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Spectroscopic Characteristics of Carbon Nitride Nanostructures Synthesized by Fast Glow Discharge-Induced Reaction of Methane and Ammonia

Hayder G. Fahad, Rand B. Lutfi, Sohaib S. Ahmed, Oday A. Hammadi

Department of Physics, College of Education, Al-Iraqia University, Baghdad, IRAQ

Abstract
In this work, the spectroscopic characteristics of carbon nitride nanostructures synthesized by the reaction of methane and ammonia gases were studied. This reaction was induced by electric power transferred to the reaction volume throughout argon fast glow discharge at high pressures at room temperature. This power was applied to the reaction as short pulses to produce carbon nitride nanoparticles without production of cyanogen molecules. A clear correlation between synthesis parameters and material properties was revealed. The refractive index measurements show that shorter pulse durations yield nanoparticles with higher refractive indices, likely due to increased material density or specific structural arrangements. These findings highlight the importance of precise pulse duration control for tailoring carbon nitride's optical properties for various applications. Longer pulse durations (1 ms) lead to higher UV-Vis absorption, suggesting increased yield or more developed π-electron systems. The consistent formation of characteristic C-N bonding was confirmed regardless of pulse duration. Most notably, shorter pulse durations (0.01 ms) result in a significantly higher refractive index, indicating a denser or more ordered material.

Keywords: Carbon nitride; Nanostructures; Glow discharge; Spectroscopic characteristics
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1. Introduction

Carbon nitride (C_3N_4) nanoparticles represent an emerging class of metal-free materials with promising applications in fields such as photocatalysis, energy conversion, environmental remediation, and biomedicine. These materials are composed primarily of carbon and nitrogen atoms arranged in various polymeric frameworks, most notably graphitic carbon nitride (g-C_3N_4). Due to their unique electronic structure, visible light responsiveness, and chemical robustness, carbon nitride nanoparticles have garnered significant interest in both fundamental research and applied science [1-3].

C_3N_4 nanoparticles, particularly in their graphitic form, possess a two-dimensional layered structure analogous to graphene. The layers are formed by heptazine or triazine units linked through tertiary amines. The interlayer stacking is typically held together by van der Waals forces, allowing for exfoliation into few-layer or even monolayer sheets. Nanoparticle morphology can vary based on synthesis conditions but generally falls within the 5–100 nm range, with high surface area and tunable porosity. C_3N_4 nanoparticles are thermally stable up to around 600°C in air and over 700°C under inert atmospheres. Their chemical resistance is also notable, showing high stability in acidic and neutral environments, although they can slowly degrade in strong alkaline solutions. This robustness makes them suitable for a range of environmental and chemical applications [4-6].

C_3N_4 is a semiconductor with a band gap typically around 2.7 eV, making it responsive to visible light. The conduction and valence bands are primarily composed of nitrogen 2p and carbon 2p orbitals, giving it a redox potential suitable for photocatalytic hydrogen production and pollutant degradation. Modifications such as doping or nanostructuring can tailor the band gap and electronic transitions to specific needs. The surface of C_3N_4 nanoparticles is rich in amine groups (-NH_2) and nitrogen vacancies, which serve as active sites for adsorption, catalysis, and functionalization. These surface features enable strong interactions with metal ions, organic pollutants, and biological molecules, facilitating applications across diverse domains [7-9].

Various methods have been developed to synthesize carbon nitride nanoparticles, with the choice depending on the desired particle size, crystallinity, and application. The most common method for preparing g-C_3N_4 involves the thermal polymerization of nitrogen-rich precursors such as melamine, urea, cyanamide, or dicyandiamide. The precursor is heated in a crucible under air or inert gas (typically 500–600°C), leading to the release of ammonia and the formation of a polymeric carbon nitride framework. By tuning the temperature and precursor, nanoparticles of varying size and crystallinity can be obtained. Solvothermal methods involve reacting precursors in sealed autoclaves with solvents at elevated temperatures and pressures. This technique can yield well-dispersed nanoparticles with controlled morphology. Hydrothermal conditions are especially effective when doping with metals or forming heterostructures with other semiconductors [10-12].

