Synthesis and Characterization of Nitrogen-Doped Carbon Quantum Dot (NCQD)/ Titanium Dioxide (TiO_2) Hybrid Nano Material for Enhanced Photocatalytic Applications

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1. Introduction

The growing demand for sustainable wastewater treatment has spurred interest in advanced nanomaterial solutions. One promising candidate is a hybrid nanomaterial combining nitrogen-doped carbon quantum dots (NCQDs) and titanium dioxide (TiO_2). NCQDs offer tunable bandgap and excellent photocatalytic activity, especially in UV light, overcoming the limitations of UV-activated TiO_2. Integrating NCQDs with TiO_2 creates a synergistic effect, enabling visible-light driven photocatalysis while maintaining the stability and reactivity of TiO_2. This hybrid approach enhances pollutant degradation efficiency and selectivity, showcasing the potential of nanomaterials in environmental remediation. The NCQD/TiO_2 hybrid exemplifies innovative strides in nanotechnology for sustainable solutions.

2. Materials/Methodology

2.1 Synthesis of Hybrid Nanomaterial

Analytical-grade chemicals and unpurified solvents were utilized in the experiments. NCQD solution was synthesized using a one-step microwave method with sodium citrate and triethanolamine, following the procedure described in (Ren,Ga and Ai, 2019). Simultaneously, TiO_2 nanoparticles were prepared using titanium isopropoxide (TTIP) and ethanol via the sol-gel method, as outlined in (Hosseini, Sadeghi, and Khazaei, 2017). The NCQD/ TiO_2 hybrid Nanomaterials were fabricated by dispersing 0.1 g of TiO_2 in 1 ml of NCQD solution using ultrasonic methods, as detailed in (Zhang et al.,2016).

2.2 Characterization

Particle size analysis of TiO_2 and NCQDs was conducted using a Particle sice analyzer (Malvern Zetasizer Ver 7.03). The crystalline phase of the synthesized TiO_2 samples was determined and estimated using an X-ray diffractometer (Rigaku Ultima 4 X-ray) with Cu-Kα radiation at a scan speed of 3.000 deg/min and 2θ range of 10^0-80^0. UV-Vis absorption spectra of NCQD, TiO_2, and NCQD/TiO_2 Nano material were acquired using JENWAY model 7310 spectrophotometer. The morphologies and sizes of both TiO_2 and NCQD/TiO_2 samples were characterized using a scanning electron microscope (Hitachi SU6600). FTIR analysis for NCQD samples was conducted using a Bruker Vertex 80 spectrometer. The bonding sites of the NCQD/TiO_2 hybrid nanomaterial were analyzed using X-ray photoelectron spectroscopy (Thermo Scientific TM ESCALAB Xi+).

3. Results and Discussion

3.1 Structural and Optical Properties of NCQDs

NCQDs were synthesized through a hydrothermal method utilizing triethanolamine and sodium citrate as precursors. The resulting NCQDs exhibited blue fluorescence under UV light (fig 3.1.a), indicative of quantum confinement effects, and were characterized by an approximate size range between 0.5 – 1.3 nm (fig 3.1.b). The electronic properties of semiconductor nanocrystals, or quantum dots, depend on their size. The bandgap energy governs the absorption of light by quantum dots, with electronic transitions occurring when the energy of incident photons matches or exceeds the bandgap

energy. Significant UV absorption was observed for the NCQDs (fig 3.1.c), with an absorption peak observed at 263 nm, indicative of a $\pi-\pi^*$ transition commonly observed in aromatic carbon-based structures. The introduction of nitrogen doping created energy levels that facilitated this transition, resulting in the observed absorption peak.

The structural and chemical composition of the synthesized NCQDs were investigated using Fourier-transform infrared spectroscopy (fig 3.1.d). The FTIR spectra revealed characteristic peaks corresponding to various functional groups within the NCQDs. Notable peaks included O-H stretching vibrations at 3289 cm^{-1}, indicating surface hydroxyl functionalities. Additionally, intense peaks corresponding to aliphatic C-H stretching vibrations were observed at 2949 cm^{-1}, 2880 cm^{-1}, and 2827 cm^{-1}, highlighting the presence of aliphatic carbon moieties within the carbonaceous framework of the NCQDs. Furthermore, bending vibrations of C-H bonds were detected at 1450 cm^{-1} and 1407 cm^{-1}, providing further evidence of aliphatic carbon functionalities. The presence of nitrogen atoms within the carbon lattice were confirmed by a peak corresponding to C-N stretching vibrations at 1282 cm^{-1}. Additionally, peaks attributed to C-O stretching vibrations at 1151 cm^{-1} were observed.

