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Synthesis, structural and morphological property of a novel Pd/g-CN nano composite for gas sensing application

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Abstract. In this paper graphitic carbon nitride (g-CN) was synthesized using urea as a precursor at temperature 550 °C in a muffle furnace. Palladium Nano-particles were introduced in the graphitic carbon nitride matrix by fairly new chemical sol-gel process followed by filtering and drying. Material characterization such as X-Ray Diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and Energy-dispersive spectroscopy (EDS) were performed. XRD indicates the formation of polycrystalline material. SEM and TEM analysis indicate the uniform Palladium nanostructures impregnated g-CN matrix. EDS analysis justifies the presence of all the elements.

1. Introduction

The demand for hydrogen as a clean energy has gained immense significance now a day due to its ready availability and eco-friendly with the nature. Moreover, hydrogen being clean, efficient, renewable, and its only by-product is water [1]. In the near future, hydrogen energy would be one of the prominent green energy sources for vehicles, industries and many other applications. Hydrogen being explored in all possible fields such as fuel cell technology, industries, militaries, research, and petroleum industries, etc. Therefore, it is also indispensable to detect the leakage of the hydrogen.

In order to overcome such requirement, a reliable sensing material is needed to detect the hydrogen gas in its lower explosion limit that is 0.1 to 4% hydrogen content in an air [1-2]. The sensing material must have better sensitivity, selectivity, reliability, durability and should be cost-effective. Many reports have employed palladium (Pd) as the active sensing material due to its strong affinity towards hydrogen [2-6]. Palladium when exposed in a hydrogen-rich environment, the hydrogen atoms react with the palladium and adsorption of hydrogen in palladium take place, as a result, palladium transforms to palladium hydride (PdH_x) [3-6]. During this process phase transition from α to β occurs [7]. These phase transitions are irreversible in nature in case of pure palladium, as a result, the lifetime and stability of the hydrogen gas sensor are affected [7]. In order to overcome such difficulty with pure palladium, alloy/composites of Pd with several other metals such as Pd-Ag, Pd-Pt, Pd-Au, Pd-Ni, Pd-Cr, Pd-Al, Pd-NiO_x, Pd-TiO₂, Pd-WO₃, Pd-SnO₂/MoS₂, Pd/(Mg-Ni and Mg-Ti) and Pd-Cu have been explored to get better repeatability, stability and durability as a hydrogen gas sensor [7-11]. In our presented report, palladium/graphitic carbon nitride (Pd/g-CN) composite was explored as a prominent and reliable sensing material. Graphitic carbon nitride (g-CN) is a semiconducting polymer having a band gap of 2.7 eV consisting of carbon and nitrogen atoms arranged in graphitic-like



structure [12-15]. g-CN can be used for an efficient gas sensor due to its stability and non-poisonous in nature [16]. g-CN possesses remarkable electronic, mechanical and optical properties as well as a high thermal and chemical stability [15-17]. g-CN being multifunctional catalyst has enormous applications in photo-catalytic activity, photo-electrochemical, energy conversion, storage, and gas sensing [18-21]. g-CN has drawn immense significance owing to its low cost and easy synthesis [18]. The g-CN fine powder can be prepared via facile Thermal poly-condensation of nitrogen-rich precursors (such as urea, thiourea, cyanamide, dicyandiamide, and melamine), electrodeposition, pulse laser deposition (PLD) and sputtering [12-18]. In our experiment urea was selected as a precursor in order to make graphitic carbon nitride matrix. Further graphitic carbon nitride matrix was modified by incorporating palladium nanoparticles as it gives strong selectivity, sensitivity and durability towards hydrogen gas. Sensing material was synthesized by thermal condensation followed by the sol-gel process.

2. Material synthesis:

2.1 Preparation of g-CN:

The g-CN powder was prepared by calcination with urea as a precursor. Typically, 10g of urea was placed inside a quartz crucible (50ml) and followed by heating at 550°C in a muffle furnace for 3h followed by step heating. This method overcomes the requirements of other supplements such as carrier gases, vacuum, etc. To get nanoparticle, prepared bulk g-C₃N₄ was ground well into the fine powder with the use of mortar and pestle, then dispersed in a solution consisting of DI water followed by the successive sonication for 12 hours. The unexfoliated g-C₃N₄ was removed by centrifugation.

2.2 Preparation of Pd/g-CN Composite:

To incorporate palladium nanoparticle into the graphitic carbon nitride matrix fairly new synthesis process was explored in which 80 mg of Graphitic carbon nitride fine powder was added into the 100 ml DI water, followed by sonication at room temperature. Ammonium tetrachloropalladate (II) [(NH₄)₂PdCl₄] fine powder was added to the g-CN solution followed by continuous sonication. A reducing agent solution was separately prepared by adding NaOH and NaBH₄ under constant magnetic stirring at 400 RPM at room temperature. As a result, the black colored solution of Pd/ g-C₃N₄ composite was obtained which was then centrifuged and dried.

