

Ammonia Sensing by Photoluminescence Study of Carbon Nanoparticles and their Composites: A Comprehensive Investigation

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Abstract—We show that bio carbon-zinc oxide nanocomposites show higher photoluminescence intensity and larger shifts in wavelength in the presence of ammonia gas compared with biomass-derived carbon. Both bamboo biomass-derived carbon and carbon-zinc oxide nanocomposite samples were prepared via a simple hydrothermal method and were characterized using various techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The findings suggest that the synthesized carbon-zinc oxide nanocomposites can be used as a potential candidate for ammonia sensing applications.

Keywords: Nanocomposite, Carbon nanoparticles, photoluminescence, ammonia sensing, hydrothermal method

1. Introduction

Ammonia gas is one of the main causes of air pollution. It is produced by nitrogen-rich animal and plant matter, the decomposition of organic material, automobiles, and industries [1]. It can cause burns and airway inflammation as well as injure the skin, eyes, and lungs. According to the Occupational Safety and Health Administration (OSHA), the maximum allowed level of NH_3 in the workplace is 50 ppm [2]. Researchers find it challenging to detect NH_3 at lower concentrations (below 50 ppm) [2]. Therefore, developing highly sensitive and selective ammonia sensors has been a topic of intense research. Various sensing methods exist for NH_3 detection, such as solid-state, electrochemical, and optical sensing [1]. Among various sensing methods, photoluminescence sensing (optical sensing) has emerged as a promising approach for detecting ammonia.

Various materials are used to fabricate ammonia sensors, including semiconductor metal oxide, catalytic metals, polymers, and carbon nanomaterials [3, 4]. Metal oxides are widely used for ammonia-sensing applications. Metal oxide-based ammonia sensors have several promising benefits, but they also have some major drawbacks that need fixing, such as low selectivity in detecting one kind of gas out of a mixture [5-7]. Therefore, researchers are searching for a material that

can replace the existing material and enhance the sensing parameters such as sensitivity, selectivity, fast response time, recyclability etc.

Carbon nanomaterials and their composites with metal oxide are currently gaining a lot of attention in the development of ammonia sensors. Also, recent studies have reported that photoluminescence-based ammonia sensors using carbon nanomaterials exhibit high sensitivity, fast response time, and low detection limits [8-10]. In this context, biomass-derived carbon nanomaterials having greater surface area, porosity and rich functional group and tunable photoluminescence properties can make the material for ammonia sensing applications [11].

The present work reports the synthesis of carbon nanoparticles (CNP) and CNP@ZnO nanocomposites using bamboo biomass as a carbon source via the hydrothermal method. The structural and morphological characterization results confirm the successful formation of CNP@ZnO nanocomposite having a spherical morphology. The sensing properties were investigated using photoluminescence spectra acquired at room temperature with a spectrofluorometer (FLS 1000 Edinberg) excited with its Xenon lamp at 260 nm. In the presence of ammonia gases, both samples show multi-color luminescence at a single excitation wavelength. This study suggests that these nanoparticles and their composites are low-cost and efficient sensing materials for detecting ammonia gas.

2. Experimental

2.1. Material synthesis

Bamboo biomass was collected from the forest division and cleaned with water and then crushed into smaller pieces and dried. A hydrothermal method was used to synthesize carbon nanoparticles. In a typical synthesis, bamboo biomass (5gm) was added into 50 ml of distilled water. Then the mixture was transferred into a Teflon-lined autoclave and heated at 180°C for 24 hours. The carbon nanoparticles were collected by

removing the large particles via centrifugation. Then the final product was dried in oven at 60°C for 24 hours. The synthesized material was powdered using a mortar and pestle and named CNP. To synthesize its composite, bamboo biomass (5 gm) was added into 50 ml solution of $ZnCl_2$ (1M) and followed the above-mentioned procedure. Then the final product was collected and named as CNP@ZnO.

2.2. Characterization

The synthesized samples were structurally investigated using an X-ray diffractometer (Bruker D8 Advance) in the 2θ ranges of 10° - 80° . The morphological properties and the surface elemental composition were obtained using Scanning electron microscope (ZEISS), Transmission electron microscope (Tecnai F20), and Energy dispersive X-ray (EDX) techniques. The photoluminescence measurements were recorded using spectrofluorometer (FLS 1000 Edinberg) at room temperature with an excitation wavelength 260 nm.