Bulk C_3N_4 can be converted into nanoparticles or nanosheets through sonication in suitable solvents such as ethanol, isopropanol, or water. The mechanical energy breaks the weak van der Waals forces between layers, yielding few-layer or nanoparticulate forms. This method is often combined with chemical exfoliation using acids or alkalis for more effective delamination. Soft and hard templates such as silica nanoparticles, block copolymers, or salt crystals are used to create porous carbon nitride nanostructures. After polymerization, the template is removed via chemical etching or thermal treatment, leaving behind nanoparticles with tunable porosity and high surface area. This method is widely used to enhance photocatalytic performance [13-16].

Nanoparticles can be doped with heteroatoms (e.g., sulfur, phosphorus, boron) or integrated with other materials (e.g., graphene, TiO_2, quantum dots) to improve their optical, electronic, or catalytic properties. Such composites are often synthesized using one-pot co-condensation methods or post-synthesis functionalization [17,18].

C_3N_4 nanoparticles are widely investigated for photocatalytic applications, particularly under visible light. They can catalyze: water splitting to generate hydrogen, degradation of organic pollutants in wastewater, reduction of CO_2 to value-added chemicals. In solar cells, C_3N_4 can be used as a photoanode material or as a sensitizer in dye-sensitized solar cells. Additionally, its high conductivity (when doped) and chemical stability make it a candidate for supercapacitors, lithium-ion battery anodes, electrochemical sensors. The biocompatibility, low toxicity, and photoluminescence of C_3N_4 make it useful in bioimaging, due to its stable fluorescence under UV light, photodynamic therapy, where it can generate reactive oxygen species under light, drug delivery, with its surface amine groups allowing for functionalization with targeting ligands or drugs [19-21]. Due to its high surface area and reactive sites, carbon nitride nanoparticles can be functionalized with recognition elements (e.g., antibodies, aptamers) for use in chemical and biosensors. Applications include detection of heavy metals, glucose sensors, DNA hybridization assays. C_3N_4 nanoparticles serve as effective adsorbents and photocatalysts for removing organic dyes, pesticides, heavy metals (e.g., Cr(VI), Pb^{2+}), from water and air. Their regeneration via sunlight adds value in sustainable waste treatment systems [22-24].

In this work, the spectroscopic characteristics of carbon nitride nanostructures synthesized by the reaction of methane and ammonia gases were studied. This reaction was induced by electric power transferred to the reaction volume throughout argon fast glow discharge at high pressures at room temperature.

2. Experimental Work

Deposition camber is first evacuated down to 10^{-5} mbar to remove any residuals or contaminants. Argon gas at pressure of 0.5 mbar was used to generate the fast glow discharge between two electrodes made of stainless steel. The dimensions of each electrode are 20x5 mm^2. Argon was chosen due to its low breakdown voltage (~190V at 35mA) compared to methane and ammonia, therefore, small amount (~0.033%) of the minimum applied power is consumed for the generation of plasma column to represent the resistor through which the remaining power (~99.96%) is transferred to the reaction volume to break the bonds in methane and ammonia molecules and soon induce the reaction between the released carbon and nitrogen atoms. The discharge power from a power supply (5-6kV, 4-5A) is applied between the electrodes as pulses of different durations (0.1, 0.25 and 1ms). A pulse forming network (PFN) was used to convert the DC signal of the power supply into short pulses. The repetition rate of discharge pulses could be determined from 1 to 100 Hz by the PFN circuit. However, all results presented here were obtained using repetition rate of 20 Hz. The methane (CH_4) and ammonia (NH_3) gases are premixed in a cooled reactor before pumped into the chamber at flow rate of 1 sccm. This reactor is cooled down to 5°C to prevent the normal reaction of methane and ammonia. The maximum pressure of gas mixture is 3 mbar. As soon as the breakdown of argon gas occurs, the remaining power induces the reaction (Eq. 2) between CH_4 and NH_3 molecules to form C_3N_4 molecules. This reaction occurs faster than the normal reaction given by Eq. 1. The synthesized nanoparticles were collected on a clean watch glass (2cm in diameter) inside the chamber. The chamber was kept closed during the application of discharge power throughout valves on the inlets of gases and outlet to the vacuum pump. More details on the experimental work can be found elsewhere [25,26].

