Facile synthesis of graphitic carbon-nitride supported antimony-doped tin oxide nanocomposite and its application for the adsorption of volatile organic compounds

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Antimony-doped tin oxide (ATO) nanoparticles with an average size of ~ 6 nm were prepared by co-precipitation and subsequent heat treatment. Graphitic carbon nitride (g-CN)/ATO hybrid nanocomposite was designed by the combination of thermally synthesized g-CN and ATO nanoparticles by ultrasonication. The materials were characterized using N2 adsorption/desorption (BET), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). A mixture of five volatile organic compounds (VOCs, chloroform, benzene, toluene, xyylene and styrene) was used to compare the adsorption capacity of the samples. The adsorption capacity of ATO nanoparticles was improved by the addition of g-CN. Experimental data showed that, among the five VOCs, chloroform was the least adsorbed, regardless of the samples. The g-CN/ATO showed nearly three times greater adsorption capacity for the VOC mixture than pure ATO. The unchanged efficiency of VOC adsorption during cyclic use demonstrated the completely reversible adsorption and desorption behavior of the nanocomposite at room conditions. This economically and environmentally friendly material can be a practical solution for outdoor and indoor VOC removal.

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metal-doped metal oxides (Ghosh et al., 2017), and metal adsorbents (Paraskeva et al., 2008). Many porous hybrid materials have also been successfully designed and used as adsorbents for removing dye molecules, heavy metals, nitrogenous gases, and VOCs (Sun et al., 2016). The materials like SiC ultrathin fibers (Wang et al., 2014a), silicon-carbon-nitrogen hybrid materials (Meng et al., 2015), MOFs (Huang et al., 2012), layered double hydroxide (LDH) (Tarutani et al., 2014) show remarkable adsorption performance due to their better surface properties like high surface area and porosity (Yu et al., 2015).

Similarly, graphitic carbon nitride (g-C₃N₄ or g-CN), a conjugated metal-free semiconducting material often used for water reduction, hydrogen storage, and oxidation (Chu et al., 2013) has many exceptional properties, such as environmentally benign, stable physicochemical property, and high adsorption capacity due to the presence of surface functional groups (Zhao et al., 2015). These metal-free semiconducting materials can be prepared using low-cost reagents such as dicyandiamide, melamine, urea, and thiourea with a simple heating process (Ge et al., 2011; Zhang et al., 2009). Also, g-CN is a soft polymeric semiconductor that can easily be applied to the surface of other materials in comparison to inorganic conjugative materials such as carbon nanotubes and graphene (Miranda et al., 2013; Yu et al., 2013). Thus, this conjugated material is also applied for the adsorption of VOCs (Hou et al., 2016; Muñoz-Batista et al., 2014). However, the pristine g-C₃N₄ has a limited specific surface area. Top-down approaches such as liquid exfoliation or thermal exfoliation are utilized successfully to break the stacking of bulk g-CN to nanosheets and increase its specific surface area. Though exfoliated nanosheets exhibit enhanced adsorption capacity, their overall VOC removal capacity can be higher if porous, high surface area containing metal oxides supported on its surface.

Thus, in our study we designed a new adsorbent hybrid nanocomposite by combining g-CN with 6 nm ATO nanoparticle. ATO is a widely studied transparent conducting oxide used to fabricate thin films to apply in gas sensor (Babar et al., 2011), electro-chromic device (Moir et al., 2013) and photocatalysis (Sun et al., 2014). Furthermore, nanoparticles provide large areas for surface adsorption and provide exceptionally high surface area as hybrid composites with 2D materials. These hybrid composites can aid gas diffusion and mass transport. However, ATO powder has never been reported as an adsorbent material only. In this paper thermally, synthesized graphitic carbon nitride is successfully exfoliated with ATO nanoparticles by ultrasonication. Thus, this study investigates the adsorption of a VOC mixture on the surface of the as-synthesized hybrid nanocomposite using a simple technique and quantifies the adsorption of VOCs using combined gas chromatography–mass spectrometry (GC/MS).