3. Results and discussions

3.1 X-Ray Diffraction

Fig. 1A and 1B show the X-ray diffraction patterns of CNP and CNP@ZnO nanocomposites respectively. Fig. 1A shows two characteristic peaks of graphite carbon observed at 2θ of 23° and 44.7° . These peaks were assigned to the (002) and (100) reflections of the graphite structure [12]. While the XRD pattern of CNP@ZnO nanocomposites (Fig. 1B) shows graphite carbon peak of graphite carbon without changing the 2θ position compared with CNP. Additionally, the major peaks observed at $2\theta = 29.4^\circ, 31.7^\circ, 34.4^\circ, 36.2^\circ, 47.5^\circ, 56.6^\circ, 62.8^\circ, 68^\circ,$ and 69.1° were indexed as the crystallographic orientations of (110), (100), (002), (101), (102), (110), (103), (112), and (201) planes respectively, which confirms the formation of hexagonal phases of ZnO [13, 14].

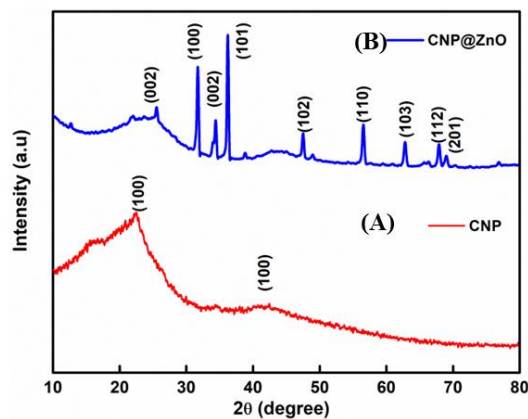


Figure 1: XRD pattern of: (A) Carbon nanoparticles and (B) CNP@ZnO composites

3.2 Microstructure and elemental composition analysis

The surface morphology of the synthesized samples was shown in Figure 2A-2F. The Scanning electron micrograph

(SEM) results clearly show that the particles are spherical in shape and agglomerated (Fig. 2A) whereas for composite, it is found that the porous nature of the material with presence ZnO nanoparticles (Fig. 2B). The particle size was obtained from the Transmission electron micrograph (TEM) images using Image J software and found to be ~ 68 nm and ~ 17 nm for CNPs and CNP@ZnO nanocomposites respectively. The elemental composition of both the samples were studied using Energy Dispersive X-ray analysis (EDAX) analysis. The results confirm the presence of C, O, K elements for CNP (Figure 2E) and C, O, Zn for the nanocomposites (Figure 2F)

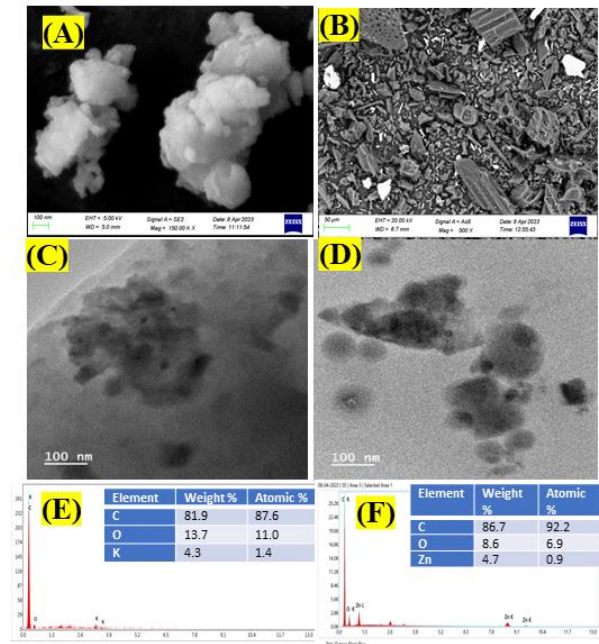


Figure 2: SEM micrograph of: (A) carbon nanoparticles (CNPs); (B) back scattered image of CNP@ZnO nanocomposites; TEM images of: (C) CNP; (D) CNP@ZnO nanocomposites; elemental composition (EDAX): (E) CNP; (F) CNP@ZnO

3.3. Photoluminescence study

The photoluminescence spectra of CNP and CNP@ZnO were shown in Fig. 3A and 3B respectively. In Fig. 3A, when the material is excited at 260 nm in absence of ammonia gas, two broad emissions occurred at ~ 473 nm (blue emission) and 616 nm (orange emission). Generally, the photoluminescence response of carbon nanostructures depend on the degree of surface oxidation and surface functional groups [15, 16]. The blue emission can be mainly assigned to the luminescence from the radiative recombination of the excited electrons from the $n-\pi^*$ transition of $C=O$ in the sp^2 region, whereas the orange emission band originates due to the presence of graphitic nitrogen and oxygen-related functional groups on the sp^2 carbon shell. However, in presence of ammonia gas, four emission lines occur at 375 nm, 474 nm, 561 nm and 623 nm corresponding to the violet, blue, green, and red emission

respectively. After the ammonia gas treatment, new surface functional groups are formed, which can be the cause of the red shifted photoluminescence response.

