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Synthesis and characterization of nitrogen-doped titania nanomaterials of homogeneous particle size

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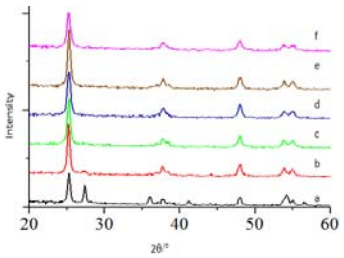
GRAPHICAL ABSTRACT



ABSTRACT

Modification of sol-gel method was used to synthesize homogeneous particle size nitrogen-doped titania (N-TiO_2) nanomaterials using tetraethyl ammonium hydroxide (TEAOH) as N source. XRD analysis showed that these N-TiO_2 (1-5 % N concentration) crystallined in anatase structure. The crystallinity of the samples decreased with increasing of N content. The calculation using Scherrer equation showed that the particle size of the synthesized N-TiO_2 ranged 15.02 - 26.85 nm, strongly suggesting attainment of nanomaterials. DR UV-Vis results indicated that the band gap energy of 5% N doped TiO_2 was only 2.58 eV, implying the sample could be a potential photocatalyst under visible light irradiation. Homogeneous particle size of the synthesized nanomaterials was evidenced through FESEM images. Meanwhile, the EDX analysis confirmed the homogenous distribution of elements Ti, N and O in 5% N doped titania sample.

Keywords: titania, nitrogen, doped, nanomaterials, homogeneous

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1. INTRODUCTION

Nanomaterial titanium dioxide (TiO_2) has been extensively used as a pigment [1] and in sunscreen [2], paints [3], toothpaste [4] *etc*. TiO_2 nanomaterial has been receiving much attention for its good photocatalytic [5] and hydrophilic properties [6]. These works on application and fundamental aspects of TiO_2 are mainly related to the self-cleaning, chemical energy generation, and photovoltaic devices.

Metal doping on TiO_2 [7] has been an important approach in band gap engineering to change the optical response of semiconductor photocatalysts. Metal doping induces a bathochromic shift (a decrease of the band gap or introduction of intra-band gap states), to increase the absorption of visible light. Doping may lead to photocatalytic systems that exhibit enhanced efficiency [8] which is desirable to maintain the integrity of the crystal structure of the photocatalyst while changing its electronic structure by doping. It is easier to replace Ti^{4+} in TiO_2 with a cation than to substitute O^{2-} with another anion because of the difference in the charge states and ionic radii.

Many techniques have been examined to achieve this purpose, including the doping of TiO_2 with transition metals [9], but these doped materials suffer from thermal instability and an increased number of recombination centres. Usage of transition metal has limited the application of textile and waste water related industries. Doping with anion atoms such as nitrogen seems to be more successful [5, 10]. The introduction of substitutional N atoms into the TiO_2 matrix improves optical absorption in the visible region, and leads to corresponding photochemical activity.

In this work, a series of nanostructured nitrogen doped titania were synthesized via sol-gel method. The properties and photocatalytic activity of the samples were presented.

2. EXPERIMENTS

2.1 Nanomaterials Preparation

The sol-gel procedure used in this study to synthesis TiO_2 consists of 1:2:100 ratio of titanium tetraisopropoxide (TTIP), acetylacetone (AcAc) and ethanol, respectively. The sol-gel procedure used for N-TiO_2 preparation consists of same ratio with 0.06, 0.13, 0.19, 0.26 and 0.32 cm^3 ratio of tetraethyl ammonium hydroxide (TEAOH) as source of nitrogen. TTIP was added dropwise into AcAc and was stirred with solvent ethanol at room temperature. The systems were stirred during the addition and then for an additional 60 min, then TEAOH was added to the solution

under vigorous stirring for 60 min. The mixture was stirred in oil bath at 80 °C until gelation was formed. The gelation was dried at 110 °C overnight, resulting formation of dry gels. The resulting dry gels were calcined at 500 °C for 5 h. Accordingly, nitrogen-doped titania containing 0.06, 0.13, 0.19, 0.26 and 0.32 cm^3 ratio of TEAOH and pure titania were labeled as 1N-TiO_2, 2N-TiO_2, 3N-TiO_2, 4N-TiO_2, 5N-TiO_2 and TiO_2, respectively.

2.2 Characterization of nanomaterials

The prepared nanomaterials were characterized via techniques of X-ray diffraction (XRD), diffuse reflectance UV-Vis (DR UV-VIS), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDX).

