EFFECT OF AGING ON THE SUSTAINABLE PHOTOCATALYTIC ACTIVITY OF ANATSE/RUTILE N-DOPED TIO_2

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ABSTRACT-Advancing photoactive metaloxides is an active area of research for enviromental application. In this study, with the special focus on the efect of aging time on physico-chemical properties, visible light active nitrogen doped titanium dioxide (N-TiO_2) nano-photocatalysts were successfully synthesized by hydrolysis of titanium tetraisopropoxide in the presence of guanidium chloride via a simple solgel method. The resulting materials were subjected to different characteration techniques; X-ray diffraction, ultraviolet–visible diffuse reflection spectroscopy, photo-luminescence, scanning electron microscopy, energy dispersive X-ray spectroscopy, and BET surface areas. Moreover, their photo-catalytic perfomation was evaluated against MB dye with the help of sunlight. The results revealed that the number of aging days dectates the crystal structure, morphology, light absorbation capacity, photogenerated charge carrier fate and photoactivities of the as-synthesized photocatalysts. Notably, N-TiO_2 exhibited a red-shift light absorption edge to visible region and enhanced photocatalytic activity for the degradation of MB. More importantly a mon the as-prepared saomples, the mosted aged, for 9 days, N-TiO_2 demostrated the best 95% MB degradation on two hours sunligh exposure. This activity mainly attributed to the higher crystal structure, anatase/rutile mixed phase, stronger light absorption sunlight, large surface and pore size, and lower photogenerated charge carrier recombination.

KEY WORDS **- Doping, N-TiO_2, Aging factor, Photodegradation, Water Purification**

INTRODUCTION

Photo-catalysts have been a hot topic in many research fields in solving environmental pollution because of their unique advantages [1].More significantly, since the conventional methods are often chemically, energetically and operationally intensive, these materials could play the indispensible role in decontaminating and mineralizing non-bio-degradable organic pollutants of various industrial effluents [2].Among the semiconductor photo-catalysts, TiO_2 has emerged the most promising materials due to its inertness to chemical environments, long-term photo-stability, non-toxicity, abundant and cheap [3]. However, due to its large band gap (3.0 eV for rutile and 3.2 eV for anatase)[4], it is not only the poor solar energy conversion efficiency but also the high charge carrier recombination rate is often a major drawback for its limited practical applications [5].

Researchers have developed different techniques doping with hetero-atom, coupling with other semiconductors, and sensitizing with organic dyes are major approaches for extending light absorption into visible wavelength region through modifying the intrinsic nature of TiO_2[6], [7]. Moreover, due to its ability to modify the morphology, electrical conductivity, refraction index and the photo-catalytic activity toward visible light absorption, nitrogen doping into TiO_2 crystal has gained specific interest nowadays [8]–[10]. Several literatures had revealed that the main research focus is on the effect of dopant type/concentration, water/alcohol ratio, and temperature on the crystal structure, morphology, electronic behavior and photoactivity[9], [11]–[15].However, the formation of oxygen vacancies,low N dopant level introduction and usage of toxic hydrazine as source of dopant,doping nitrogen in to TiO_2calls a new synthesis approach.In this study, with the special focus on the effect of aging on physico-chemical properties and photocatalytic active of N-TiO_2were systematically synthesized by hydrolysis of titanium tetraisopropoxide in the presence of guanidium chloride via a simple solgel method,; and analyzed by different spectroscopy techniques.

METHOD

The nitrogen TiO_2 was prepared as follows: to 30mL ethanoic solution, 4mL of tetrabutyltitanate (TBT) was added and stirred vigorously for 30 minutes. 2g guanidinium chloride was added and mixed to a pre-prepared solution by mixing 10mL ethanol and 0.3mL conc. HNO_3 (69%). Then to this mixture, the TBT solution was added and stirred vigorously for 2 hours. This mixture was sealed vials and aged for 1, 3, 6 and 9 days. Finally, it was dried at 80^0C for a day and heated at 400^0C for 4 hours in tubular furnace at 1^0C/min heat rate. The as-prepared samples were denoted as N_X-TiO_2, where x is the aging days, and N_0-TiO_2 without guanidinium chloride, a control sample is prepared.