3. Results and Discussions:

3.1 X-ray diffraction analysis:

The X-ray diffraction (XRD) pattern of the graphitic carbon nitride polycrystalline bulk powder and nanoparticle was done using a Smartlab Rigaku diffractometer (CuK α , λ =1.5405Å) and obtained graph is shown in the fig (1). From the graph it implies that the bulk graphitic carbon nitride shows a strong peak at 27.5 which corresponds to interlayer diffraction of the conjugated aromatic systems and a weak peak at 13.01 corresponds to in-planar repeated tri-s-triazine units [12-15], the peak shows that the intensity of the interlayer diffraction reduces as it goes from bulk to nanoparticle. The interlayer spacing for a peak at (002) was calculated 0.323nm using Bragg's law similarly the interlayer spacing for the (100) peak was calculated as 0.679nm respectively.

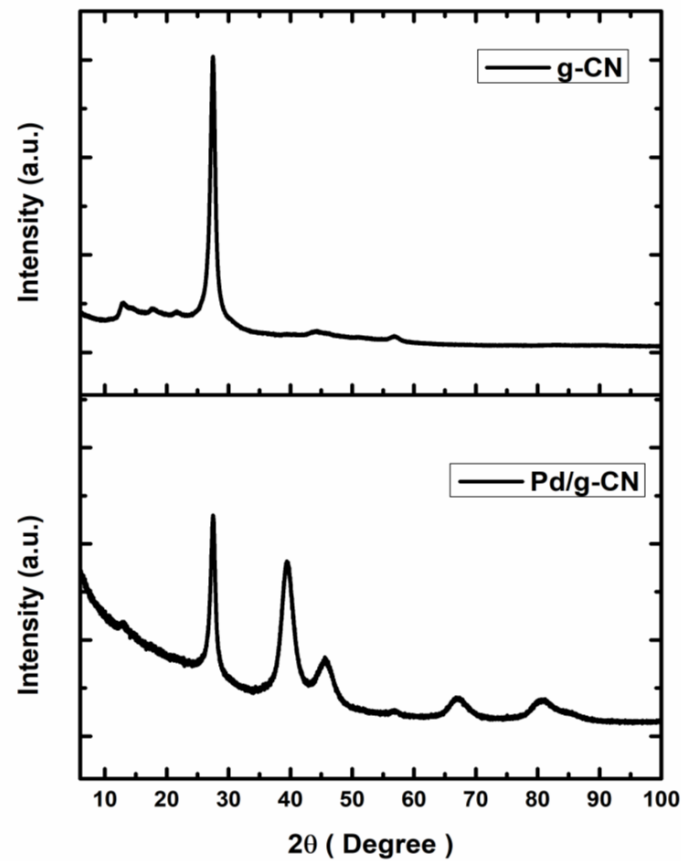


Fig. 1: XRD image of g-CN and Pd/g-CN material.

Introduction of Palladium at g-CN matrix gives rise to sharp palladium peaks at 39.64°, 45.73°, 67.12°, 80.95° and 85.58° which correspond to palladium (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) FCC crystal planes [8].

Crystallite size of metal particles was calculated using Scherrer's formula:

$$d(\text{\AA}) = k\lambda/(\beta \cos \theta)$$

Where $k = 0.9$ (a coefficient); $\lambda = 1.5405 \text{ \AA}$ (wavelength of $K\alpha$ radiation); β = full width at half maximum of corresponding peaks; θ = peak position. The calculated average crystallite size is around 3-5 nm.

3.2 Energy-dispersive X-ray spectroscopy:

The Energy-dispersive X-ray spectroscopy (EDS) analysis shown in the fig (2) justifies the presence of carbon (C), nitrogen (N), and palladium (Pd), with the support of following data it is concluded that palladium nanoparticles are present in the graphitic carbon nitride matrix.

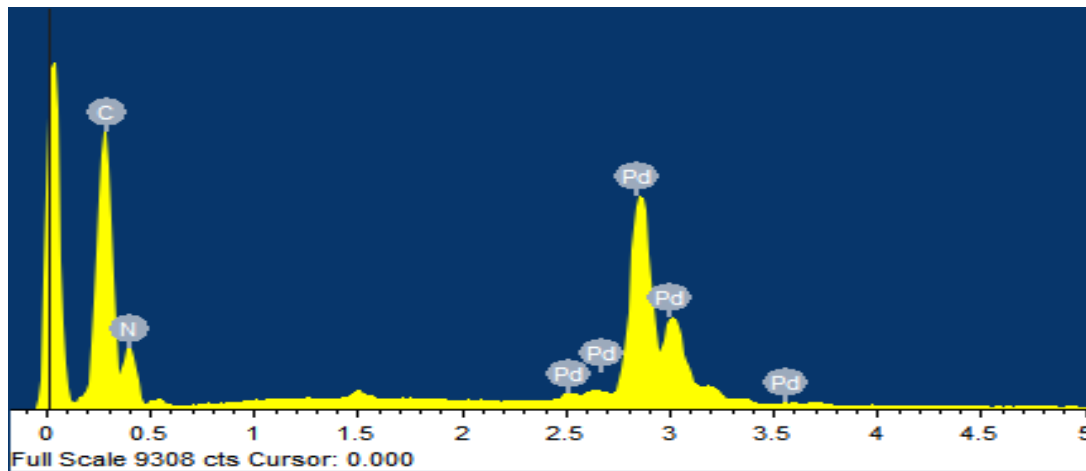


Fig. 2: EDS image of g-CN and Pd/g-CN material.