Mainly, if there are more surface defects, more electrons and holes can be trapped. Therefore, the red-shifted emission results from the recombination of trapped excitons. Also, the shift in wavelength and the formation of three distinct optical centers can be attributed to the changes in the electronic structure of the carbon nanoparticles caused by ammonia treatment. Ammonia is known to react with surface functional groups of carbon nanoparticles, leading to the formation of new surface species that can affect the electronic properties of the nanoparticles [17].

Fig. 3B shows the PL spectrum of CNP@ZnO nanocomposite samples. Before the ammonia treatment, one PL peak was observed at 473 nm (blue emission) with higher intensity compared to CNP, attributed to recombination of electron-hole pairs. While in the presence of ammonia gas, a red emission occurs at 621 nm with higher intensity. This red shift can be due to the reaction of ammonia gas with carbon to form amine functional groups by nucleophilic substitution, in which an ammonia molecule replaces a carbon atom on the surface of the nanoparticles. The formation of nitrogen-containing functional groups can occur via electrophilic substitution, in which the nitrogen atom of ammonia attacks the carbon atoms on the surface of the nanoparticles [18, 19]. This interaction between the surface functional groups within the synthesized material and the ammonium groups can cause an increase in the intensity and formation of new optical centers.

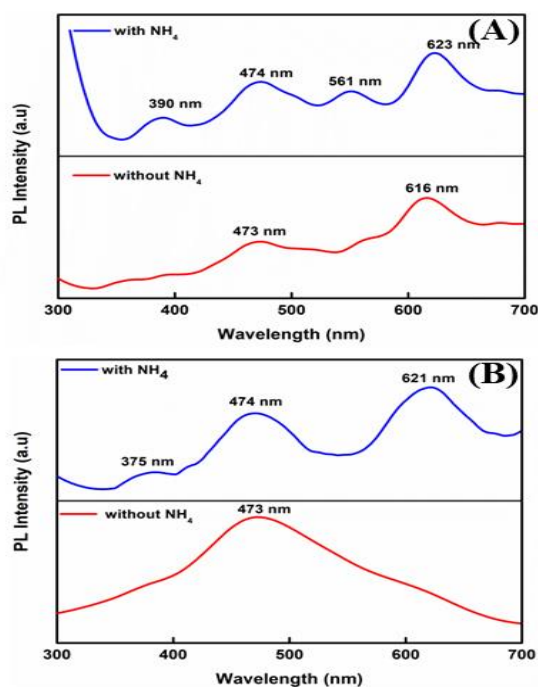


Figure 3: Photoluminescence spectra of: (A) carbon nanoparticles (CNPs) and (B) CNP@ZnO nanocomposites

Conclusions

Low-cost, high-quality, non-invasive, biodegradable, nontoxic sensor technology is a fundamental and critical factor for health diagnostics, food quality monitoring and industrial applications. The presence of ammonia in air, water, and the body has long been associated with liver, kidney, and gastrointestinal complications. Detection of ammonia with non-invasive methods is of particular interest to researchers and typically metal oxides among different materials have been used for this purpose. However, with renewable, nontoxic, low-cost, and abundant precursors, biomass derived carbon nanostructures are emerging cases of porous materials and have shown great potential for various applications. We prepared activated carbon and their nanocomposites with zinc oxide. Due to formation of nanocomposites, the carbon materials were functionalized with suitable emission sites. The renewed surface functional groups in the nanocomposites caused a significant change in luminescence response, shifting from blue to red peaks, making them excellent candidates for ammonia sensing. This intense red shift resulted due to the reaction of ammonia gas with carbon forming amine functional groups by nucleophilic substitution of an ammonia molecule replacing a carbon atom on the surface, creating new optical centers.

References.