Interestingly, the absence of a characteristic peak at 1600-1800 cm^{-1}, typically associated with carbonyl (C=O) groups, suggested their absence in the NCQD sample compared to the reference material. This absence indicated a possible reaction involving the carbonyl group of sodium citrate during the synthesis process. Specifically, mixing sodium citrate with triethanolamine may have facilitated complex reactions, leading to the carbonization of cross-linked polymer structures derived from condensation reactions and the subsequent synthesis of nitrogen-doped carbon quantum dots.

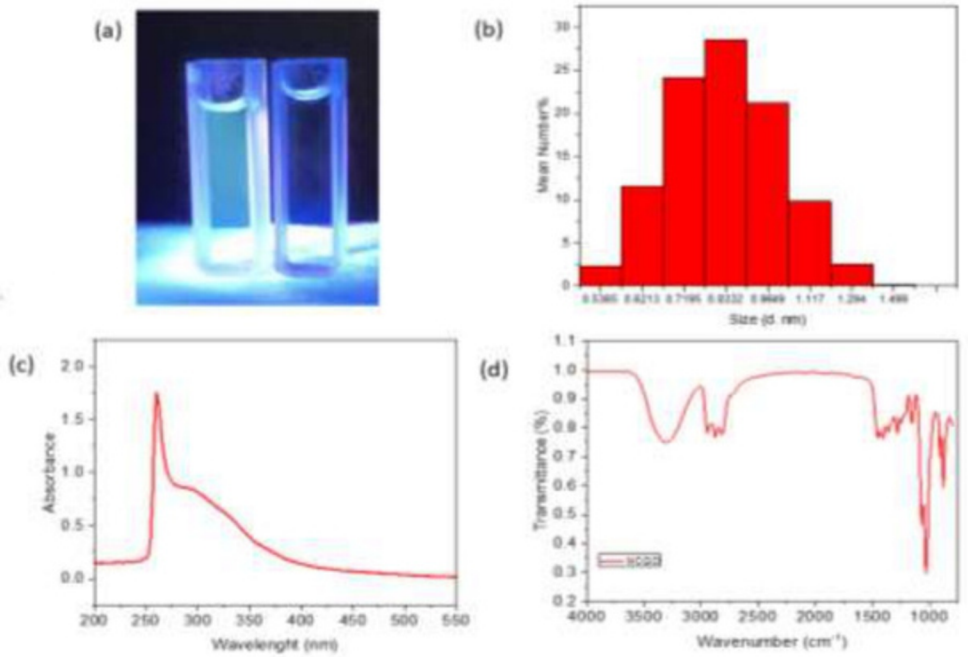

Fig. 3.1 – (a) Blue florescence of NCQD Solution under UV light with reference (b) Particle size distribution graph of NCQDs (c) UV-Vis absorption spectra of NCQDs (d) FTIR analysis of NCQDs

3.2 Structural and Optical Properties of TiO_2 Nanoparticles

TiO_2 nanoparticles synthesized via the sol-gel method were comprehensively characterized using various analytical techniques. Particle size analysis was conducted (fig 3.2.a), and it revealed a mean particle size ranging from approximately 25-100 nm. SEM analysis further elucidated the structural characteristics, revealing a spherical morphology with well-dispersed particles (fig. 3.2.b). The observed morphology corroborates the successful synthesis of TiO_2 nanoparticles via the sol-gel method, highlighting the uniformity and homogeneity of the synthesized sample.

X-ray diffraction analysis was employed to investigate the crystalline nature of the synthesized nanoparticles (fig 3.2.c). The XRD pattern exhibited characteristic diffraction peaks corresponding to the synthetic rutile phase of TiO_2, confirming the crystallinity and purity of the synthesized nanoparticles. The absence of additional peaks suggests the absence of impurities or secondary phases, further validating the high-quality synthesis of TiO_2 nanoparticles.