3. Results and Discussion

The UV-Visible absorption spectra shown in Fig. (1) illustrate the optical properties of carbon nitride nanoparticles synthesized using a glow discharge method, with variations in the pulse duration. This is a critical parameter in plasma-assisted synthesis, as it directly influences the energy input, reaction kinetics, and ultimately, the structural and electronic properties of the resulting nanomaterials. The three distinct curves correspond to pulse durations of 1 ms (blue), 0.1 ms (red), and 0.01 ms (black), allowing for a comparative analysis of their optical behavior. All three spectra exhibit a broad absorption band in the ultraviolet region, extending into the visible, which is characteristic of carbon nitride materials. This strong absorption in the UV range, typically below 450 nm, is generally attributed to $\pi \rightarrow \pi^*$ electronic transitions within the graphitic-like C-N frameworks (such as triazine or heptazine rings) that form the backbone of carbon nitride. These transitions involve the delocalized electrons in the conjugated system, and their energy directly relates to the material's band gap [27,28].

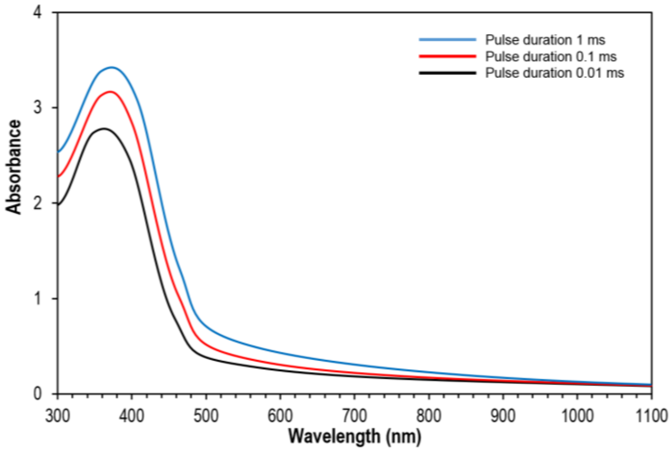

Fig. (1) UV-visible-NIR absorption spectra of the carbon nitride nanoparticles synthesized using different glow discharge pulse durations

A closer examination of the spectra reveals a prominent absorption peak, or shoulder, around 350-380 nm for all samples. This feature is particularly pronounced for the nanoparticles synthesized with a 1 ms pulse duration, showing the highest absorbance. As the pulse duration decreases to 0.1 ms and further to 0.01 ms, there is a clear reduction in the overall absorbance across the entire spectrum. This trend suggests that longer pulse durations might lead to a higher concentration of absorbing species (i.e., more carbon nitride nanoparticles or a denser structure), or potentially to a more developed conjugated system within the nanoparticles, enhancing their light absorption capabilities.

The observed decrease in absorbance with shorter pulse durations could be due to several factors related to the plasma synthesis process. A shorter pulse duration implies less energy delivered per pulse and potentially a shorter time for the reactive species (from methane and ammonia) to interact and form stable C-N bonds. This might result in lower yield since fewer carbon nitride nanoparticles might be formed, leading to a lower concentration in the measured solution and consequently reduced absorbance. This might also result in smaller particle size as shorter plasma exposure or less time for growth could lead to smaller nanoparticles. While quantum confinement effects in very small nanoparticles can sometimes shift absorption to higher energies (shorter wavelengths), a general reduction in absorbance might indicate fewer light-absorbing units [29]. Different stoichiometry and structure might be resulted because varying pulse durations could influence the C/N ratio or the degree of polymerization and ordering within the carbon nitride network. Shorter pulses might lead to more amorphous structures, or structures with fewer extended π-electron systems, which would absorb less light. For instance, a less developed graphitic structure or a higher proportion of sp^3 hybridized carbon might contribute to lower absorbance. Finally, reduced defect states might be resulted as the presence of defects (e.g., nitrogen vacancies, structural imperfections) in carbon nitride can introduce localized energy states within the band gap, potentially leading to absorption in the visible region. If shorter pulse durations result in a "cleaner" or less defective material, this could contribute to the reduced absorbance observed at longer wavelengths [30].

Beyond the main UV peak, all spectra show a gradual decrease in absorbance towards the near-infrared region (up to 1100 nm), with a tail extending into the visible light range. This tail absorption is typical for semiconductor materials and can be attributed to various factors, including defect states, band tailing, or possibly a very weak scattering component. The absorbance in the visible region is also highest for the 1 ms sample and lowest for the 0.01 ms sample, following the same trend as the UV peak. This suggests that the same factors influencing the UV absorption are likely responsible for the differences in visible light absorption. Figure (2) shows the values of energy band gap of the synthesized nanoparticles.

