Characterization

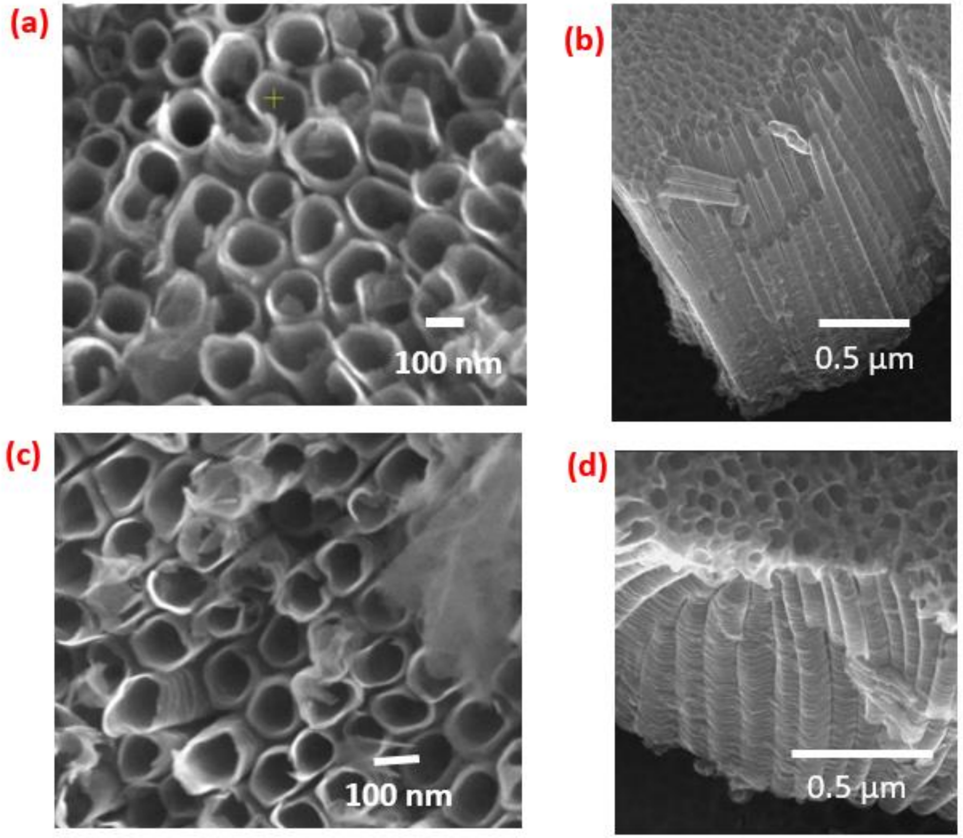


Figure 1. FESEM Image- Pure TiO_2 nanotube array (a)Top View (b)Side View, GO- TiO_2 nanotube hybrid (c) Top View (d)Side View.

- FESEM confirmed the formation of highly ordered and uniform nanotubes in both the samples (Figure 1).
- 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.