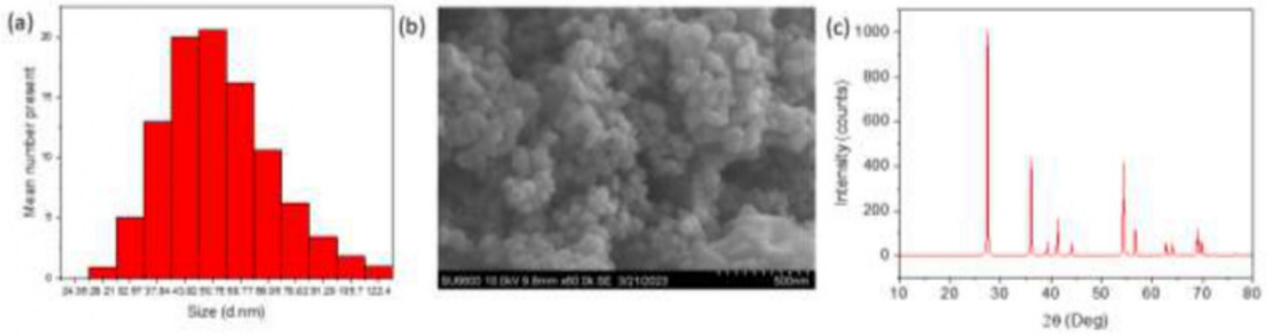

Figure 3.2 – (a) Particle size distribution of TiO_2 Nano particle (b) SEM analysis of TiO_2 (c) XRD spectrum of TiO_2

3.3 Structural Properties of NCQD/TiO_2 Hybrid Nanomaterial

The structural properties of the NCQD/TiO_2 hybrid Nano material were investigated, primarily focusing on the presence or absence of chemical bonding between carbon and titanium, which is crucial for determining the adsorption behavior of quantum dots onto TiO_2. The XPS analysis revealed distinctive peaks corresponding to C 1s, Ti 2p, O 1s, and N 1s, with binding energies of 286.4, 459.0, 532.8, and 401.0 eV, respectively (fig 3.3.a). In the Ti 2p survey, two prominent peaks at 459.3 and 465.1 eV were observed, representing the Ti 2p3/2 and Ti 2p1/2 states of TiO_2, respectively. Notably, the absence of a Ti^{3+} peak in the Ti 2p3/2 spectra indicated that NCQD/ TiO_2 hybrid Nano materials predominantly consisted of Ti^{4+} species (fig. 3.3.b).

In the C 1s survey, four distinct peaks were observed, corresponding to different carbon species. The primary peak at 285.97 eV indicated the presence of graphitic carbon or carbon-carbon double bonds in the NCQD/ TiO_2 sample. Peaks at 287.2 eV and 289.04 eV were attributed to C-O/C-N and C=O/C=N bonds, respectively, while the peak at 289.87 eV indicated the presence of C–N bonds. Importantly, the absence of a C-Ti bond peak in the Ti 2p and C 1s spectra suggested that NCQDs were not chemically linked to TiO_2 (fig. 3.3.c). Analysis of the O 1s spectrum revealed five fitted peaks, providing insights into oxygen-containing species present in the sample. The peak at 531.94 eV suggested the presence of oxygen atoms in Ti-O bonds, indicative of TiO_2 nanoparticles or TiO_2 related species in the NCQD/ TiO_2 sample. Peaks at 533.26 eV and 536.66 eV were attributed to surface adsorbed or physisorbed oxygen and oxygen atoms in carbonyl or carboxylate groups, respectively. Additionally, the peak at 534.53 eV indicated the presence of hydroxyl groups or adsorbed water molecules on the sample surface (fig. 3.3.d).

SEM images revealed a rough surface for the NCQD/ TiO_2 Nano material, suggesting predominant deposition of NCQDs onto the TiO_2 surface. Due to their small size, NCQDs appeared challenging to distinguish through SEM imaging (fig. 3.3.e, f). These quasi-spherical nanoparticles were composed of amorphous to nanocrystalline materials.