RESULT AND DISCUSSION

XRD

The crystal phase and degree of crystallinity of the as-prepared photocatalysts are given in figure 1. It consists of several narrow sharp diffraction peaks at 25.4^0, 37.8^0, 48.3^0 which can be indexed to anatase phase (A) (JCPDS: 21-1272)[16] . It is clearly seen that the introduction of nitrogen in the TiO_2 crystal matric for samples N_1-TiO_2, N_3-TiO_2, and N_6-TiO_2 without changing the pure titania crystal structe,N_0-TiO_2. However, when Ti and N precursors aged for longer 9 days, it was observed a phase change- a new peak at 27.5^0 for rutile phase (R). Thus, unlike the first samples which has single pure anatase phase, N_9-TiO_2 has a mixed anatase/rule phase. It is assumed that the aging time was too short for anatase to rutile phase transformation for the N_1-TiO_2, N_3-TiO_2, and N_6-TiO_2. Nevertheless, the xrd revealed that all photocatalysts are highly crystalline.

UV-VIS DIFFUSE REFLECTANCE

From the UV-vis spectra, Fig 1: (b) it is clearly seen that both the pure and doped photo-catalysts has strong absorption in uv region; however, the N-TiO_2 samples showed a red shift unlike the undoped sample. Meaning, due to the incorporation of N species into the lattice of TiO_2, all the N-TiO_2 samples enhance their visible absorption with threshold of 500nm. Moreover, it was noted that the N_9-TiO_2sample showed a relatively higher absorption in visible region- boosts the effective utilization of solar light.

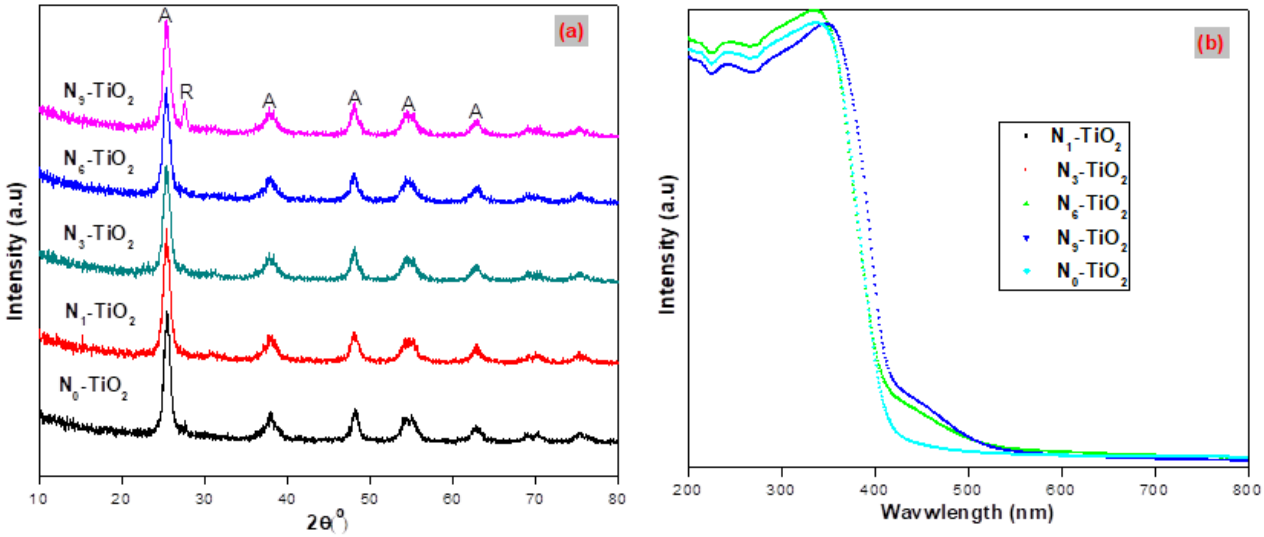

Figure 1: (a) XRD patterns and (b) UV-vis diffuse reflectance spectra of as-prepared N_0-TiO_2, N_1-TiO_2, N_3-TiO_2, N_6-TiO_2, N_9-TiO_2 from bottom to top.

