Chapter 6

Summary, conclusion and scope of future work

6.1 Summary of the current work

In the present work, the aim was to fabricate (i) low temperature (≤150 ˚C) organic vapour sensors with good stability and repeatability, (ii) sensors with fast response time and recovery time (iii) sensors providing high response magnitude (iv) sensors having the detection range down till ppb level with fair response magnitude. Different techniques were followed to develop different kinds of nanocomposites with two different TiO_2 nanostructures (0-D-TiO_2 nanoparticles and 1-D-TiO_2 nanotubes). The *p*-type anatase TiO_2 nanoparticles were synthesized by sol-gel method and highly oriented *n*-type TiO_2 nanotubes were synthesized by electrochemical anodization route. To fabricate sensors with high response magnitude and low operating temperature, internal doping (intrinsic property) was altered via oxygen vacancy modulation in TiO_2 nanotubes. To new methods – chemical reduction and cathodization were applied to induce oxygen vacancy type defects in TiO_2 nanotubes or make the TiO_2 nanotubes more *n*-type. Cathodic reduced TiO_2 nanotubes exhibited a high response magnitude of 99.64 % and 60 % to 100 ppm of ethanol at 200 ˚C and 50 ˚C. Whereas the chemically reduced TiO_2 nanotubes showed a moderate response magnitude of 75.4 % and 80 % at 150 ˚C and 200 ˚C. The developed sensor offered a dynamic range of 20 ppm to 200 ppm for selective detection of ethanol.

Different nanoforms of carbon were taken into account to form nanocomposites with TiO_2 nanostructures. All the fabricated nanocomposites were subjected to various characterization including morphological (SEM and TEM), structural (XRD, Raman spectroscopy, PL and UV Vis) and chemical (XPS and EDS). Three device structures were fabricated based on the morphology of the synthesized nanocarbon- TiO_2 nanostructures composite such as a) planar/ resistive (b) vertical (MIM) and c) field effect transistors.

Electron beam deposition technique was adopted to deposit gold (Au) electrodes on the sensing layer. 100 -150 nm thick Au contacts were deposited, as per the structure of device. In general, vertical device structure (Metal Insulator Metal structure) was fabricated for the 1-D dominated (e.g. TiO_2 nanotubes) sensors and planar structure and FET structure was considered for 0-D and 2-D materials (e.g. TiO_2 nanoparticles and graphene) based sensors.

Table 6.1 The sensing performance of various fabricated devices under different environmental conditions

Sr. No.	**Sensors**	**Conductivity**	**Device Structure**	**Target VOC**	**Detection Range (ppm)**	**Opt. Temp (˚C)**	**Res. Mag. (%) in 100 ppm**	**Res/Rec Time (s) (in 100 ppm)**
1	Cathodic Reduced TiO_2 nanotube	*n*-type	Vertical (MIM)	Ethanol	200-20	150	90	371/4967
2	Chemically Reduced TiO_2 nanotube	*n*-type	Vertical (MIM)	Ethanol	200-20	150	75.4	155/779
3	GO loaded TiO_2 nanotubes	*n*-type	Vertical (MIM)	Methanol	1000-10	RT	28	34/40
4	GO (95 vol %) implanted *p*-TiO_2 nanoparticles	*p*-type	FET	Ethanol	300-1	100	40	147/900
5	GO (99 vol %) implanted *p*-TiO_2 nanoparticles	*p*-type	FET	Ethanol	300-0.5	100	115	184/3008
6	C_{60}(0.2 wt%)-TiO_2 nanotube composite	*n*-type	Vertical (MIM)	Formaldehyde	100-0.01	150	93	4/7
7	C_{60}(0.5 wt%)-TiO_2 nanotube composite	*n*-type	Vertical (MIM)	Formaldehyde	100-0.01	150	99	44/989
8	C_{60} encapsulated TiO_2 nanoparticle	*p*-type	Planar	Formaldehyde	1000-1	150	117	12/331

Response magnitude = $(|R_a-R_g|/R_a) \times 100$, 90% of the maximum change under the exposure and the removal of the VOCs were considered to calculate the response and recovery time for all the sensors, RT: Room temperature.

