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Proceeding Paper

Preparation of Mesoporous Bicrystalline N-Doped TiO_2 Nanomaterials for Sustainable RhB Degradation under Sunlight †

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† Presented at the 4th International Online Conference on Nanomaterials, 5–19 May 2023; Available online: https://iocn2023.sciforum.net/.

Abstract: N-doped titanium dioxide (N/TiO_2) nanomaterials were successfully prepared using titanium butoxide and guanidinium chloride using the simple sol-gel method. The significance of the annealing gas environment (air, argon, or nitrogen) on their physicochemical and photocatalytic degradation properties was investigated. Indeed, the gas type governed the crystal/phase nature from monophase anatase with a low crystallinity to dual-phase anatase/rutile with a higher crystallinity. Moreover, results revealed that the introduction of N in the TiO_2 matrix led to a red shift towards visible-light, narrowed the bandgap (2.35 eV), and suppressed recombination. Nobly, the N/TiO_2 prepared in air demonstrated the highest RhB degradation performance (99%) with the highest rate constant (0.0158 min^{-1}), which was twice faster than the undoped TiO_2.

Keywords: doping; TiO_2; photocatalysis; rhodamine B; anatase and rutile; wastewater; degradation

1. Introduction

Due to rapid urbanization and industrialization, a growing number of toxic contaminants are entering into water bodies and this trend is expected to be further worsened. For instance, RhB is one of the most ubiquitous and industrial effluents. It is particularly challenging and dangerous to degrade through deploying the conventional techniques as it is hazardous and generates carcinogenic species [1,2]. Meanwhile, advanced oxidation process techniques (such as heterogeneous-catalysis, photocatalysis, electrochemical oxidation, and Fenton) have played indispensable roles in neutralizing such dyes [3,4]. Particularly owing to its high chemical inertness, strong oxidizing power, and abundance, TiO_2 remains a promising photocatalyst in tackling such environmental problems [5].

Unfortunately, its large bandgap, low solar conversion, and high charge carrier recombination rate limits its practical application [6], and in alleviating these problems, considerable research has been conducted [7]. Among nonmetal doping, N-doping into a TiO_2 matrix has gained specific attention; consequently, various N/TiO_2 nanostructures have demonstrated a better catalytic performance compared to typical TiO_2 under visible light [8]. To suppress the charge recombination, preparing mixed-phase TiO_2 has been recommended more than its monophasic nanostructure, since the former materials have demonstrated a better photocatalytic performance [9]. However, preparing these mixed-phase nanomaterials requires a high temperature (>600 °C), and follows multistep reactions; especially for the brookite counterpart, is quite challenging [7]. The disadvantage of such a high temperature synthesis method is that it significantly reduces the active surface area of the catalyst. Thus, preparing the phase-heterojunction N/TiO_2 at lower energies still remains imperative. With this aim, in this study, the effect of annealing gas

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Citation: Assayehegn, E.; Gidey, A.T. Preparation of Mesoporous Bicrystalline N-Doped TiO_2 Nanomaterials for Sustainable RhB Degradation under Sunlight. *Mater. Proc.* **2023**, *14*, 32. https://doi.org/10.3390/IOCN2023-14490

Academic Editor: Jian-Gan Wang

Published: 5 May 2023

type on the physicochemical properties of N/TiO_2 was investigated. A variety of N/TiO_2 nanocrystals were synthesized via the sol-gel method using guanidinium chloride (GUA) as an eco-friendly N-dopant source and were then characterized via different techniques. Additionally, their RhB photodegradation performance under direct sunlight was explored.

2. Materials and Method

2.1. Synthesis of N/TiO_2 Nanocatalysts

The nanomaterials were prepared through our previous modified method [10,11]; which is typically as follows:

- Titanium butoxide (11.4 mmol, Sigma Aldrich, Bengaluru, India branch) was added into ethanolic solution (30 mL, ethanol/water 5:1) step-wise while vigorously stirring;
- In another beaker, an equimolar amount of guanidinium chloride (98%, Sigma Aldrich, Bengaluru, India branch) was added to a solution of ethanol (10 mL) and 5 drops of conc. HNO_3 while stirring;
- To this solution, the above white solution was added step-wise while stirring for 2 h;
- The resultant mixture was then sealed and aged for 12 days;
- Finally, it was heated at 400 °C for 4 h in a furnace under a different gas environment with a flow rate of 150 cm^3/min (Table 1). The samples prepared in atmospheric air, Ar, and N_2 were denoted as NT-A, NT-Ar, and NT-N, respectively. Following the same procedure, a control sample was prepared in air without adding the N-dopant and was designated as N-0.

Table 1. Synthesis parameters and XRD results of as-obtained photocatalysts.

