Synthesis and Characterization of a g-C₃N₄ Coupled Hybrid Nanocomposite for the Photocatalytic Effects

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Abstract. Photodegradation of organic pollutants using nanoparticles with suitable band gap is one of the most studied technologies in last few decades. About 8 nm antimony-doped tin oxide (ATO) nanoparticles, as the photocatalyst for organic degradation, is prepared by the calcination of the stoichiometric mixture of precursor hydroxides of Sn⁴⁺ and Sn³⁺. ATO was combined with thermally synthesized graphitic carbon nitride (g-C₃N₄ or g-CN) and the resulting Z-scheme g-CN/ATO nanocomposite was utilized for the decomposition of salicylic acid (SA) in aqueous solution. All the samples were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR) and the progress of the photocatalytic degradation reaction was measured by using UV-Visible spectroscopy. The rate constant measurements showed that the rate of degradation of SA is enhanced with hybrid nanocomposite.

1. Introduction
Heterogeneous photocatalysis has been regarded as the sustainable renewable technology to solve the global energy and environmental crisis, in which semiconductor materials generate reactive electron-hole pair by band gap excitation in presence of sunlight [1]. TiO₂ is considered most promising photocatalyst due to its low cost, high stability and non-toxicity as well as suitably placed band position and excellent surface properties. However, practical application of TiO₂ is hindered due to its wide band gap (Eg = 3.2 eV) which can only absorb UV light (λ < 380 nm) which is merely a 4% of the whole sunlight [2-5]. Thus, quest of alternative photocatalysts that can utilize the major portion of the sunlight i.e. visible light is another major strategy in the photocatalysis. Antimony doped tin oxide (Sb₂SnO₅: ATO) is one such semiconductor with excellent charge mobility and narrow band gap (Eg = 2.65 eV) that can absorb major portion of sunlight [6, 7]. However, firstly the band position of ATO is not appropriately placed with conduction band (CB, +0.95 V) and valence band (VB, +3.6 V); it cannot generate the reactive species in aqueous medium. Secondly, the recombination of electron-hole is faster than the electron transport [8].

Coupling of two semiconductors with matching band position can decrease the recombination rate due to the charge transfer and thus the photogenerated electron-hole pair becomes more available for higher catalytic efficiency [9, 10]. A notable strategy to overcome this limitation was applied by combining it with TiO₂ for the decomposition of Methylene Blue in a visible-light photocatalytic mechanism [11]. Next, graphitic carbon nitride (g-C₃N₄ or g-CN) could be a potential material for yet
another strategy, \( g\text{-C}_3\text{N}_4 \) has sufficiently negative conduction band position to utilize the photogenerated electron and its exfoliated 2D flat-structure provides more reactive sites that reduces \( e-\text{h} \) recombination rate [12]. Thus, a new z-scheme type ATO/\( g\text{-C}_3\text{N}_4 \) system is designed. The photocatalytic decomposition of a model organic compound salicylic acid (SA) was studied and the origin of the enhanced photoactivity was suggested in a mechanism.

2. Material and methods

2.1. Materials
All the reagents, melamine, tin chloride (\( \text{SnCl}_4 \cdot 5\text{H}_2\text{O} \)), sodium bicarbonate (\( \text{NH}_4\text{HCO}_3 \)), acetic acid (\( \text{CH}_3\text{COOH} \)), antimony chloride (\( \text{SbCl}_3 \)), ethanol, salicylic acid (SA) and \( \text{NH}_4\text{OH} \) were purchased from Sigma-Aldrich and used directly for experiments without any further purification.

2.2. Synthesis of \( g\text{-CN} \) nanosheet
Melamine was thermally polymerized at 550 °C for 3 hr in a muffle furnace resulting yellowish graphitic carbon nitride (\( g\text{-CN} \)) [13]. \( g\text{-CN} \) powder was crushed into fine powder and again heated at 550 °C for 3 hr to complete the polymerization of the remaining melamine. Next, the bulk \( g\text{-CN} \) powder was stirred overnight with oxalic acid (1.0 M). Thus, exfoliated \( g\text{-CN} \) nanosheet was separated from the suspension by filtration, freeze-dried and heated at 300 °C to remove the residual oxalic acid.