1. Materials and methods

1.1. Materials

The commercial reagents ethanol (EtOH), tin(IV) chloride pentahydrate (SnCl₄·5H₂O), ammonium bicarbonate (NH₄HCO₃), acetic acid (CH₃COOH), antimony(III) chloride (SbCl₃), ammonium hydroxide (NH₄OH) solution were obtained from Sigma-Aldrich and used as received.

1.2. Preparation of antimony-doped tin oxide (ATO)

The ATO nanoparticles were synthesized by co-precipitation and subsequent heat treatment (Bai et al., 2006). During the synthesis of ATO, 18.54 mmol of SnCl₄·5H₂O and 2.498 mmol of SbCl₃ (Sn:Sb ratio = 5 mol.%), 11 g NH₄HCO₃ and 3.54 g CH₃COOH were dissolved into 100 mL of anhydrous EtOH. The solution pH was maintained at 7 by adding NH₄OH (25 wt.%) and stirred vigorously for about 4 hr. The resulting white precipitate of the Sn⁴⁺ and Sb³⁺ hydroxide suspension was centrifuged, washed with distilled water, and heated at 550°C for 8 hr in the muffle furnace. This process resulted in the desired bluish-gray ATO nanopowder.

1.3. Preparation of g-C₃N₄ (g-CN)

The graphitic carbon nitride (g-C₃N₄) nanosheet was prepared using melamine that had previously reported. Melamine was put in a crucible with a lid under ambient pressure in air. After thermal treatment at 550°C for 3 hr, the yellow colored g-C₃N₄ was obtained. The obtained powder was crushed into fine powder and again heated at 550°C for 3 hr to complete the thermal polymerization of all melamine. Then, the sample was washed with nitric acid (0.1 mol/L) and water several times and dried at 80°C for 6 hr.

1.4. Preparation of g-CN/ATO hybrid nanocomposite

For the formation of g-CN/ATO hybrid nanocomposite structures, 1:1 ratio by weight of the ATO nanoparticle and g-CN was ultrasonicated in a 50 mL ethanol for 2 hr. The sample was then dried slowly at 90°C for 24 hr, and subsequently heat-treated at 150°C for 3 hr.

1.5. Characterization

The products were first characterized with X-ray powder diffraction (XRD, Rigaku, Japan) under ambient conditions over a 2θ range of 20–80° at a scan rate of 2°/min (monochromatic Cu Kα, 40 kV, 20 mA). The morphological features of the samples were analyzed using a field-emission scanning electron microscope (FE-SEM, S-7400, Hitachi, Japan) and high-resolution transmission electron microscope (HRTEM, JEM-2010F, JEOL, Japan). The surface areas were measured by Brunauer–Emmett–Teller (BET) method whereas the pore volumes and pore sizes were measured by Barrett–Joyner–Halenda (BJH) method using Micromeritics ASAP 2420, USA. The Fourier transform infrared (FTIR) spectra of the samples were recorded using an ABB Bomen MB 100 spectrometer (Bomen MB 100, Bomen, Canada).

1.6. VOC adsorption experiment

VOC adsorption measurement was carried out according to the standard method described in previous article (Kim et al., 2013) with some modification as shown in Scheme 1. In this experiment, 0.5 g of a powder sample was placed into a closed
container with two valves and two compartments partitioned by a perforated aluminum foil. The container was degassed with the help of a vacuum pump and filled with the nitrogen gas for inert environment. A VOC test mixture (100 mg/L) containing equal amount of chloroform, benzene, toluene, o-xylene and styrene compounds was prepared. The mixture was diluted several times in methanol to produce the 4 μg of VOCs, injected into the container containing the prepared nanocomposite and kept for the adsorption for 1 hr at 60°C for evaporation of VOCs. The container was cooled to room temperature; unabsorbed remnant VOCs were collected into the Tenax absorber (Tenax-GR, Japan Analytical Industry, Japan) with continuous N2 flow at 0.065 L/min flow rate. The trapped VOCs were analyzed using GC/MS (GC/MS QP 2010 plus, Shimadzu, Kyoto, Japan) for quantitative and qualitative analysis. The gas chromatographic and mass spectral data were used to identify and quantify the traces of the individual compounds by comparing the data to that of reference database registered by National Institute of Standards and Technology. The adsorbed amounts of each of the volatile compounds were calculated by comparing with blank experiment.

