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HIGHLY HOMOGENEOUS NITROGEN DOPED TITANIA NANOMATERIALS: SYNTHESIS AND CHARACTERIZATION

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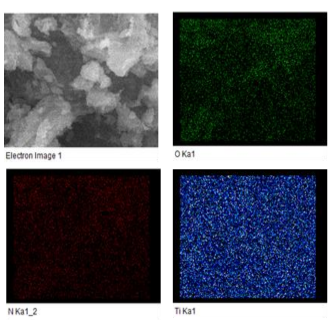
Graphical abstract



EDX mapping of 5N-TiO_2

Abstract

A series of nitrogen doped titania nanomaterials were synthesized via sol-gel method by using tetraethyl ammonium hydroxide as N source. Doping of N into TiO_2 was confirmed via X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR) analyses. Mixture of anatase and rutile phases appeared in the unmodified TiO_2 which was calcined at 773 K. The addition of N to TiO_2 matrix led to formation of single phase of anatase. It has been demonstrated thatTiO_2 and all the N-doped TiO_2 materials were in nanoscale ranging 15.91 – 20.82 nm. Change in surface morphology after N doping was detected by field emission scanning electron microscope (FESEM). Results of EDX mapping analysis indicated homogeneous distribution of N dopants.

Keywords: Titania, nitrogen, nanomaterial, homogeneous

1.0 INTRODUCTION

Since its profitable production in the early twentieth century, titanium dioxide (TiO_2) has been extensively used as a pigment in sunscreen, paints, toothpaste [1-3]. Nanomaterials of titanium dioxide have been receiving much attention for their good photocatalytic and hydrophilic properties [4-5]. These works on application and fundamental aspects of TiO_2 are mainly related to the self-cleaning, chemical energy generation, and photovoltaic devices. Titania has advantages including being non-poisonous, easy to prepare, inexpensive and strong oxidation–reduction reactions [6]. It could restrain virus activity and eliminates the planktons in the air [7]. Titania has also the features of anti-pollution, deodorisation, dust-proof, and self-clean and currently great interest has been dedicated to the use of TiO_2 based photocatalyst for the degradation of dyes in aqueous solutions[8]. The benefit derived from TiO_2 and doped TiO_2 have drawn much research in the field.

Different methods are available for the preparation of TiO_2 photocatalysts, such as hydrothermal [9], solvothermal [10], direct oxidation [11], chemical vapor deposition [12], physical vapor deposition [13], electrodeposition[14], sol [15] and sol-gel [16-17]. Nonetheless, the advantages derived from preparation of TiO_2 using sol-gel method, which include effective control of particle size, shape and properties, synthesis of nanocrystalline powder with high purity at low temperature, better homogeneity of raw materials, preparation of composite materials, andproduction of homogeneous materials have motivated many researchers to the use of the method in preparing TiO_2 [18-19].

The sol-gel method is a wet-chemical technique widely employed in making various ceramic materials [18]. In a typical sol-gel process, hydrolysis and polymerization of precursors will form a colloidal suspension or sol. The liquid phase to solid gel phase transition occurs after complete polymerization [19]. Many studies reported that different modifications of sol-gel method have been used to produce pure thin films or powders in large homogeneous concentration [17].

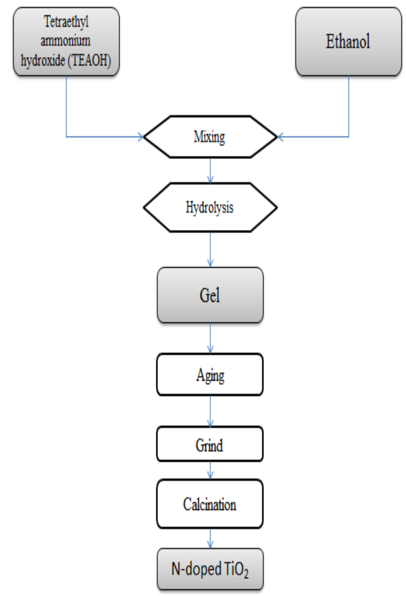
Doping with non-metal such as nitrogen seems to be more successful [20]. The introduction of substitutional N atoms into the TiO_2 matrix improves optical absorption in the visible region, leading to corresponding photochemical activity. The solar energy contains only 3-4% of UV light (λ < 380nm), while the visible light made up of 47% [21]. Thus, many new approaches have been carried out by researchers to enhance the nanomaterials efficiency in visible light region. Successful evidence in various researches shows that modification of titania nanomaterials by doping could enhance the absorptivity of intensity in visible region. Development of TiO_2 responsive to visible light by doping it with various anions as a substitute for oxygen in the TiO_2 lattice has been ongoing studied. The mixing of the p states of the doped non-metal (anions) with O 2p states shifts the valence band edge upwards which narrowed the band gap of $TiO_2$with conduction band [22]. Unlike metal ions, non-metal are less likely to recombine, thus non-metal ions contributes to better enhancing ability of the photocatalytic activity of titania. In this work, an attempt was carried out to synthesize homogeneous N-doped titania nanomaterials via sol-gel method. The properties of these materials were presented in this paper.