2.3. Synthesis of ATO nanoparticles and ATO/\( g\text{-CN} \) nanocomposite
In the synthesis of ATO nanoparticles as reported in [14], 50 ml of ethanol was vigorously stirred with 3.25 g of \( \text{SnCl}_2 \cdot 5\text{H}_2\text{O} \), 5 mol% \( \text{SbCl}_3 \), 5.5 g \( \text{NH}_4\text{HCO}_3 \) and 1.75 g \( \text{CH}_3\text{COOH} \) in a 100 ml beaker for 4 hr. The pH of the solution was adjusted at 7 by adding ammonia solution. The white suspension of the \( \text{Sn(OH)}_3 \) and \( \text{Sb(OH)}_3 \) was centrifuged and washed 3 times with distilled water and calcined at 550 °C for 8 hr. The bluish grey powder confirmed the formation of ATO nanopowder. For the synthesis of ATO/\( g\text{-CN} \) nanocomposite, ATO NP and \( g\text{-CN} \) were separately sonicated in ethanol: water (1:1) solution for 30 min and mixed together before a hydrothermal treatment at 180 °C for 4 hr. The resulting composite with 1%, 5% and 10% by weight of \( g\text{-CN} \) was washed several times and dried.

2.4. Characterization
The crystal phase of the prepared samples was identified by X-ray powder diffraction (Rigaku Multiflex diffractometer). Likewise, the surface morphology of all samples was analyzed by a field-emission scanning electron microscope (FE-SEM, S-7400, Hitachi, Japan). Furthermore, the morphology and crystal phase were also analyzed using high-resolution transmission electron microscope (HR-TEM, JEM-2010F-JEOL Japan).

2.5. Photocatalytic measurement
The photocactivity of the samples was studied in terms of the photodegradation of SA with visible light source [15]. 1 mg/l of the catalyst and 50 ml of the 10 mg/l SA aqueous solution were stirred in a 100 ml photo-reactor for 30 min in dark to attain the adsorption-desorption equilibrium between the catalyst and SA. The solution was irradiated with visible light from A 300 W Xe lamp (DY, Tech., Korea) equipped with a UV and IR cut-off filters (Edmund optics, USA). After certain time interval, 2 ml aliquot of the solution was drawn out with a syringe fitted with a filter and the absorbance was measured in a UV-Visible spectrophotometer. The concentration of the remaining SA corresponding to the absorbance at 297 nm was calculated from the Beer-Lambert Law. Finally, the rate of the photodegradation of the various samples was compared by the following equation:

\[
\text{Degradation efficiency} \,(\%) = 1 - \frac{C}{C_0} \times 100\%
\]

Here, \( C_0 \) is the concentration of SA at 0 min, and \( C \) is the concentration of residual SA at a certain time \((t)\). The dark reaction was also performed for the comparison.
3. Results and discussion

3.1. Morphological studies

XRD pattern in figure 1(a) shows the diffraction peaks of SnO$_2$ with tetragonal rutile structure corresponding to the JCPDS card number 01-072-1147. No impurity peaks related to Sb$_2$O$_3$ or Sb$_2$O$_5$ and the bluish grey color of the powder indicated successful doping of Sb on the crystal lattice of SnO$_2$ and indicated the presence of the new energy band of ATO below the conduction band minima, originated from outer orbitals (5d and 6s) of Sb. Thus, the CB minima of SnO$_2$ is lowered and band gap of ATO as 2.55 eV [16]. XRD pattern of 10% ATO/g-CN composites revealed no characteristic diffraction g-CN in the nanocomposite likely due to the low g-CN content as shown in figure 1(b)) [17].

![Figure 1. XRD spectra of (a) ATO nanoparticles, (b) 10% ATO/g-CN nanocomposite and (c) g-CN nanosheet.](image)

The shape size and the crystalline nature of the as-prepared nanoparticle and nanocomposites were investigated in detail by FESEM and TEM/HRTEM as shown in figure 2. Figure 2(a) and 2(b) showed FESEM images of monodispersed ATO with high aggregation and 5% ATO/g-CN nanocomposite respectively. The image of 5% ATO/g-CN nanocomposite shows the good attachment of ATO nanoparticles and the g-CN sheet. The intercalation of ATO NPs on g-CN sheet resulted in less agglomeration in the nanocomposite which would significantly increase the surface area and surface characteristics like porosity of the nanocomposite compared to individual components. A TEM image in figure 2(c) shows clusters of uniform 8 nm ATO nanoparticles. Figure 2(d) shows the TEM image of exfoliated g-CN sheet. Figure 2(e) shows the TEM image of the 5% ATO/g-CN nanocomposite [18]. HRTEM of 5% ATO/g-CN nanocomposite shows well-developed lattice fringes of ATO nanoparticles which underlines high crystallinity in figure 2(f). The d-spacing of 0.335 nm corresponds to the 101 planes of the tetragonal rutile crystal (JCPDS: #01-072-1147).
3.2. **Photocatalytic activity**