An attempt was also made to fabricate a sensor having the synergistic properties of both nanocarbon and TiO_2 nanostructures. This work mainly concerns the sensors based on nanocarbon-TiO_2 composites for the detection of volatile organic compounds. Graphene, the fascinating 2-D nanoform of carbon and the mother of all allotropes of carbon, was utilized to form nanocomposites with both TiO_2 nanoparticles and TiO_2 nanotubes. Firstly, TiO_2 nanoparticle -graphene oxide nanocomposite was synthesized where, the concentration of both TiO_2 NPs and GO were varied systematically to find the appropriate ratio where the nanocomposite could exhibit excellent VOC sensing as well as FET behaviour. The planar structure-based *p*-type anatase TiO_2 nanoparticles implanted on few layer graphene oxide sensor having 50 vol% *p*-TiO_2 and 50 vol% GO exhibited best response magnitude of 40 % to 100 ppm of ethanol at 100 C. Pure graphene oxide based sensor depicted a poor response magnitude of 3 % to 100 ppm ethanol at 100 ˚C and was unable to sense below 100 ppm. Table 6.1 enlists the novel sensors fabricated with their type of conductivity, structure, response magnitude towards target VOC, operating temperature and response/recovery time.

6.2 Conclusion

- This work aims in the development of highly sensitive, selective and stable VOC sensors considering different nanocomposites based on different nanoforms of TiO_2 and two different nanoforms of carbon.
- Metal oxide semiconductors are adequate for VOC sensing but they have certain drawbacks like high operating temperatures (150-400 ˚C), poor selectivity, moderate response magnitude and poor detection range.
- On the other side carbon nanostructures based sensors have the potential to detect VOCs but suffer from long response/ recovery time, low response magnitude and are not so powerful to detect the VOC in low ppm level. Independent nanocarbon based sensors are not sufficient for VOC sensing.
- Composites of nanocarbons with metal oxide provide superior performance in terms of high sensitivity, selectivity, repeatability, quick response time and recovery time and detection till ppb level. TiO_2 is a potential nanomaterial for VOC sensing whose sensing performance can be improvised by doping or forming nanocomposite with carbon nanostructures.
- Oxygen vacancy modulation is the way to induce non-intentional doping inside metal oxide-TiO_2. Increasing the number of oxygen vacancies, increases the number of interaction sites to the surface that makes the metal oxide highly reactive. Out of the new techniques applied for oxygen vacancy modulation, cathodic reduction of nanotubes offered very high response magnitudes of 99.64 % and 60% in the exposure to 100 ppm of ethanol at 200°C and 50°C, respectively. Chemically reduced TiO_2 nanotubes offered moderate response magnitude of 75.4% and 80% at 150°C and 200°C to the exposure of 100 ppm ethanol which was found to be the best among all the sample due to appreciably fast response (155 s) and recovery time (779 s).

Developed MIM sensors depicted adequate stability and selectivity towards ethanol with moderate dynamic range (20 to 200 ppm ethanol) of detection.