Catalyst	$Ti(OBu)_4$ (mmol)	GUA (mmol)	Temp. (°C)	Gas Type	Phase Comp. (%)		Crystal Size (nm)	
					Anatase	Rutile	Anatase$^{(101)}$	Rutile$^{(110)}$
N-0	11.4	0	400	Air	96	4	9.3	-
NT-Ar		11.4		Argon	98	2	8.5	-
NT-N		11.4		Nitrogen	98	2	8.5	-
NT-A		11.4		Air	53	44	10.2	36.3

2.2. Characterization Techniques of Catalysts

The following techniques were deployed for this study: X-ray diffractometer (Bruker D8 Advance, Cu-Kα), field emission scanning electron microscopy (FESEM) (SEM (Quanta 400 FEG SEM)), photoluminescence, PL, (JASCO FP-6500), and Jasco V-650 spectrophotometer for the UV-Vis diffused reflectance (DRS), respectively.

2.3. Photocatalysis Study

Under natural sunlight, these experiments were conducted at CSIR-NIIST, Thiruvananthapuram, India in January, 2018. 50 mg of as-synthesized photocatalyst were dispersed to RhB solution (200 mL, 20 mg L^{-1}). The dye-catalyst suspension was magnetically stirred for 30 min in the dark; it was then exposed to direct sunlight irradiation (11 am to 4 pm) while stirring. At regular time intervals, aliquots of the suspension were withdrawn. After removing the catalysts by centrifugation, the solution was then analyzed with a UV-vis spectrophotometer (UV-2401-PC-Shimadzu).

3. Results and Discussion

3.1. Structural Analysis

Figure 1 depicts the XRD patterns of the as-prepared materials. It can be clearly seen that both NT-Ar and NT-N have 98% anatase phase (JCPDS: 21-1272) similar to N-0; whereas NT-A comprises a mixture of 53% anatase and 44% rutile phases (JCPDS: 21-1276) with trace amount of brookite (Table 1) [12]. Comparing their respective XRD peaks, the N-doping is occurred without altering the crystal structure in the cases of NT-Ar and NT-N; however, it is caused a significant phase change in NT-A. Moreover, this difference in gas environment influences the degree of crystallinity and particle size; NT-A displays the highest crystallinity nature of all as-synthesized powders with a larger anatase nanoparticle size (10.2 nm) than that of NT-Ar and NT-N (8.5 nm) (Table 1). This strongly suggests that calcining TiO_2 nanoparticles in atmospheric air favors particle growth; while in Ar and N_2, hinders the growth of the nanoparticles.

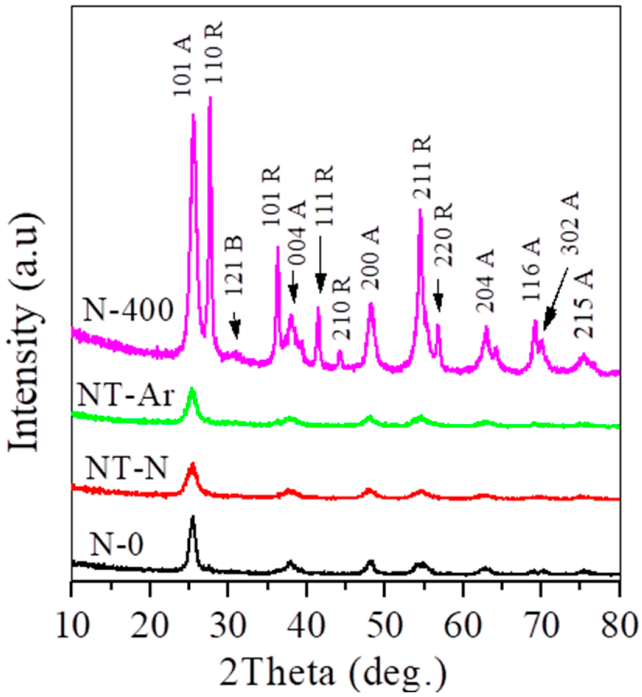

Figure 1. XRD data of as-prepared nanomaterials (A: anatase, and R: rutile).

3.2. Morphological Analysis

The field-emission SEM images and elemental analysis of TiO_2-based materials are presented in Figure 2. The undoped sample has roughly spherical particles with aggregates (Figure 2a). Importantly, both the NT-Ar and NT-N doped samples (Figure 2b,c) have a spherical shape, which infers to their surface stability by the respective gas type. Whereas NT-A has a coral-like structure (Figure 2d); in this particular sample, particle coarsening and neck formation among the particles were observed due to the surface energy increment under annealing in air. Consequently, its particle size was increased, which is in agreement with the previous XRD discussion. Meanwhile, according to the EDAX elemental results (as shown in Figure 2e–h), N-0 has both Ti and O, however the N/TiO_2 materials were found to have a third additional N element with a 6.8–10.1 atomic % range, thereby confirming that nitrogen was effectively incorporated. Moreover, the doped-N was homogenously distributed.