Structural and Optical Characterization

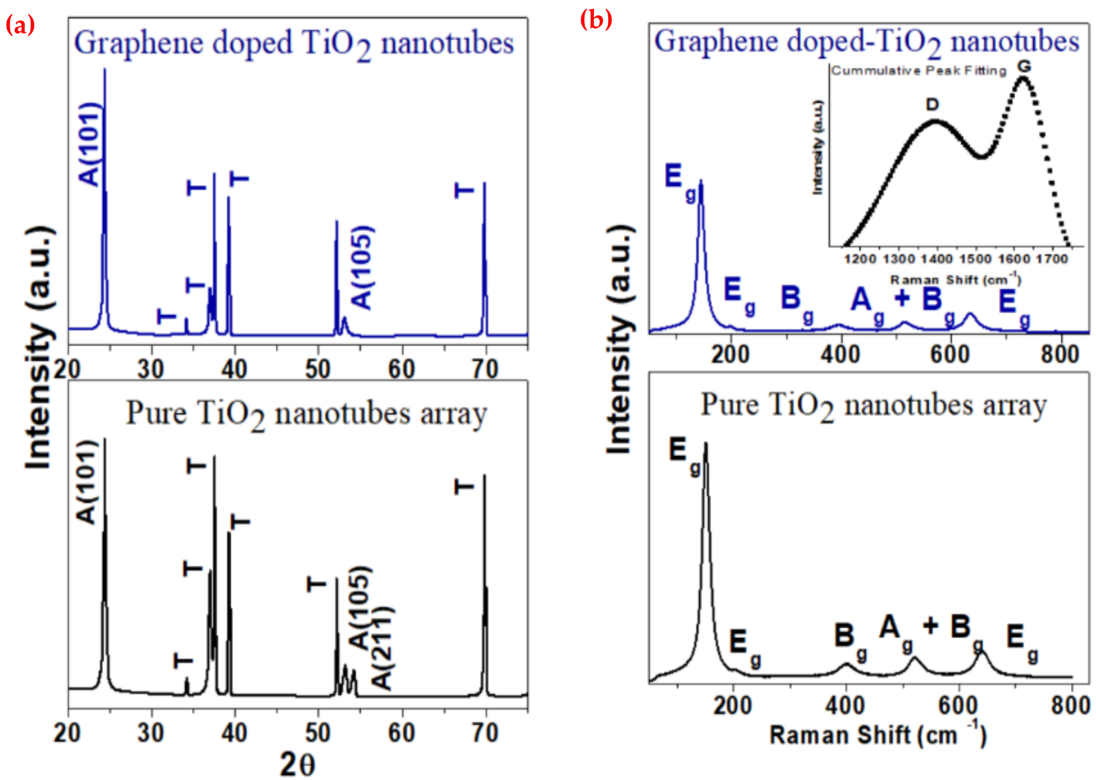


Figure 2. Pure TiO_2 nanotube array and Graphene doped TiO_2 nanotube array (a) XRD Spectra, (b) Raman spectra.