2. Results and discussion

The XRD patterns of the particles synthesized at 550°C from the reaction mixtures containing 5% molar ratios of Sb and Sn are shown in (Fig. 1). The ATO nanoparticles clearly show the diffraction peaks corresponding to SnO2, as matched with the JCPDS card number 01-072-1147 to confirm the tetragonal rutile structure. Crystalline byproducts such as Sb2O3 or Sb2O5 are not indicated in the XRD, which further suggests that the antimony doping most probably occurs by substituting tin atoms within the crystal structure of SnO2. Thus, the energy band structure of ATO, originating from Sb 5d and 6s, may be present below the CB of SnO2. As a result, the band gap of ATO is reported to be 2.55 eV or less (Rana et al., 2016). A small change at XRD was also used to measure the mean grain size (D) of the as-prepared ATO nanoparticles. The crystallite size for each sample was calculated using the Scherrer equation, defined as:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]

where D is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, K is a dimensionless shape factor with a typical value of about 0.9, λ is the X-ray wavelength, and \( \beta \) is the line broadening at half the maximum intensity (FWHM) (El-Sheikh et al., 2017). Calculated from the Scherrer equation, the crystallite size of the ATO nanoparticles prepared by sol–gel process was determined to be 5 nm. The measurement is in good agreement with the size determined by TEM. Similarly, the XRD patterns of g-CN/ATO hybrid nanocomposite revealed the coexistence of ATO and g-CN phases. Presence of small broad peak at 27.5° indicates the presence of g-CN in the g-CN/ATO nanocomposite.

Fig. 1 – X-ray diffraction (XRD) patterns of g-CN, ATO and g-CN/ATO.
The detailed morphologies and structures of the as-prepared hybrid nanocomposite were imaged using FE-SEM/EDS (energy dispersive spectroscopy) (Fig. 2) and TEM/HRTEM (Fig. 3). Fig. 2a shows the uniform but highly aggregated surface morphology of ATO particles. Fig. 2b shows the porous and irregular surface of the g-CN/ATO indicating aggregation.

**Fig. 2** – Field-emission scanning electron microscopy (FESEM) images of (a) ATO and (b) g-CN/ATO. Inset: Energy-dispersive X-ray spectroscopy (EDS) spectrum showing the elemental composition of g-CN/ATO where C, N, O, Sn, Sb, S represent the elements carbon, nitrogen, oxygen, tin, and antimony, respectively; K and L represent the first and second shell number of an atom and ZAF refers to the correction method in which Z, A and F represent the atomic number correction, absorption correction and fluorescence correction during EDS, respectively.

**Fig. 3** – Transmission electron microscopy (TEM) images of (a) ATO, (b) g-CN, and (c) g-CN/ATO and (d) high-resolution TEM (HRTEM) of ATO nanoparticles.
of ATO nanoparticles minimized largely. EDS analysis of the g-CN/ATO hybrid nanocomposite (Fig. 2) revealed only the existence of C, N, Sn, Sb, and O in hybrid nanocomposite, suggesting both successful synthesis and high purity.

Fig. 3a shows a TEM image of ATO nanoparticles with uniform size and shape and with partial agglomeration. Fig. 3b shows an overview image of thermally synthesized pristine g-CN sheet which provides the scaffolding of the sheets during sonication. In contrast to the individual nanoparticles, enough contact with the g-CN sheet resulted in less agglomeration of ATO nanoparticles in the hybrid nanocomposite. Such reduced agglomeration on the g-CN sheets enhances the surface area and porosity-related characteristics of the composite above that of bare ATO nanoparticles. HRTEM imaging gives further insight into the structural features of the ATO (Fig. 3d). The well-developed lattice fringes are randomly oriented, which underlines the high crystallinity of the ATO nanoparticles. Thus, the particle size of ATO is confirmed in the range of 6 nm.