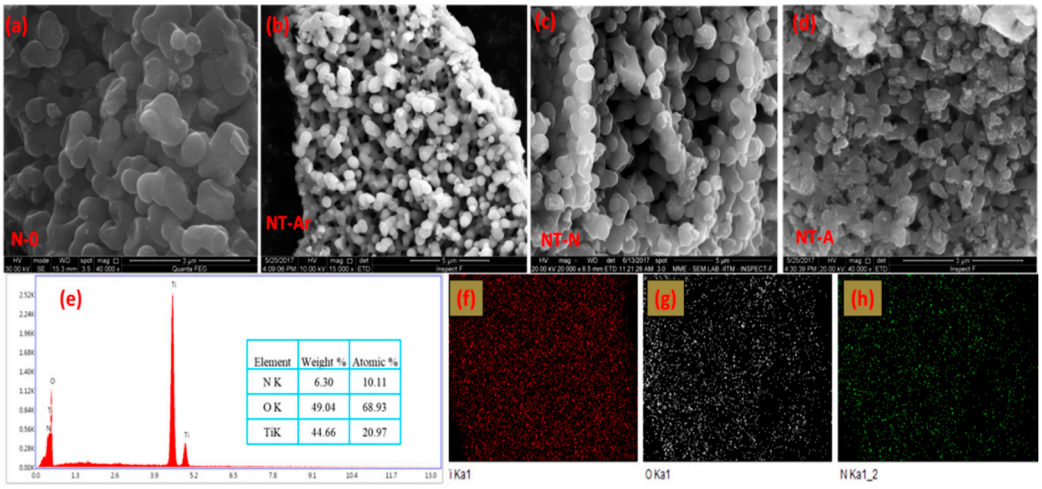

Figure 2. FESEM images of N-0 (**a**), NT-Ar (**b**), NT-N (**c**), NT-A, and (**d**) and EDAX of NT-A (**e**), with its elemental mapping of titanium (**f**), oxygen, and (**g**) nitrogen (**h**).

3.3. Optical-Response Analysis

The DRS, Kubelka-Munk, and PL measurements of N-0, NT-Ar, NT-N, and NT-A are depicted in Figure 3; as shown, the unmodified white TiO_2 had an absorption peak in the UV region (~400 nm). However, all the as-obtained N-doped catalysts were found to have two peaks: a sharp peak at ~420 nm, and an abroad one in the range of 420–600 nm, displaying an extended red shift to the visible light region. Meanwhile, based on the Kubelka–Munk plot (Figure 3b), all the N/TiO_2 materials exhibited a lower band gap energy (E_g) than TiO_2; NT-N particularly demonstrated the lowest E_g of 2.35 eV. Thus, incorporating N in the TiO_2 matrix not only led to a red shift (towards visible light) but also narrowed the band gap.

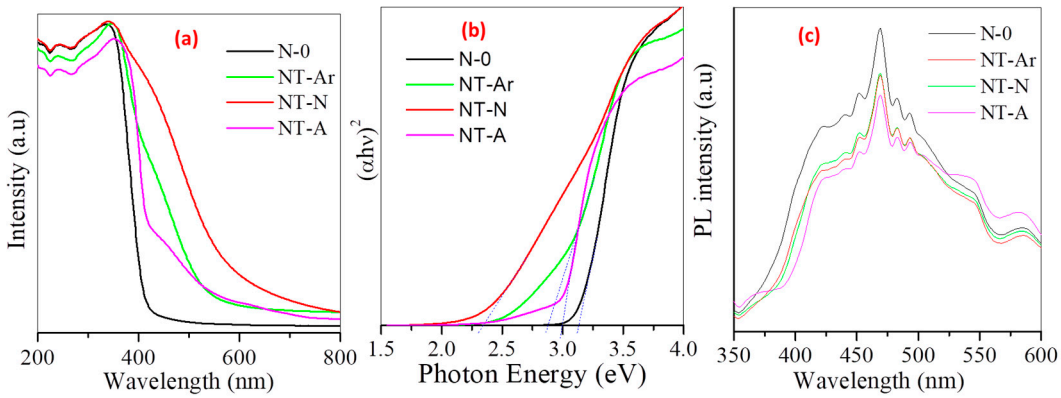

Figure 3. (**a**) DRS spectra; (**b**) tauc plot; and (**c**) PL spectra of the as-obtained TiO_2 and N/TiO_2 nanomaterials.