SEM, EDAX, and BET

The SEM images of the TiO_2 nanomaterials, figure 2, were revealed that effect of aging time on their morphology keeping the rest synthesis condition same. However, the aging day varies from 1 to 9 days.

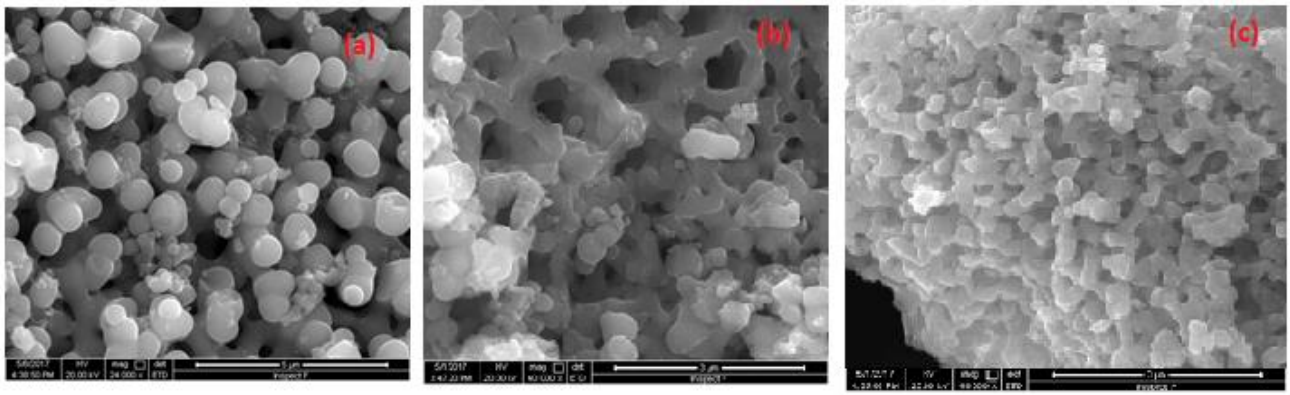

Figure 2: FESEM images of as-synthesized N-TiO_2 aged (a) 1 day (b) 6 days (c) 9 days

As it can be seen in figure, the N-TiO_2 has a spherical shape with a particle size ranges from 250 to 500nm with some aggregation. However, as the as the aging days increases, the microsphere particles, figure2:(a) for N_1-TiO_2, were observed that they grow and connected one another, Fig 2:(c) for N_9-TiO_2. Moreover, from BET surface data, Table 1, the N-TiO_2 nanomaterials have large surface area; and observed there is marginal surface area reduction up on aging while the BJH pore radius is quite similar.

From the elemental analysis of Energy Dispersive Spectroscopy (EDAX) results, it is assured that the N-titania powders are effectively doped with N wt4%, Table 1. Moreover, it is observed that aging time didn't affect N percentage.

Table 1: BET and EDAX data of N-TiO_2 with different aging 1, 3, 9 days.

Aging Time	BET surface area (m^2/g)	BJH Pore Radius (nm)	Ti K Wt%	O K Wt%	N K Wt%	C K Wt%
1 days	83.46	2.63	54.31	37.43	4.17	4.09
3 days	73.62	2.69	54.82	36.50	4.01	4.66
9 days	79.80	2.81	59.18	28.11	4.22	8.49

PHOTOLUMINESCENCE

The Photoluminescence (PL)emission measurement is the key technique to understand whether the defecthas affect the fate of the photo-excited charge carries phenomenon (like e^-/h^+ trapping, migration and transfer) [17]. The PL spectra, Fig 3 of the undoped and nitrogen-doped TiO_2 with different aging time is given and can be seen that there is a broad region ranging 420-550nm which is ascribed to the emission signals due to the charge carriers recombination originating from the charge-transfer transition of an oxygen vacancy trapped electrons [11] .