The FTIR study provides information about the presence of g-CN and ATO as shown in Fig. 4. In case of the pure g-CN, the FTIR spectrum showed a broad range of 3600–3000 cm\(^{-1}\), corresponding to either adsorbed moisture or the stretching modes of terminal N–H groups at the defect sites of the aromatic ring. This is most likely wholly attributable to residual N–H groups, although the presence of adsorbed water molecules may also need to be considered. In the 1600–1200 cm\(^{-1}\) regions, we can observe several contributions primarily associated with the N–C stretching modes of heterocyclic compounds. The absorption band at 1635 cm\(^{-1}\) can be ascribed to the C–N stretching vibration modes, while the peaks at 1571, 1402, 1322 and 1241 cm\(^{-1}\) represent the C–N heterocyclic stretching of g-CN. The peak located at 810 cm\(^{-1}\) can be attributed to the characteristic out-of-plane skeletal bending modes of the triazine cycles, which is consistent with the reported value (Yan et al., 2009; Zhang et al., 2011). In the spectrum of pure ATO (Fig. 4), absorption bands at 3400 and 1630 cm\(^{-1}\) are characteristic of O–H bending modes of adsorbed water and hydroxyl groups, respectively. In the spectrum of g-CN/ATO (Fig. 4), the presence of the characteristic peaks of both g-CN and ATO indicates that the carbon nitride component maintains its primary structural characteristics in the g-CN/ATO materials. The FTIR spectrum of the composite g-CN/ATO shows the broadened peak in the range of 3600–3000 cm\(^{-1}\) due to the presence of the O–H vibration of ATO nanoparticles, implying an increase in surface hydroxyl groups. The characteristic peaks of ATO in the range of 400–800 cm\(^{-1}\) are also broadened due to the Sn–O vibration, confirming the presence of ATO (Volosin et al., 2011).

To study the adsorption capacity of ATO nanoparticles on g-CN/ATO, we further studied the surface properties like BET surface area, pore volume and pore size of the samples using nitrogen adsorption–desorption analysis (Table 1). N\(_2\) adsorption–desorption analysis indicates the nature of the curves are of Type IV isotherm (Fig. 5), the characteristic feature of which is Type H3 hysteresis loop associated with capillary condensation taking place in the mesopores due to aggregates of plate-like g-CN and ATO nanoparticle in composite g-CN/ATO. Three well-distinguished regions of the adsorption isotherm (Fig. 5) are evident: (i) monolayer–multilayer adsorption, (ii) capillary condensation on the pore walls, and (iii) multilayer adsorption on the outer particle surfaces. Sharp increase in adsorbate volume at low relative pressure (\(P/P_0\)) indicates the presence of microspores along with mesopores. The capillary condensation occurs at a higher relative pressure (\(P/P_0 \approx 0.98\)) (Sing, 1985). In addition, the pore size
distribution calculation based on the Barrett–Joyner–Halenda (BJH) method using adsorption branch of isotherm (Fig. 5), g-CN/ATO hybrid nanocomposite possess larger mesopores with a pore diameter of 34.2 nm as compared to ATO nanoparticles (18.4 nm) and g-CN sheet (25.9 nm) shown in Table 1. The high measured pore size of ATO nanoparticles indicates these particles are actually grain clusters or polycrystals (Zhou et al., 2009). The results illustrate that the BET surface area of g-CN/ATO composite is significantly higher than those of bare ATO and g-CN. The larger surface area of the hybrid nanocomposite is attributed to the exfoliation of stalked g-CN sheets and less aggregate of ATO nanoparticles in between the sheets. This increased the porosity of the hybrid nanocomposite significantly (Wang et al., 2014b).