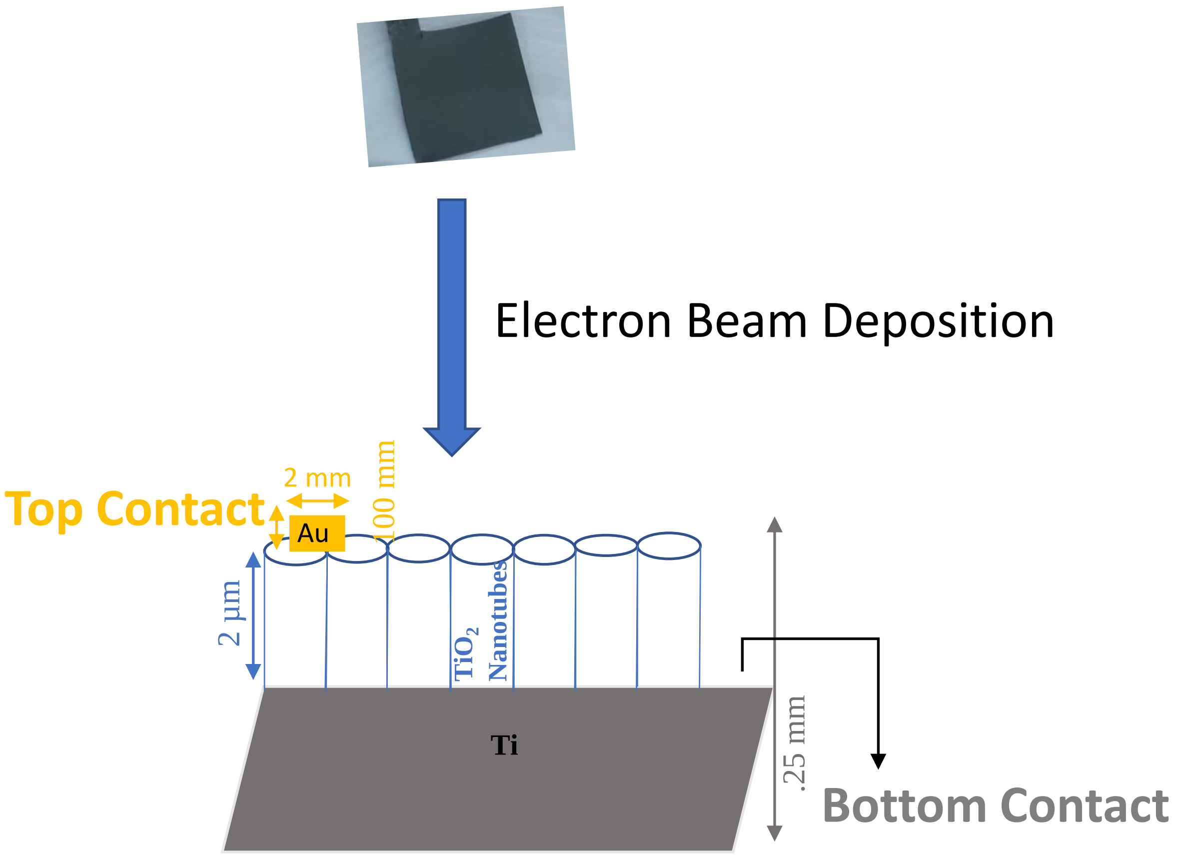
XRD spectra

- The sharp intensity peak at 25.3˚ in both the samples attributes to the anatase crystallinity of TiO_2 nanotubes (Figure 2a).
- 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.

Raman Spectra

- 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.
- 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.

Device Fabrication



Au-TiO₂ nanotubes-Ti (Sandwich structure)

- Metal-Insulator (oxide)-Metal (MIM) structured sensors were fabricated by using both pure and graphene doped TiO_2 nanotubes.
- In both the devices, Ti substrate was considered as the bottom electrode and e-beam deposited porous Au was considered as the top electrode.