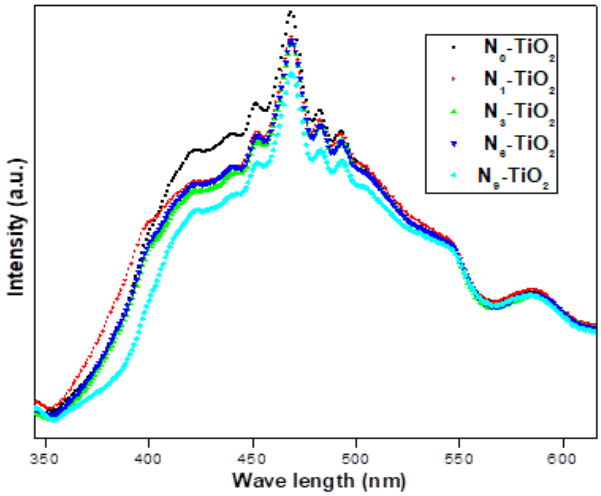

Figure 3: PL spectra of as-prepared from top to bottom, undoped N_0-TiO_2, N_1-TiO_2, N_3-TiO_2, N_6-TiO_2, N_9-TiO_2.

It is clearly seen that all the N-TiO_2 samples have lower PL peak intensities than the pure TiO_2; revealing the introduction of the N species in the TiO_2 crystal lowers the photo-generated charge carriers' recombination rate rather than creating recombination sites. Notably, N_9-TiO_2 sampleshowed the most PL quenching. This could be due its anatse/rutile phase composition which has charge carries separation property as reported elsewhere [18], [19]

PHOTOACTIVITY TEST

The photocatalytic degradation over N-doped titania catalysts was tested against model pollutant methyl blue. The catalyst dose was 80mg while dye concentration was10ppm in 100mLof aqueous solution. After the suspension was magnetic stirred for an hour in the dark to ensure the mixture had reached adsorption equilibrium, and then the solution was exposed to sunlight, as light source, from 12 p.m. to 2 p.m. during the summer season at Trivandrum, India. Every 30minutes, 3ml of solution was taken and analyzed UV- visible spectroscopy after the solution had been centrifuged. The change in the characteristic absorption band of MB at 664 nm was used to calculate the photodegradation efficiency, as presented in figure 4 [20].

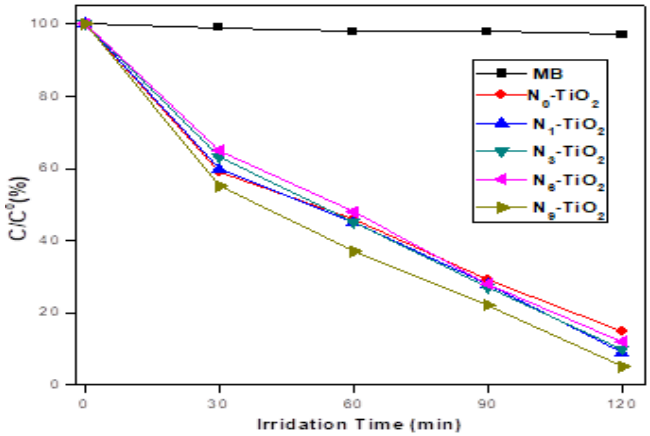

Figure 4: MB degradation for N_x-TiO_2photocatalysts as a function of irradiation time.

It's clearly understood from the figure that the photostable MB has been degraded by the as-prepared photocatalysts and N_9-TiO_2 demonstrated the highest performance, 95%.The others N_3-TiO_2, N_1-TiO_2, N_6-TiO_2 were recorded 90, 89, and 88% degradation. It is noted that the aging didn't brought a significant degradation change among the N-TiO_2 samples, though all N-TiO_2 shown better degradation that the pure one, 85%.

As conclusion, it is observed that aging time had an effect on the crystal phase, morphology, optical, electronic properties and photodegradation during nitrogen doping titania though it is not such significant. However, the most aged, 9days, nitrogen dope titaniademonstrated better photoactivitywhich was attributed due to the synergetic effect of mixed anatase/rutile phase, high sunlight absorption, lower PL.

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