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SYTHESIS AND CHARACTERIZATIONS OF GCN (GRAPHITIC CARBON NITRIDE) AND ZnO MODIFIED GCN

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ABSTRACT

The polymeric GCN (Graphitic Carbon Nitride) materials were fabricated by the pyrolysis of urea. GCN is composed of tri-s-triazine based structure and a potential metal-free photocatalyst that can be used to address both the energy crisis and environmental issues. GCN has a small surface area and low charge carrier mobility. The most stable form of carbon nitrides, GCN, has attracted a lot of attention. Moreover, because to its high condensation level, it exhibits remarkable thermal stability and chemical inertness. Due to its distinctive band structure, creating a heterojunction composite by coupling it with a wide band gap semiconductor offers a viable technique to enhance charge separation and increase surface area. A common heterogeneous catalyst with strong catalytic activity that is non-toxic and insoluble is zinc oxide (ZnO). The wide band gap semiconductor ZnO has potential uses. Zinc acetate dihydrate is pyrolyzed to produce ZnO. ZnO is used in the one pot pyrolysis method to modify GCN. Using XRD, Raman spectroscopy and SEM the structural, chemical and elemental composition of GCN, ZnO, and ZnO modified GCN were investigated.

Keywords: GCN, ZnO, ZnO- GCN

INTRODUCTION

Graphitic carbon nitride (GCN), a semiconductor polymeric photocatalyst, has attracted growing interest in the field of visible light-induced hydrogen evolution reaction (HER) because of its straightforward synthesis process, low band gap energy, light absorption in the visible spectrum, and ease of application. These days, a semiconductor material with a structure akin to graphite is called graphitic carbon nitride (GCN). Its tris-s-triazines-based 2D-planar layers are stacked one on top of the other by weak Van der Waals forces [1]. GCN is a cheap substance that can be easily and sustainably produced in huge quantities. Precursors can include melamine [2], urea [3], and cyanimide [4], among other chemical molecules with a high nitrogen concentration. Despite being one of the first synthetic polymers carbon nitrides were not widely used at the time due to their unknown structure [5]. Due to extensive research conducted most recently, the fundamental structure of carbon nitrides is gradually being established. Due to its distinct visual and photocatalytic capabilities, GCN, the most stable allotrope of carbon nitrides, has drawn a lot of interest [6]. Moreover, because to its high condensation level, it has exceptional thermal stability and chemical inertness. Previous studies [7-11] have described its promising applications in fluorescence spectroscopy [12–13] and photo-catalysis [7–11]. Moreover, this useful substance has applications in electrochemistry such as electrocatalysis and electrochemiluminescence [14–17]. GCN was usually used in the fabrication of sensitive electrochemical sensors based on its catalytic activity [18-19]. In a variety of industrial processes, zinc oxide (ZnO) is a frequently used heterogeneous catalyst with high catalytic activity that is non-toxic, insoluble, and reasonably priced [20]. On the other hand, ZnO and its mixed-metals have been employed as photocatalysts that break down halogen compounds, and the photocatalytic activity increased as the size of ZnO particles approached nanoscale levels [21-22]. Moreover, constructing a heterojunction coupling between GCN and semiconductors with compatible band structures is an excellent way to separate photogenerated charges effectively and broaden the absorption spectrum [23-24]. Using urea and the zinc acetate dihydrate $[ZnCO3]2•[Zn(OH)2]3$, we attempted to produce a ZnO-GCN composite. In this study, the zinc acetate dihydrate and urea one pot pyrolysis reaction was used to easily synthesis the ZnO-GCN composite.

MATERIALS AND METHODS

Materials

Urea, Zinc acetate dehydrate were obtained from Nice Chemicals Private Limited.

Synthesis of GCN

GCN is produced by calcined 10g of urea at 400°C for three hours in a muffle furnace.

Synthesis of ZnO

A crucible containing 5g of zinc acetate dihydrate was placed in a muffle furnace and calcined to 400°C for three hours.