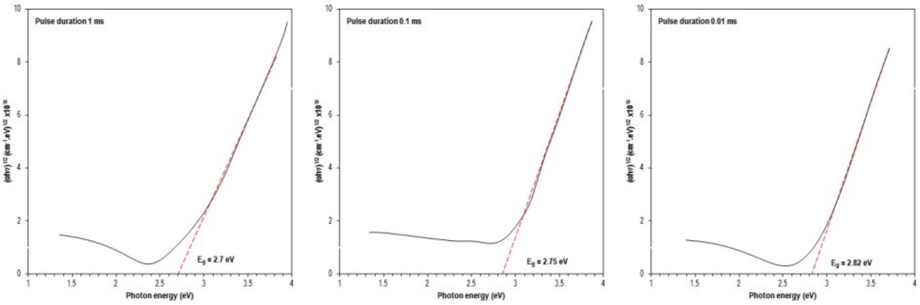

Fig. (2) determination of energy band gap for the carbon nitride nanoparticles synthesized using different glow discharge pulse durations

The FTIR spectra seen in Fig. (3) showcase the vibrational modes of carbon nitride nanoparticles synthesized using varying glow discharge pulse durations: 1 ms, 0.1 ms, and 0.01 ms. These spectra are crucial for understanding the chemical bonding and structural evolution of the nanoparticles under different synthesis conditions. All three spectra exhibit characteristic absorption bands associated with carbon nitride. A broad absorption band centered around 3200 cm^{-1} is observed, corresponding to N-H stretching vibrations and potentially O-H stretching from adsorbed water or residual functional groups. This band's intensity appears somewhat consistent across the different pulse durations, suggesting a similar degree of N-H functionalities or hydration. The most prominent features are observed in the fingerprint region between approximately 1200 cm^{-1} and 1700 cm^{-1}. The strong band at around 1637 cm^{-1} is typically assigned to the stretching vibrations of C=N bonds, often associated with the triazine or heptazine ring structures in graphitic carbon nitride. The shoulder at 1587 cm^{-1} further supports the presence of such conjugated C=N systems. The multiple sharp peaks at 1426, 1332, and 1241 cm^{-1} are characteristic of the stretching modes of C-N heterocycles and possibly C-NH-C bridging units within the carbon nitride framework. Finally, the sharp peak at 808 cm^{-1} is a hallmark of the breathing mode of the triazine or heptazine units, confirming the formation of graphitic-like carbon nitride structures [31].

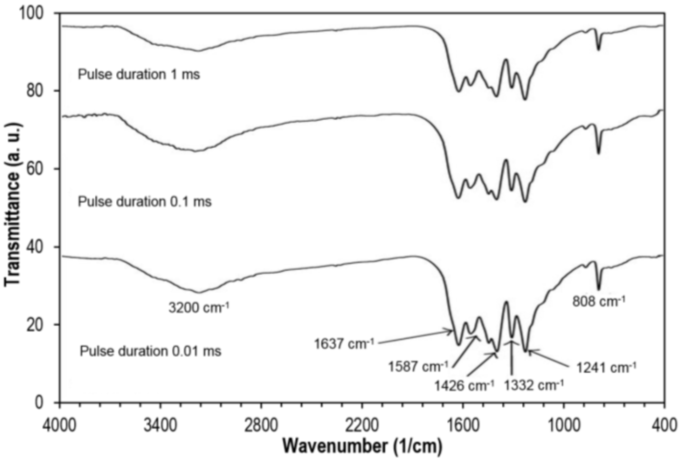

Fig. (3) FTIR spectra of the carbon nitride nanoparticles synthesized using different glow discharge pulse durations

Comparing the spectra, there are no dramatic shifts in the peak positions, indicating that the fundamental chemical bonding motifs of carbon nitride are maintained across the different pulse durations. However, subtle differences in the relative intensities and broadness of these peaks might suggest variations in the degree of polymerization, crystallinity, or the presence of specific C-N configurations. For instance, the sharpness and prominence of the characteristic peaks appear somewhat similar across all pulse durations, implying that the core carbon nitride structure is consistently formed, regardless of the pulse length within this tested range. This consistency in FTIR indicates that the glow discharge method is robust in producing the fundamental C-N framework [32].