4. Morphological analysis:

4.1 SEM Analysis:

Morphological analysis of the g-CN and Pd/g-CN powder samples were investigated with the use of sophisticated FESEM and TEM facilities. SEM analysis of the g-CN and Pd/g-CN was done using JSM-7600F (FEG) instrument shown in the fig (3), which gives the morphological background of the particles. SEM image reveals the irregularity in the layers and porosity. Pt coating of 5nm thickness on the g-CN and Pd/g-CN was done in order to overcome the charging effect. In case of Pd/g-CN it was found that Pd nanoparticles around 3-5nm were formed and uniformly settled on a g-CN matrix. Though in some places Pd cloud was noticed due to uneven loading.

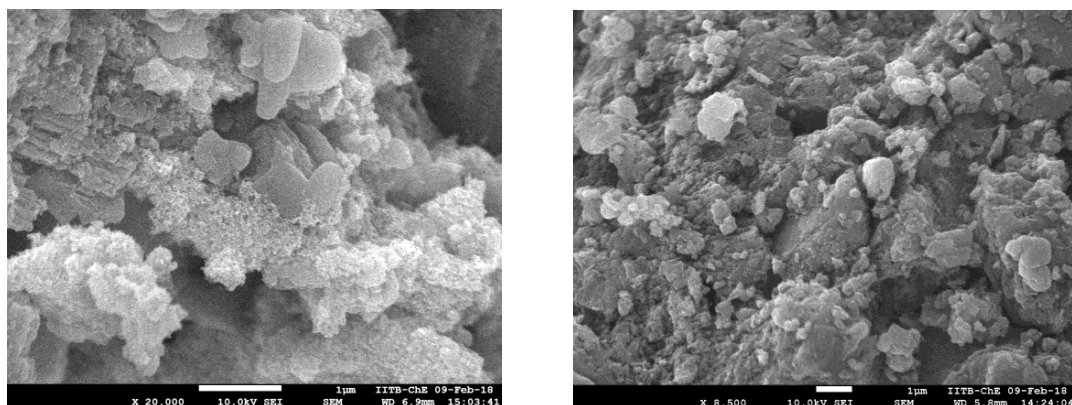


Fig. 3: SEM image of g-CN and Pd/g-CN material

4.2 TEM Analysis:

TEM images of the samples were taken using **Philips CM 200** instrument. TEM image of g-CN is shown in the fig (4) it indicates g-CN sheets which overlies. Pd/g-CN TEM image justifies the Pd nanoparticle size which is around 3-5nm is closely matches with the particle size, which was calculated using Scherrer's formula of the obtained XRD data.

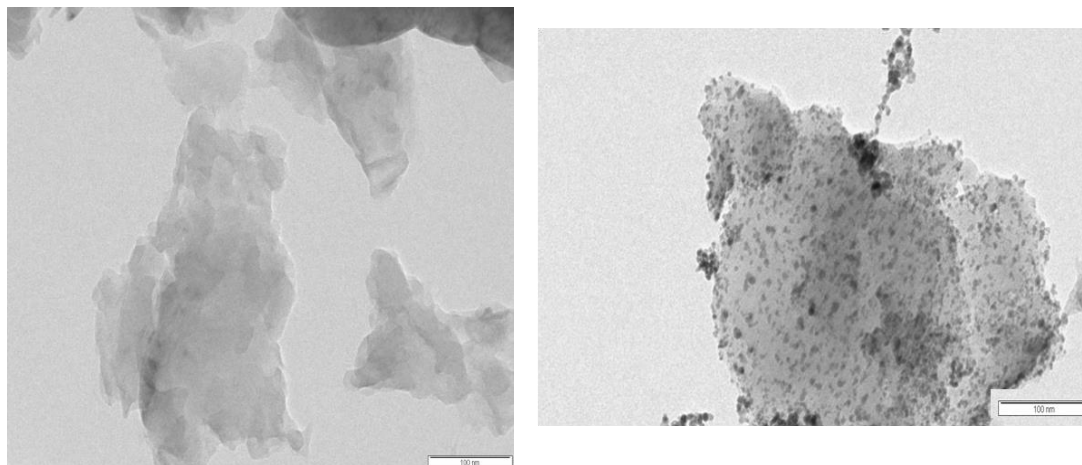


Fig. 4: TEM image of g-CN and Pd/g-CN material.

5. Conclusion

Pd/g-CN nano-composite was prepared and characterizations were done, which justify the presence of Pd and g-CN. XRD data justifies the presence of Palladium and g-CN with signature peaks at reported 2θ values and material showed polycrystalline in nature, indicating the inter-planer stacking of repeated tri-s-triazine rings. SEM and TEM images show the uniform dispersion of Pd nanoparticle on the g-CN lattice. XRD, TEM studies confirm the particle size of palladium to be in 3-5 nanometres. This novel composite can be utilized as a prominent hydrogen gas sensing material.

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