Methanol Sensing

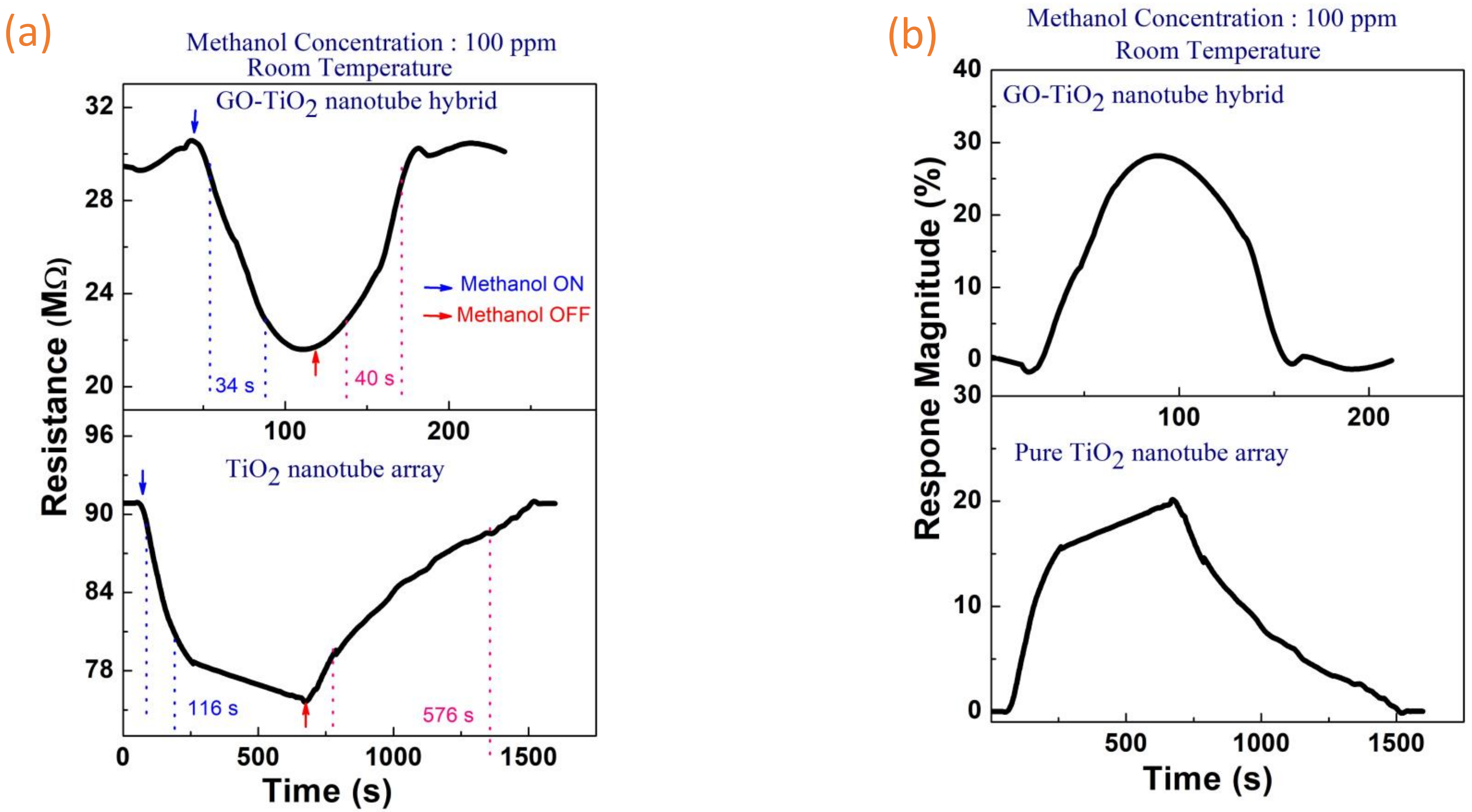


Figure 3 (a) Transient response and (b) Response magnitude of pure TiO_2 nanotube array and GO-TiO_2 nanotube hybrid in exposure to 100 ppm methanol at room temperature