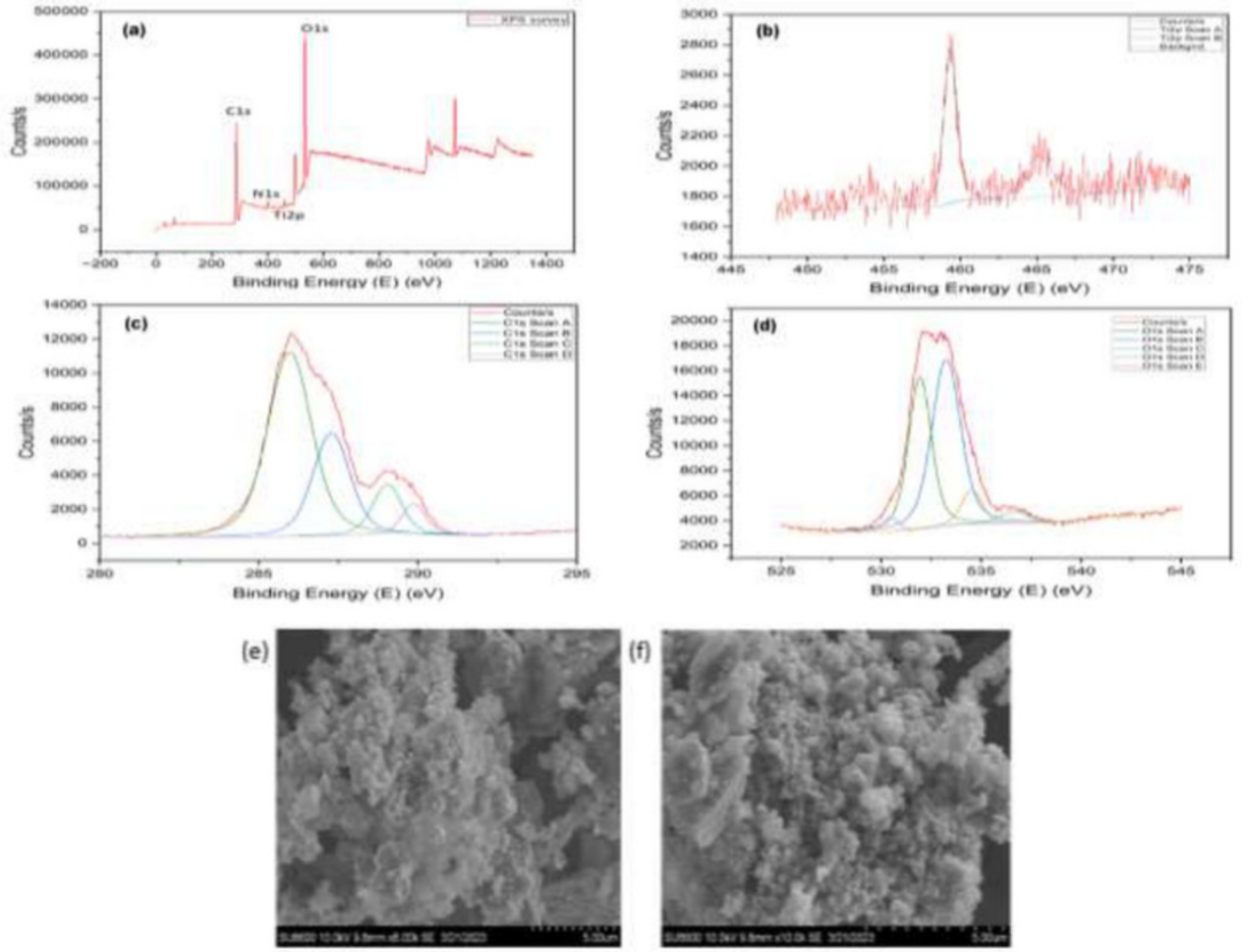

Figure 3.3 – (a) XPS full range survey spectrum (b) Ti 2p survey (c) C 1s survey (d) O 1s survey (e), (f) SEM images of NCQD/ TiO_2 hybrid composite