Figure (4) displays the refractive index of carbon nitride nanoparticles as a function of wavelength, highlighting the impact of different glow discharge pulse durations during synthesis. This plot clearly illustrates the phenomenon of dispersion, where the refractive index changes with the wavelength of light. For all three pulse durations (1 ms, 0.1 ms, and 0.01 ms), the refractive index generally exhibits a decreasing trend as the wavelength increases from 300 nm to 1100 nm. This normal dispersion is typical for most transparent or semi-transparent materials in regions far from their absorption bands, indicating that the material interacts more strongly with shorter (higher energy) wavelengths [33]. Crucially, the pulse duration significantly affects the magnitude of the refractive index. The carbon nitride nanoparticles synthesized with a 0.01 ms pulse duration consistently show the highest refractive index, hovering around 1.85-1.9 over the entire wavelength range. This suggests that very short, intense pulses might lead to a denser or more ordered structure, or a specific C-N network configuration that results in higher polarizability. Conversely, the nanoparticles produced with a 1 ms pulse duration exhibit the lowest refractive index, ranging from approximately 1.6 to 1.45. The 0.1 ms sample falls in between, with refractive index values around 1.7 to 1.6.

This clear trend indicates that shorter glow discharge pulse durations lead to higher refractive indices for the carbon nitride nanoparticles. This could be attributed to several factors: shorter pulses might result in a more compact or less porous material, different C/N ratios, or a higher degree of graphitization, all of which can increase the material's density and electronic polarizability, thereby raising its refractive index. These variations are critical for applications where precise control over optical properties, such as in antireflection coatings or optical waveguides, is desired [34,35].

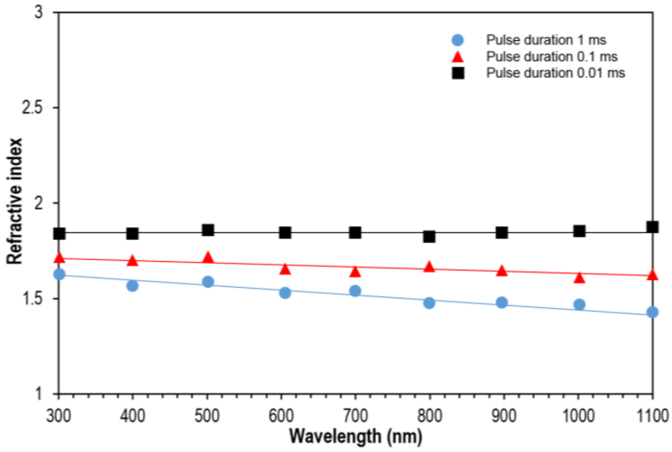

Fig. (4) Dispersion curves of the carbon nitride nanoparticles synthesized using different glow discharge pulse durations

4. Conclusion

The comprehensive analysis of carbon nitride nanoparticles synthesized via glow discharge reveals a clear correlation between synthesis parameters and material properties. The UV-Vis spectra demonstrate that longer pulse durations enhance overall light absorption, suggesting higher yield or more developed conjugated systems. FTIR analysis confirms the consistent formation of characteristic C-N bonding motifs across all pulse durations, indicating the robustness of the synthesis method. Crucially, the refractive index measurements show that shorter pulse durations yield nanoparticles with higher refractive indices, likely due to increased material density or specific structural arrangements. These findings highlight the importance of precise pulse duration control for tailoring carbon nitride's optical properties for various applications. The provided analyses of carbon nitride nanoparticles synthesized by glow discharge reveal a direct relationship between pulse duration and optical properties.

Longer pulse durations (1 ms) lead to higher UV-Vis absorption, suggesting increased yield or more developed π-electron systems. FTIR confirms the consistent formation of characteristic C-N bonding regardless of pulse duration. Most notably, shorter pulse durations (0.01 ms) result in a significantly higher refractive index, indicating a denser or more ordered material. These findings underscore the critical role of glow discharge pulse duration in precisely tuning the optical characteristics of carbon nitride nanoparticles for targeted applications.

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