Synthesis of ZnO modified GCN

Zinc acetate dehydrate was dissolved in 10 ml of distilled water and thoroughly stirred. 10g of urea was dissolved, then mixed once more. The solution was heated to 60°C for two hours in an oven. The powder was extracted, thoroughly ground, and deposited in a crucible in a muffle furnace where it was calcined at 400°C for three hours.

CHARACTERIZATIONS

A Field-Emission Scanning Electron Microscope (HITACHI, SU-6600, FESEM) were used to examine the structural morphology of the products . Using X-ray diffraction (Bruker Kappa APE XII) the crystalline structure of the as-prepared samples was examined. Using a confocal Raman instrument (CRM200), Raman spectra between 400 and 2000 cm1 were obtained.

RESULTS AND DISCUSSION

XRD

GCN-pure and ZnO-GCN composite samples' X-ray diffraction (XRD) patterns Figure 1 demonstrated graphitic stacking of C_3N_4 and displayed a prominent peak at 27.3°, which corresponds to the (002) plane [25-26]. The introduction of ZnO may limit the formation of GCN-pure crystals because the intensity of the (002) peak was shown to diminish with increasing amount of $Zn(CH_3CO_2)_2 \cdot 2H_2O$ in the precursor system [27]. At 13.1°, which corresponds to the (100) plane, a second, less powerful peak also occurred. This peak might be related to the distance between nitride pore pores, which is an in-plane structural paacking motif of GCN [28].When ZnO was added, the smaller peak's strength decreased, indicating a significant link between the GCN-pure host and the new ZnO. Peaks of the wurtzite hexagonal phase of zinc oxide are shown in Figure 2 [29]. No additional ZnO peaks were seen in the ZnO-GCN sample, which may have been caused by the ZnO content of the ZnO-GCN composite being so low.

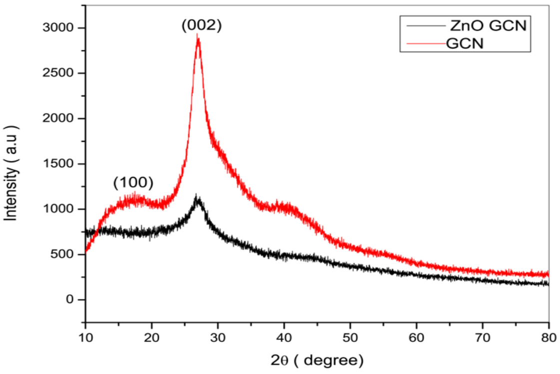

Fig 1: XRD of GCN and ZnO-GCN

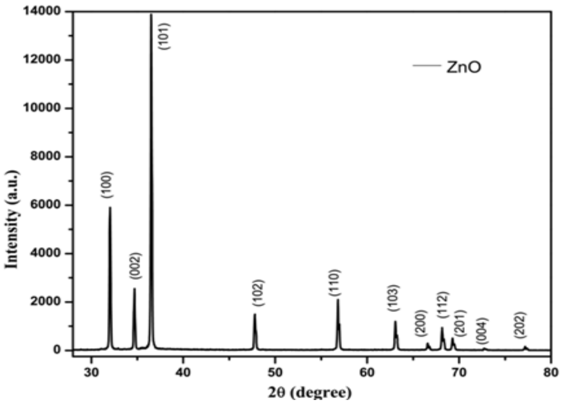

Fig 2: XRD Of ZnO

Raman Spectra

The structural differences between pure ZnO and GCN, as well as ZnO-GCN nanocomposite, are visible using Raman spectroscopy. The disordered (D) band at 1374 cm-1 and the graphitic (G) band at 1582 cm-1 are two distinct peaks that were identified for the ZnO-GCN nanocomposite, indicating the presence of the carbon phase shown in Figure 4. The presence of sp2 C-C bonds and aromatic six-membered sp2 clusters corresponds to the occurrence of the D and G bands in the spectral area between 1300 cm-1 and 1600 cm-1 [30]. Similar distinctive peaks and greater shifts in the Raman spectra of the ZnO-GCN nanocomposite indicate the same crystalline structure. These changes can also be attributed to how ZnO and GCN interact chemically. The spectrum of pure ZnO is shown in Figure 3 and the hexagonal wurtzite phase of ZnO is represented by the peaks at 323 cm1, 422 cm1, and 523 cm1. ZnO oxygen shortage flaws are represented by the peak about 523 cm1 [31].