2.0 METHODOLOGY

N-doped TiO_2 Preparation. A series of N-doped TiO_2 materials were synthesized via sol gel method as shown in Scheme 1. Firstly, tetraethyl ammonium hydroxide (TEAOH, 40% w/w) as N source was mixed with ethanol with mol ratio 1:20. After 5 minutes stirring, the solution was added with titanium tetraisopropoxide (TTIP, >97%) at N mol% of 1 - 5. The mixture underwent constant stirring at room temperature until the hydrolysis was fully completed after one hour. The gel then was left ageing for 15 hours or up to several days at room temperature until the gel was completely dry. The dried material underwent calcination in air at 773 for 5 hours. The samples were notated as xN-TiO_2, x refers to mol% of N in the sample.

For comparison purpose, pure TiO_2 was also prepared via sol gel method. Typically, TTIP was mixed with acetylacetone and ethanol. The mixture underwent constant stirring until gel was formed. After drying process, the gel was calcined at 773 K for 5 hours.

Characterizations. The prepared N-doped TiO_2 were characterized using X-ray diffraction (XRD), fourier transform infrared (FTIR) spectroscopy, nitrogen adsorption-desorption analysis, field emission scanning electron microscopy (FESEM) and energy dispersive x-ray spectroscopy (EDX). The properties of the materials including crystal structure, crystallinity, crystallite size, surface morphology and sample's homogeneity were examined.



Scheme 1 Preparation of N-TiO_2

3.0 RESULTS AND DISCUSSION

Synthesis of TiO_2 and N-TiO_2nanomaterials. All synthesized samples were white and fine powder. Figure 1 shows the XRD patterns of TiO_2 and N-doped TiO_2 which were calcined at 773 K. Mixture of anatase and rutile phases appeared in the unmodified TiO_2 which was calcined at 773 K. The diffraction peaks at 2θ = 25.3°, 37.7°, 48.0°, 53.8° and 54.9° were corresponded with typical pattern of anatase-type TiO_2. Meanwhile, the peak at 2θ = 27.4° was associated to rutile phase. Apparently, introduction of N to TiO_2 has retarded the formation of rutile phase. Rao *et al*. [20] reported that the presence of dopants inhibited the anatase-rutile transformation by stabilizing the anatase phase. As evidenced, only pure anatase phase was obtained in the N doped TiO_2 samples. It has been previously reported that N doping hindered anatase-rutile transformation by O vacancies formation [21]. The N dopant ions could enter the anatase lattice and influenced the level of oxygen vacancies, thereby inhibiting the transformation anatase to rutile. Crystallite size of the materials was calculated using Scherrer equation (Table 1). The results showed that TiO_2 and all the N-doped TiO_2 materials were in nanoscale ranging 15.91 – 26.82 nm.

The crystallite size of the N-doped materials decreased with increasing of N dopant amount in the samples, implying that the incorporation of N ions suppressed the growth of TiO_2 nanomaterials. This phenomenon could be explained by smaller ionic radii of N as compare to that of Ti. N atoms substitute for the Oatoms in TiO_2 lattice to form O-Ti-N because N is only ~6% larger than O [21].

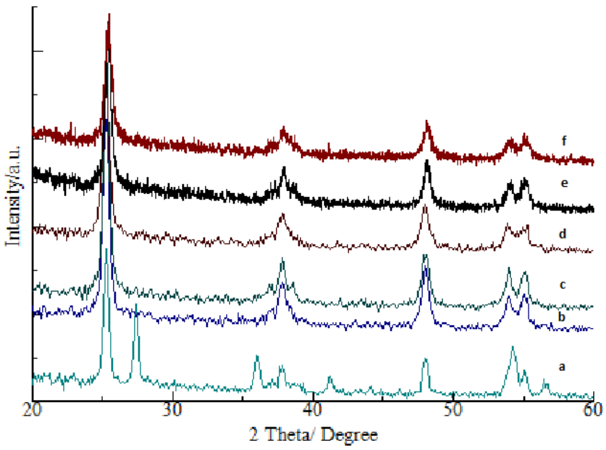


Figure 1 XRD patterns of (a) TiO_2, (b) 1N-TiO_2,(c) 2N-TiO_2, (d) 3N-TiO_2, (e) 4N-TiO_2 and (f) 5N-TiO_2