Methanol Sensing

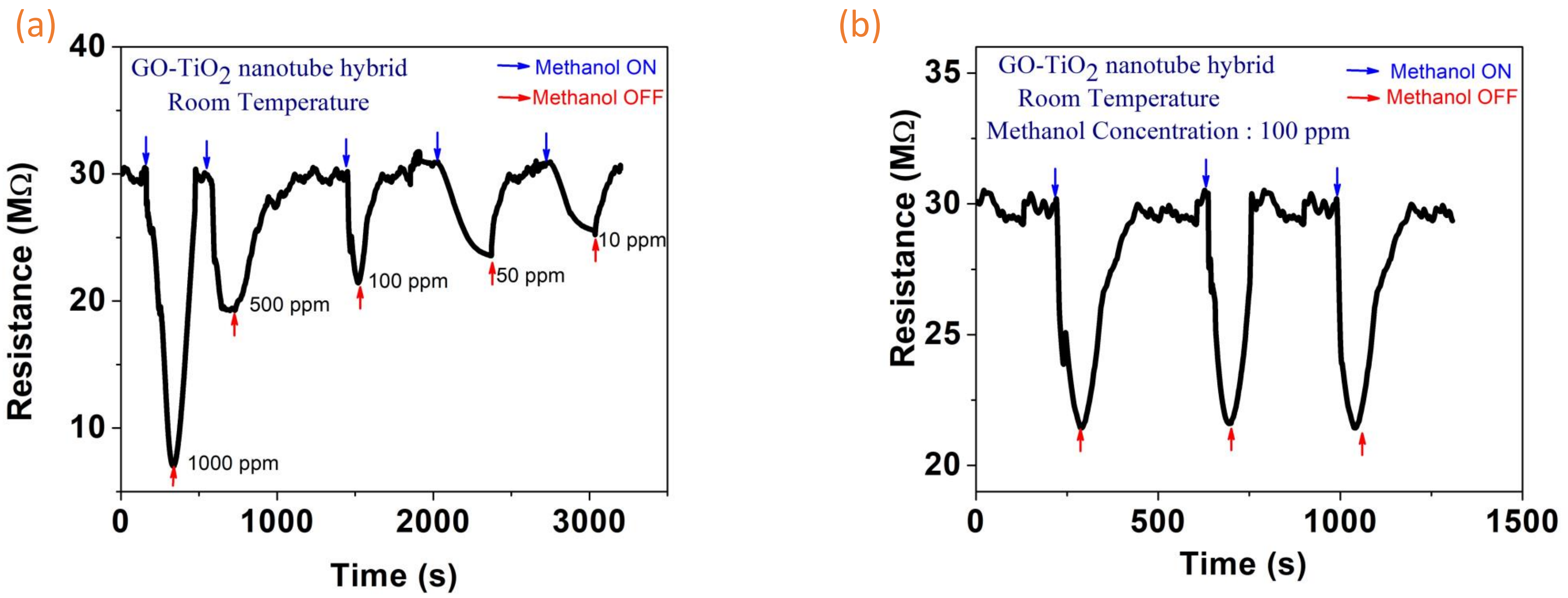


Figure 4. GO-TiO_2 nanotube hybrid (a) Transient response in methanol concentration range from 1000 ppm to 10 ppm (b) Repeated cycles in 100 ppm methanol at room temperature.

Sensing Mechanism

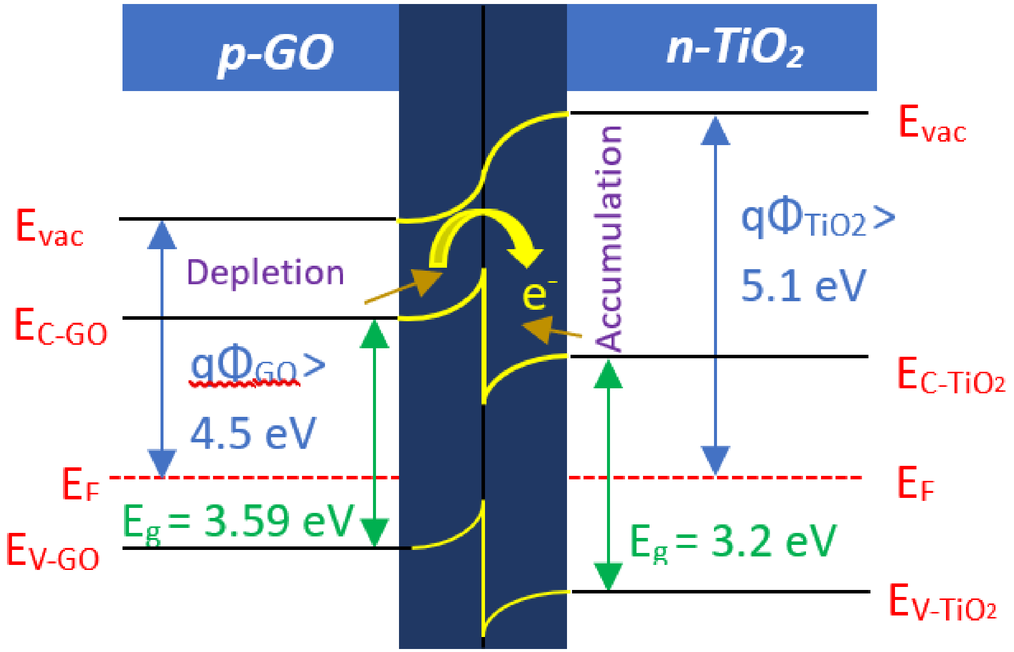


Figure 5. Heterojunction formed between *p*-type GO and n-TiO_2 nanotubes with electron depletion in GO and electron accumulation in TiO_2. Energy band diagram of *p*-GO and *n*-TiO_2.

Sensing Mechanism

- On the formation of heterojunction 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 (Eq1-3) 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.

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

$$CH_3OH + O_2^- \rightarrow HCOOH + H_2O + e^-$$

- On the formation of heterojunction between TiO_2 and GO, electrons are transferred to TiO_2 and holes are accumulated in GO.
- When methanol vapors reacts with the oxygen species it gets oxidized 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

Conclusion

- A highly ordered and oriented graphene doped TiO_2 nanotubes array was synthesised by electrochemical anodization route.
- Due to the constant availability of GO in the electrolyte, graphene was doped uniformly in the TiO_2 nanotubes without affecting the morphology of 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 (116s/576s) in the same conditions.
- 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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Thank You!