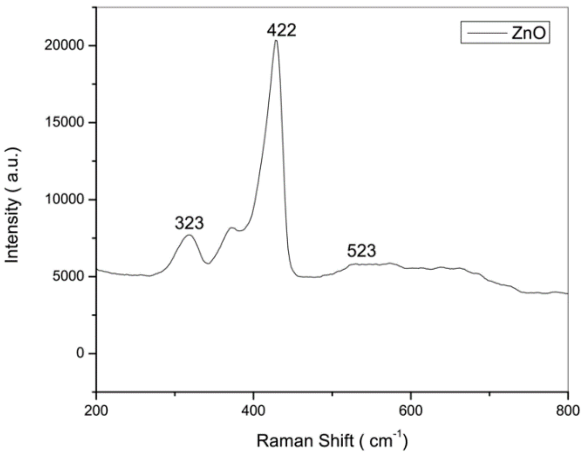

Fig 3: Raman spectra of ZnO

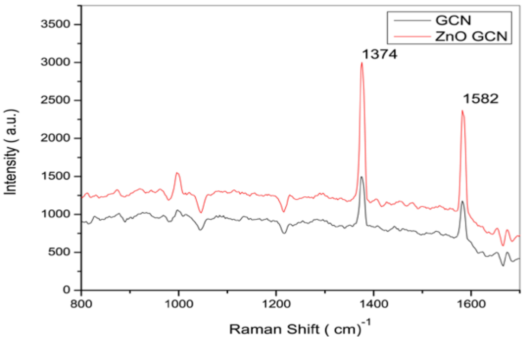

Fig 4: Raman spectra of GCN and ZnO-GCN

SEM

SEM was used to examine the morphological and microstructural characteristics of the samples for GCN pure and ZnO-GCN. The stacked layer morphology of GCN formed from urea was found to be identical to the SEM image Figure 5 of GCN's pure layered structure [32]. Figure 6 shows the evolution of ZnO-GCN into a loosely interconnected network of elongated fibres with a mean diameter of 20–60 nm after ZnO was added to GCN-pure. According to SEM examination, the thermal polymerization reaction between $Zn(CH_3CO_2)_2 \cdot 2H_2O$ and urea resulted in the production of a loose structure of ZnO-GCN with a greater surface area and porosity, which most likely happened because of the influence of released gases during the reaction.

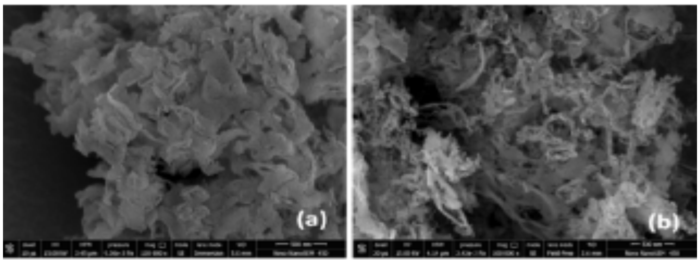

Fig 5: SEM of a) GCN and b) ZnO-GCN

CONCLUSION

The ZnO-GCN composite was easily made, and it was studied using the XRD, SEM, and Raman spectra. XRD and Raman investigations showed that ZnO strongly coordinated with GCN-pure and that the addition of ZnO caused some degradation in the crystalline structure of GCN-pure. The Raman spectra of the ZnO-GCN nanocomposite show similar distinct peaks and larger shifts, which point to the same crystalline structure of GCN. SEM analysis revealed that the thermal polymerization process between Zn(CH3CO2)2•2H2O and urea produced a loose structure of ZnO-GCN with a higher surface area and porosity, which most likely occurred due to the influence of released gases during the reaction. Eventually, ZnO was used to successfully modify the structural properties of GCN, and images from a scanning electron microscope (SEM) were used to identify the ZnO content in the GCN.

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