- [1] Kwak, D., Lei, Y. and Maric, R., 2019. Ammonia gas sensors: A comprehensive review. *Talanta*, 204, pp.713-730.
- [2] Maity, D. and Kumar, R.T.R., 2018. Polyaniline anchored MWCNTs on fabric for high-performance wearable ammonia sensor. *ACS sensors*, 3(9), pp.1822-1830.
- [3] Lawaniya, S.D., Kumar, S., Yu, Y. and Awasthi, K., 2023. Ammonia sensing properties of PPy nanostructures (urchins/flowers) towards low-cost and flexible gas sensors at room temperature. *Sensors and Actuators B: Chemical*, 382, p.133566.
- [4] Aarya, S., Kumar, Y. and Chahota, R.K., 2020. Recent advances in materials, parameters, performance and technology in ammonia sensors: a review. *Journal of Inorganic and Organometallic Polymers and Materials*, 30, pp.269-290.
- [5] Timmer, B., Olthuis, W. and Van Den Berg, A., 2005. Ammonia sensors and their applications—a review. *Sensors and Actuators B: Chemical*, 107(2), pp.666-677.
- [6] Korotcenkov, G., 2007. Metal oxides for solid-state gas sensors: What determines our choice? *Materials Science and Engineering: B*, 139(1), pp.1-23.
- [7] Srivastava, V. and Jain, K., 2008. Highly sensitive NH₃ sensor using Pt catalyzed silica coating over WO₃ thick films. *Sensors and Actuators B: Chemical*, 133(1), pp.46-52.
- [8] Travlou, N.A., Seredych, M., Rodríguez-Castellón, E. and Bandosz, T.J., 2015. Activated carbon-based gas sensors: effects of surface features on the sensing mechanism. *Journal of Materials Chemistry A*, 3(7), pp.3821-3831.
- [9] Travlou, N.A., Ushay, C., Seredych, M., Rodriguez-Castellon, E. and Bandosz, T.J., 2016. Nitrogen-doped activated carbon-based ammonia sensors: effect of specific surface functional groups on carbon electronic properties. *ACS sensors*, 1(5), pp.591-599.

- [10] Luo, W., Zhao, T., Li, Y., Wei, J., Xu, P., Li, X., Wang, Y., Zhang, W., Elzatahry, A.A., Alghamdi, A. and Deng, Y., 2016. A micelle fusion–aggregation assembly approach to mesoporous carbon materials with rich active sites for ultrasensitive ammonia sensing. *Journal of the American Chemical Society*, 138(38), pp.12586-12595.
- [11] Fan, J., Kang, L., Cheng, X., Liu, D. and Zhang, S., 2022. Biomass-Derived Carbon Dots and Their Sensing Applications. *Nanomaterials*, 12(24), p.4473.
- [12] Moseenkov, S.I., Kuznetsov, V.L., Zolotarev, N.A., Kolesov, B.A., Prosvirin, I.P., Ishchenko, A.V. and Zavorin, A.V., 2023. Investigation of amorphous carbon in nanostructured carbon materials (A Comparative Study by TEM, XPS, Raman Spectroscopy and XRD). *Materials*, 16(3), p.1112.
- [13] Meena, Parmeshwar Lal, Krishna Poswal, Ajay Kumar Surela, and Jitendra Kumar Saini. "Synthesis of graphitic carbon nitride/zinc oxide (g-C3N4/ZnO) hybrid nanostructures and investigation of the effect of ZnO on the photodegradation activity of g-C3N4 against the brilliant cresyl blue (BCB) dye under visible light irradiation." *Advanced Composites and Hybrid Materials* 6, no. 1 (2023): 16.
- [14] Ebrahimi Naghani, M., Neghabi, M., Zadsar, M. and Abbastabar Ahangar, H., 2023. Synthesis and characterization of linear/nonlinear optical properties of graphene oxide and reduced graphene oxide-based zinc oxide nanocomposite. *Scientific Reports*, 13(1), p.1496.
- [15] Kozawa, D., Miyauchi, Y., Mouri, S. and Matsuda, K., 2013. Exploring the origin of blue and ultraviolet fluorescence in graphene oxide. *The journal of physical chemistry letters*, 4(12), pp.2035-2040.
- [16] Eda, G., Lin, Y.Y., Mattevi, C., Yamaguchi, H., Chen, H.A., Chen, I.S., Chen, C.W. and Chhowalla, M., 2010. Blue photoluminescence from chemically derived graphene oxide. *Advanced materials*, 22(4), pp.505-509.
- [17] Xu, Q., Li, W., Ding, L., Yang, W., Xiao, H. and Ong, W.J., 2019. Function-driven engineering of 1D carbon nanotubes and 0D carbon dots: mechanism, properties and applications. *Nanoscale*, 11(4), pp.1475-1504.
- [18] Tuci, G., Zafferoni, C., Rossin, A., Milella, A., Luconi, L., Innocenti, M., Truong Phuoc, L., Duong-Viet, C., Pham-Huu, C. and Giambastiani, G., 2014. Chemically functionalized carbon nanotubes with pyridine groups as easily tunable N-decorated nanomaterials for the oxygen reduction reaction in alkaline medium. *Chemistry of Materials*, 26(11), pp.3460-3470.
- [19] Khare, B.N., Wilhite, P., Quinn, R.C., Chen, B., Schingler, R.H., Tran, B., Imanaka, H., So, C.R., Bauschlicher, C.W. and Meyyappan, M., 2004. Functionalization of carbon nanotubes by ammonia glow-discharge: experiments and modeling. *The Journal of Physical Chemistry B*, 108(24), pp.8166-8172.