3.4 Photocatalytic Properties of NCQD/TiO_2 Hybrid Nanomaterial

When considering the peaks of TiO_2 and NCQD/ TiO_2 hybrid nanomaterial, the presence of a peak at 356 nm in the UV-Vis spectroscopic analysis indicates that both materials exhibit light absorption in the ultraviolet region. It is observed that upon adsorbing the quantum dots to TiO_2, there is no significant change in the UV-Vis analysis. Based on the results obtained, it can be inferred that the NCQD/ TiO_2 hybrid Nano material does not undergo an electron excitation mechanism under visible light, as it exhibits absorption only in the ultraviolet range and not in the visible region. It can be observed that the NCQD/ TiO_2 hybrid Nano material exhibits slight absorption in the visible range. However, the absorption is relatively lower compared to pure TiO_2. This suggests that the hybrid Nano material may have a reduced capability for electron excitation under visible light. Consequently, it can be hypothesized that the photodegradation efficiency of the hybrid Nano material may be enhanced compared to pure TiO_2 due to the presence of NCQD.

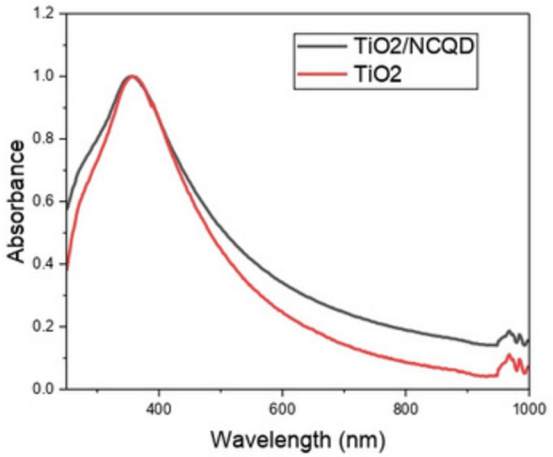

Figure 3.4 - UV-Vis analysis graph of TiO_2 and NCQD/ TiO_2 hybrid Nano material

3.5 Proposed Photocatalytic Mechanism for NCQD/ TiO_2 Hybrid Materials

The photocatalytic mechanism of NCQD/ TiO_2 hybrid materials encompasses several essential steps. Initially, molecules or pollutants from the environment, like organic dyes or contaminants, are adsorbed onto the hybrid material's surface. Upon exposure to light, both the TiO_2 and NCQDs within the material absorb photons, leading to electron excitation and the formation of electron-hole pairs. Subsequently, excited electrons from the NCQDs migrate to the conduction band of TiO_2, creating positively charged holes in the NCQDs. This charge separation prompts the migration of electrons and holes to the material's surface, facilitated by internal electric fields and charge transfer pathways. At the surface, these separated charges engage in redox reactions with adsorbed molecules or pollutants, where electrons reduce and holes oxidize them. This process drives the photodegradation of pollutants into less harmful substances, leveraging the material's photocatalytic activity. Moreover, some excited electrons react with oxygen molecules to generate reactive oxygen species like superoxide radicals and hydroxyl radicals, which further contribute to pollutant degradation. Overall, the synergistic interaction between TiO_2 and NCQDs enhances light absorption, charge separation, and ultimately, the photocatalytic efficacy of the material for environmental remediation purposes.

Conclusion

The research into the NCQD/ TiO_2 hybrid nanomaterial has opened up a promising path for improving photocatalytic applications, especially in cleaning up the environment. This hybrid combines the unique features of NCQDs and TiO_2, making it very effective at breaking down pollutants. The study shows that when NCQDs are combined with TiO_2, they create a powerful catalyst that makes use of their strengths in photocatalysis. Through meticulous structural and optical characterization, this investigation has validated the successful synthesis of both NCQDs and TiO_2 nanoparticles, alongside their integration into a cohesive hybrid nanomaterial. This is an important step forward because it means that this hybrid material can work well under UV light, making it much more versatile for cleaning up pollutants.

Understanding how this hybrid material breaks down pollutants is also crucial. The study found that it works by separating charges and which helps break down pollutants effectively. This understanding gives us valuable insights into how to make these materials even better at cleaning up pollution in the future. Overall, this research is a significant contribution to finding sustainable ways to treat wastewater. By using the combined strengths of NCQDs and TiO_2, this study offers a new solution for dealing with pollutants and lays the groundwork for future research to make these materials even more effective. As the world grapples with the challenges of environmental pollution, the development of such innovative nanomaterials is critical, offering hope for more effective and sustainable remediation strategies.

Keywords: NCQD, TiO_2, hybrid nanomaterial, photocatalysis, environmental remediation

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