- The planar structured p-TiO_2 nanoparticle-GO nanocomposite depicted a moderate response magnitude of 40 % to ethanol at 100 ˚C. A total of seven composites were synthesized where the nanocomposite having 50 vol% p-TiO_2 and 50 vol% GO (0.2 wt%) exhibited best response of ~40% among all the seven composites in 100 ppm ethanol at 100°C.
- Nanocomposites with high percentage of graphene oxide depicted the ambipolar behaviour where 5 vol% p-TiO_2+95 vol% GO and 1 vol% p-TiO_2+99 vol% GO were found having adequate field effect behaviour. 5 vol% p-TiO_2+95 vol% GO nanocomposite sensor and 1 vol% p-TiO_2+99 vol% GO nanocomposite sensor exhibited 41% and 115% response at V_{GS}=0.6 V and 0.7 V respectively where ethanol concentration (100 ppm), temperature (100°C) and V_{DS} (0.5 V) were constant. The lower detection limit were extended up to 1 ppm and 500 ppb for 5 vol% p-TiO_2+95 vol% GO nanocomposite sensor and 1 vol% p-TiO_2+99 vol% GO nanocomposite sensor respectively due to sensitivity amplification by gate electrostatic potential in FET structure. The response magnitude is highly amplified by 7 and 34 times in 5 vol% p-TiO_2+95 vol% GO sensor and 1 vol% p-TiO_2+99 vol% GO sensor by the use gate voltage compared to the two terminal planer structure.
- Moreover, 5 vol% p-TiO_2+95 vol% GO nanocomposite depicted a remarkable increase in on/off current ratio of 2800 (I_{ON} at V_{GS}=0 V and I_{OFF} at V_{GS}=1.2 V), the acceptable transconductance of 0.286 µS and high transport gap of 54.2 meV at room temperature. Whereas on/off for pure graphene oxide was measured as 66 at room temperature.
- Low detection till 100 ppb towards formaldehyde was achieved by MIM structured C_{60}-TiO_2 nanotube composites sensors. All the C_{60}-TiO_2 nanotube composite sensors having different concentrations of fullerene particles depicted selectivity and ultra-high response magnitude (> 92%) towards 100 ppm of formaldehyde at 150 ˚C. In general, all the C_{60}-TiO_2 nanotube composite sensors showed a high selectivity towards formaldehyde with high sensitivity with the concentration range of 100 ppm to 100 ppb. One major thing achieved with C_{60} (0.02 wt%)-TiO_2 nanocomposite was ultra-fast response time and recovery time (4 s/7 s). MIM structured devices support fast response time and recovery time as compared to planar structured devices.
- Planar structured based C_{60}-encapsulated TiO_2 nanoparticles hybrid sensor exhibited double response magnitude (117 %) than the pure TiO_2 nanoparticle (48%) and pure

C_{60} particles (40 %) and appreciably fast response/ recovery (12 s /331 s) towards 100 ppm of formaldehyde at 150 ˚C. Detection range of 1 ppm to 1000 ppm was covered by C_{60}-encapsulated TiO_2 nanoparticles hybrid sensor with good response magnitude. C_{60}-encapsulated TiO_2 nanoparticles hybrid sensor exhibited a natural selectivity towards formaldehyde.

- Based on the different nanoforms synthesized, three different device structures (vertical, planar and FET) were fabricated. Three different VOCs – ethanol, methanol and formaldehyde were considered for selective sensing. TiO_2 nanotubes by cathodic reduction depicted a high response magnitude but suffered from long recovery/response time. All the nanocomposite sensors fabricated were able to operate in moderate temperature range (100 -150 ˚C). Detection range down till 500 ppb was achieved with *p*-TiO_2 nanoparticles implanted GO (99 vol %) nanocomposite sensor in FET configuration. Low detection range till 100 ppb was achieved with MIM structured C_{60}-TiO_2 nanotube composites. The maximum detection range for nanocomposite sensor was 1000 ppm. Nanocarbon-TiO_2 nanotube composite sensors depicted *n*-type conductivity and nanocarbon-TiO_2 nanoparticle composite sensor depicted *p*-type conductivity.

6.3 Scope of future work

I. In this work, first of all oxygen modulated TiO_2 nanotubes were fabricated by two new techniques. Similar oxygen modulation can be performed in TiO_2 nanoparticles via different techniques. Oxygen modulated TiO_2 nanoparticles based sensors might provide excellent results in terms of sensitivity, repeatability and low temperature sensing.

II. In this present study, 2-D graphene and 0-D fullerene structures were utilized to form nanocomposites with TiO_2 nanostructures. 1-D CNT has a lot of potential in chemical sensing. Both CNT-TiO_2 nanotube composite and CNT-TiO_2 nanoparticle composite based sensors can provide repeatability, stability and high sensitivity towards volatile organic compounds with quick response time and recovery time at low operating temperature.

III. Relatively less explored Fullerene C_{60} could be tested for FET behaviour. C_{60} encapsulated loaded TiO_2 nanoparticles FET behaviour could be studied through electrical characterization and might be utilized for amplified VOC sensing.

IV. In general, the detection of toxic and harmful VOC may be a good future work. Room temperature sensing should be more focused on (Metal Oxide-Carbon nanostructures) composites. This might be improved by forming hetero/ternary structures or synthesizing new nanostructures.