Table 1 Crystalline size of TiO_2 and nitrogen doped TiO_2 calculated using Scherrer equation

Sample	Crystalline size(nm)
TiO_2	20.13
1N-TiO_2	20.82
2N-TiO_2	20.41
3N-TiO_2	16.10
4N-TiO_2	15.93
5N-TiO_2	15.91

Figure 2 shows FTIR spectra of all the samples. Several broad bands centered at 500-700 cm^{-1}were due to vibration of Ti-O bonds in TiO_2 lattice. Peaks at ~ 1633 $cm^{-1}$and ~3446 cm^{-1}were assigned to the residual of adsorbed water. The weak band at around 1360 cm^{-1} could be attributed to nitrogen oxide species, thus confirming the successfulness loading of N into TiO_2.

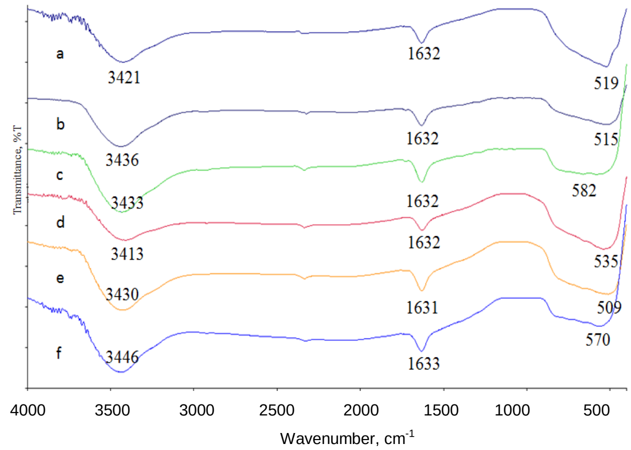


Figure 2 FTIR spectra of (a) TiO_2, (b) 1N-TiO_2, (c) 2N-TiO_2, (d) 3N-TiO_2, (e) 4N-TiO_2 and (f) 5N-TiO_2

Homogeneity of N-doped TiO_2. Morphology and the dispersion of particles were determined by using FESEM and energy dispersive X-ray analysis (EDX), respectively. Figure 3 depicts the FESEM images of TiO_2 and 5N-TiO_2. Figure 3 shows that TiO_2 has smooth surface, which most probably indicated aggregation of TiO_2. Meanwhile, 5N-TiO_2 has rough surface, implying dispersion of nitrogen onto the surface of titania. The EDX mapping image verified successful doping of nitrogen into TiO_2 (Figure 4). The nitrogen was homogeneously dispersed at TiO_2 surface.

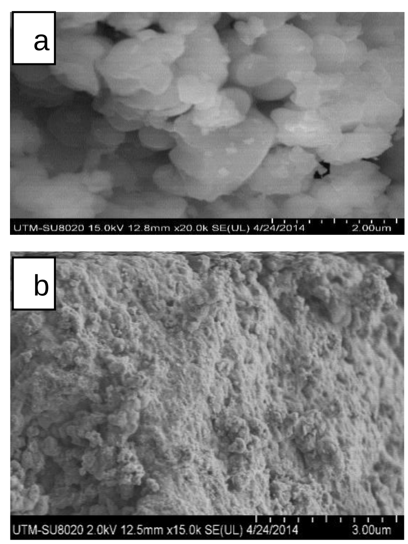


Figure 3 FESEM images of (a) TiO_2 and (b) 5N-TiO_2

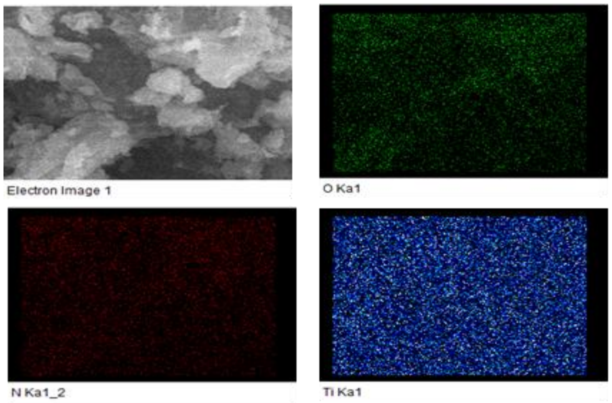


Figure 4 EDX mapping of 5N-TiO2

4.0 CONCLUSION

The synthesis of homogeneous nitrogen doped titania nanomaterials were successfully synthesized via sol gel method. These N-doped TiO_2crystallined in pure anatase phase with crystallite size ranged 15.91 – 20.82 nm. TiO_2 has smooth surface while N-doped titania has rough surface, indicating dispersion of nitrogen on the surface of titania. Homogenous dispersion of N was confirmed though the EDX analysis.

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