Understanding how N-doping into the TiO_2 structure affects the rate of excitons is crucial; the PL spectra of the as-prepared materials are illustrated as shown in Figure 3c. It is noted that all the doped materials exhibited a lower PL intensity in the range of 350–550 nm compared to the unmodified sample, N-0. The lower PL values displayed by N/TiO_2 indicates that they possess lower charge carrier recombination rates, which subsequently leads to a high accessible e^-/h^+ density. Particularly, NT-A was recorded to have the lowest PL intensity due to the A/R heterojunction through which the e^-/h^+ can be easily separated unlike the other monoanatase phase. Consequently, this visible light active material could perform better photocatalytic activities.

3.4. Evaluation of Sunlight-Driven Degradation

RhB has become a common deleterious environmental pollutant. As shown in Figure 4a,b, the concentration of the RhB and characteristics of the RhB peak intensity were reduced by the function of irradiation time. In particular, NT-A displayed the highest photocatalytic efficiency of 99% within 300 min sunlight irradiation (Figure 4c). It was noted that the RhB degradation performance was in the following order: NT-A > NT-N > N-0 > NT-Ar. Moreover, according to the photodegradation kinetics (Figure 4d), NT-A also had the highest apparent rate constant (0.0158 min^{-1}) which was two times higher than the bare TiO_2. Such enhanced RhB discoloration over the NT-A surface was ascribed to its higher degree of crystallinity, formation of A/R heterojunctions, lower recombination rate, higher accessible e^-/h^+ density, and higher aqueous-disperse character.

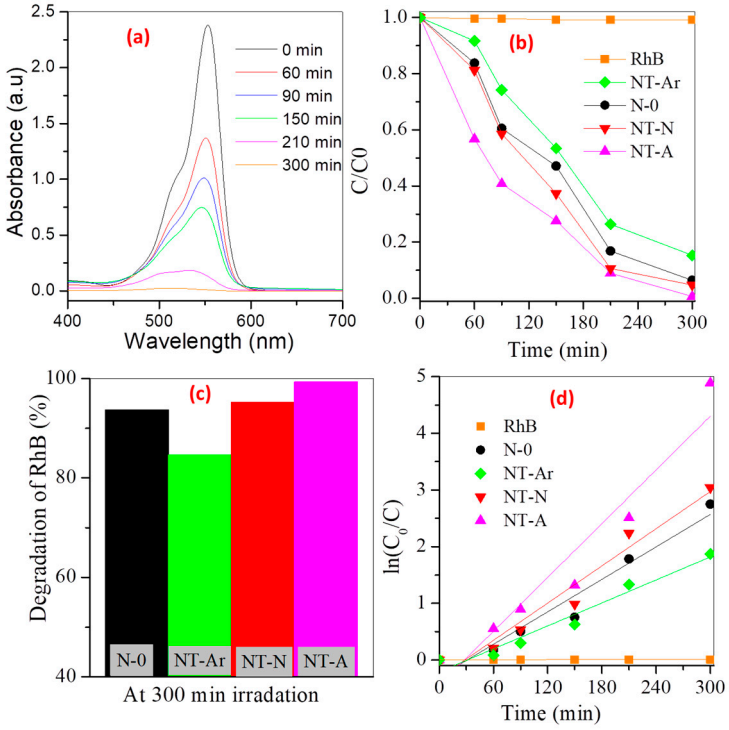

Figure 4. (**a**) UV-Vis spectra of RhB solutions after their respective irradiation time over NT-A; (**b**) RhB degradation rate under sunlight; (**c**) RhB photodegradation performance under 300 min irradiation; and (**d**) pseudo first-order of the as-synthesized catalysts.

4. Conclusions

Visible active N-doped titanium nanomaterials were successfully prepared via the sol-gel method using guanidinium chloride as the N-source. The N/TiO_2 powders were optimized at different annealing gas types (air, argon, and nitrogen) which profoundly influenced their physicochemical and photocatalytic properties. Among the variety of as-obtained photocatalysts, the N/TiO_2 annealed in air displayed the highest RhB degradation performance (99%) within 5 h of sunlight irradiation. This improved catalytic activity was mainly ascribed to the N-introduction into the TiO_2 structure that led to a higher crystallinity, optimal anatase/rutile phase composition, and well separated charge carriers.

Author Contributions: E.A.: conceptualization, methodology, investigation, software; validation, formal analysis, resources, data curation, project administration, and writing-original draft preparation; A.T.G.: software, validation, visualization, funding acquisition, supervision, writing-review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by The World Academy of Sciences, Italy (CSIR-TWAS, FR No.: 3240293587), The Centre for Science & Technology of the Non-aligned and Other Developing Coun-

tries, India (RTF-DCS, No. NAM-05/74/16), and Mekelle University, Ethiopia (PG/CNCN/PhD/MU-NMBU/024/2019).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors express their sincere acknowledges to CSIR-NIIST, IIT Madras, Ethiopian Ministry of Education, and Mekelle University.

Conflicts of Interest: The authors declare no conflict of interest.

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