The hybrid nanocomposite samples adsorbed appreciable amounts of all five VOCs present in the test mixture (Kim et al., 2013) represented in Scheme 1. The VOC adsorption capacity of the composite was greater than the pure ATO nanoparticles. This was attributed to the decreased agglomeration of the ATO nanoparticles prepared by the sol–gel method resulting greater BET surface area (Table 1) and additional pores created between ATO and g-CN. The kinetic diameter of the VOC molecules is significantly less than the sheet-like pores of the nanocomposite and can diffuse into the pores easily. The physisorption of VOCs mixture is mainly because of three reasons: (1) The surface polarity of the nanocomposite might be higher that can effectively adsorb the VOC molecules via π–π interaction, (2) the exposed metal cation sites of ATO in pores can interact with non-polar VOC molecules through cation–π interaction, and (3) additionally the presence of surface functional groups on g-CN can also interact via π–π interaction and enhances the adsorption capacity. The trend in VOC adsorption capacity was similar for all three particles, with each material best adsorbing styrene, then xylene, toluene, benzene, and finally chloroform (Fig. 6) (Barresi and Baldi, 1994). Since all the VOCs are non-polar, adsorption due to H-bonding or any other polar interactions might be absent. Thus Van der Waals interaction and chemical structures and structural effects (electronic and steric effects) of these aromatic hydrocarbons might be responsible for their different adsorption kinetics on the surfaces of the particles (Phuong et al., 1986; Pinto et al., 2004). The surface nanoparticles might form a π-complex with aromatic part of the organic compounds. This π-complex is a non-covalent weak π–π interaction between the benzene ring of the organic compounds and the metal oxide nanoparticles (Elschenbroich et al., 2003). Considering the kinetic and thermodynamic aspects of styrene, xylene, toluene and benzene, the adsorption of styrene is expected to be more favorable than that of xylene, with an order of styrene, xylene, toluene, and then benzene. In case of toluene and benzene, since toluene has more distorted structure, the π-complex of toluene with nanocomposite should be more than benzene. Thus, toluene is more strongly adsorbed than benzene which is also consistent with findings in the literature (Zhong et al., 2012). Moreover, electron donor alkyl groups increase the electron density in the aromatic ring thereby lower the ionization potential (IP) of the donor molecule and promote the formation of charge transfer complexes. Thus the IP of benzene is highest and adsorption over the nanocomposite surface is minimum followed by toluene, xylene, and styrene, which theoretically justifies the observed result (Valdés et al., 2014). Chloroform (a non-aromatic compound) had the smallest adsorption capacity among the VOCs tested, which is attributed to its lack of π-complex formation (Wang et al., 2014c).

To study the reproducibility of the g-CN/ATO hybrid nanocomposite, the sample was reused four times for VOC adsorption under conditions like those described in the experimental section. After each adsorption test, the recovered sample was dried at 80°C for 6 hr to allow desorption of the adsorbed VOCs on the surface. Fig. 7 shows that all the samples have nearly equal adsorption efficiency over four cycles, demonstrating the complete reversibility of the adsorption and desorption behavior.

3. Conclusions

In summary, we synthesized deep blue, visible light active ATO nanoparticles of approximately 6 nm size using co-precipitation and subsequent heat-treatment. ATO nanoparticles were then

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Fig. 6 – Adsorption of different VOCs on ATO, g-CN and g-CN/ATO.

Fig. 7 – Readsorption behaviour of different VOCs on the surface of g-CN/ATO.
incorporated into a g-CN/ATO hybrid nanocomposite. XRD, FE-SEM and TEM images showed that individual nanoparticles were homogeneously dispersed, reducing the agglomeration of the ATO particles alone. Similarly, the incorporation of ATO in g-CN/ATO significantly increased the surface area of the hybrid nanocomposite. The adsorption of VOCs was greatest for the g-CN/ATO hybrid nanocomposite. This optimal VOC adsorption capacity indicates that the hybrid nanocomposite can be used for commercial VOC adsorption for indoor and outdoor air. Moreover, the ATO hybrid nanocomposite demonstrated a high degree of reproducibility.

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