The photodecomposition of SA with different samples was assessed under visible-light irradiation. The concentration of the remnant SA was quantified from the absorption peak at 297 nm in the UV-Visible spectra with respect to different samples. Then, the concentration of solution with several photocatalytic samples was plotted as a function of photoreaction time as displayed in figure 3.

![Figure 3](image3.png)

**Figure 3.** The absorption spectra of SA degradation over $^{5}$ATO/g-CN, and the Photoactivity of different samples.
ATO/g-CN nanocomposites demonstrated higher photoactivity than the bare ATO or g-CN. Approximately 75% of SA was removed in the 1.5 hr irradiation time, whereas the bare ATO or g-CN could only remove 9% and 38% respectively. The photoactivity of ATO/g-CN nanocomposites is increased by increasing the g-CN content from 1 to 5 wt% by weight however but it is decreased above 5 wt% as in figure 3b. In brief, approximately 48%, 75%, and 54% of the SA is mineralized by 1 wt%, 5 wt% and 10 wt% ATO/g-CN nanocomposites respectively in 1.5 hr photoreaction time. Based on the above results, the photocatalytic mechanism of ATO/g-CN nanocomposite was proposed in figure 4. The narrow band gap ATO nanoparticles (2.65eV) and g-CN (2.6eV) can both absorb visible light leading to the formation of e-h pairs. Since the CB minimum of the g-CN (-1.13V) is quite negative compared to that of ATO (+0.95 V), the photogenerated electrons from the CB of g-CN to the CB of ATO cannot jump due to the steep downhill in the energy level, but CB electron of ATO easily jump to the VB of g-CN (+1.47 V). In this way, the recombination rate in both semiconductors is significantly decreased.

This suggests to the well-known Z-scheme photodegradation process in which the holes in the VB of ATO (+2.9V) and the electrons in the CB of g-CN take part in the degradation process. This leads to the reduction of O₂ at the CB of g-CN to produce the active species superoxide (•O₂⁻) and oxidation of water to the hydroxyl (•OH) radical [19]. These reactive species subsequently oxidize the adsorbed SA on photocatalyst surface. Additionally, holes generated in the ATO VB also oxidize SA to CO₂ and H₂O and other simpler inorganic molecules. Thus hydroxyl (•OH), superoxide (•O₂⁻) and h⁺ are the three predominant active species responsible for the enhanced photodegradation of SA as elaborated in the following equations:

\[
\text{Photo-excitation:} \quad \text{Photocatalyst} + hν \rightarrow (e^- + h^+) \]
Photo-reduction:
\[ \text{O}_2 + e^- \rightarrow \cdot \text{O}_2^-; \]
\[ \cdot \text{O}_2^- + e^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2; \]
\[ \text{H}_2\text{O}_2 + e^- \rightarrow \cdot \text{OH} + \cdot \text{OH} \]

Photo-oxidation:
\[ 2\text{h}^+ + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \cdot \text{OH} \]

Photo-degradation:
\[ \cdot \text{O}_2^-; \cdot \text{OH} + \text{SA} \rightarrow \text{Degradation products.} \]

Based on above experiments the photocatalytic scheme has been designed as shown in figure 4.

4. Conclusion
Thus, monodisperse 8 nm bluish ATO nanoparticles were synthesized and applied with g-CN for the photocatalysis. Z-scheme ATO/g-CN nanocomposite showed the higher photoactivity compared to the ATO nanoparticles towards salicylic acid mineralization. The higher photocatalytic activity of ATO/g-CN over g-CN and ATO under visible light irradiation is attributed to the well-aligned band position and increased surface properties. This ultimately accelerated charge-carrier transfer rate, lowered recombination rate and subsequently enhanced photoactivity.

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