3. RESULTS AND DISCUSSION

3.1 Synthesis of TiO_2 and N-TiO_2 Nanomaterials

TTIP was used as precursor and TEAOH was used as nitrogen dopant source. Acetyl acetone (AcAc) acted as chelating agent to control hydrolysis of titania precursor (TTIP) and precipitation of titania by forming chelate bond with TiO_2 (*aq*). Figure 1 shows DR UV-Vis spectra of TiO_2 and N dopedTiO_2. The absorbance showed to be below 360 nm. The calculated band gap energy of the synthesized TiO_2, 4N-TiO_2 and 5N-TiO_2 nanomaterials are 2.93, 2.82 and 2.58 eV, respectively. The synthesized TiO_2 nanomaterials band gap energy is larger than the value of 2.58 eV for the 5N-TiO_2 nanomaterials. The narrower band gap is due to excitation of an electron from valence band to conduction band in N-TiO_2 and thus increasing its photocatalytic activity [5,9].

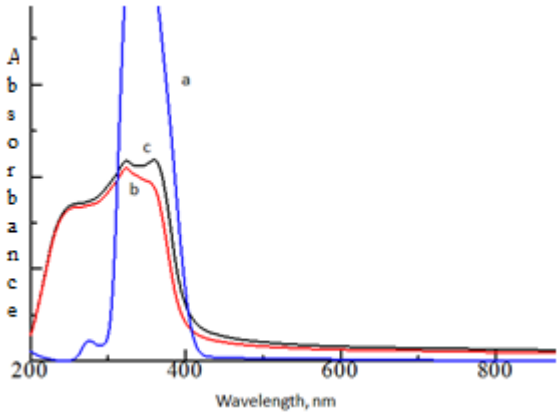

Fig. 1 DRUV-Vis spectra of (a) TiO_2, (b) 4N-TiO_2 and (c) 5N-TiO_2

XRD was used to investigate the changes of phase structure of the pure TiO_2 and nitrogen doped TiO_2 after heat treatment at different mol concentration of nitrogen. Figure 2 shows the effect of nitrogen doping on the phase structure of pure titania. The XRD patterns of all samples contained diffraction peaks that appeared at 25.3, 37.7, 48.0, 53.8 and 54.9°, which were corresponded with typical pattern of anatase-type TiO_2. There is a small peak at 27.4° correspond to rutile phase was detected in TiO_2 sample only. Apparently, introduction of nitrogen has hindered the formation of rutile phase, thus only anatase phase existed in these nitrogen doped TiO_2 materials. Besides, the increase of N amount has reduced slightly the crystallinity of the materials. The width of the intense peak at $2\theta = 25.3°$ was used to determine the crystallite size of the materials. As listed in Table 1, the crystallite size of TiO_2 and N doped TiO_2 ranged 15.02 - 26.85 nm. The crystallite size of the materials was inversely proportional to the N content in the materials.

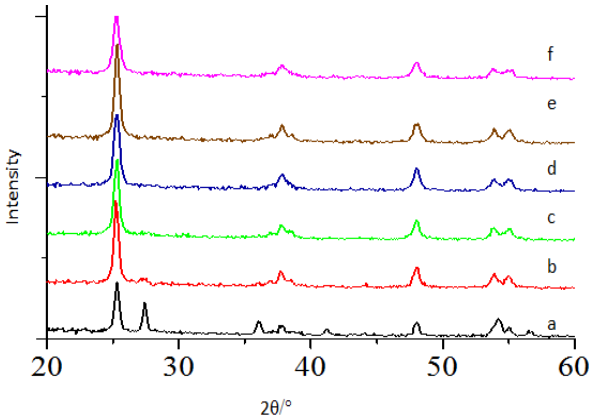

Fig. 2 XRD patterns of (a) TiO_2, (b) 1N-TiO_2 (c) 2N-TiO_2, (d) 3N-TiO_2 (e) 4N-TiO_2, and (f) 5N-TiO_2

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

Sample	Crystallite size(nm)
TiO_2	20.25
1N-TiO_2	26.85
2N-TiO_2	20.33
3N-TiO_2	16.20
4N-TiO_2	15.95
5N-TiO_2	15.02

3.2 Homogeneity of Nanomaterials

Morphology and the dispersion of particles were determined by using FESEM and energy dispersive X-ray analysis (EDX), respectively. Elemental composition analysis was carried out using with EDX. Figure 3 depicts the FESEM images for TiO_2 and 5N-TiO_2. Barbe *et al.* gave evidence that hindering the aggregation of anatase particles would suppress the formation of rutile [12]. Figure 3(a) shows that TiO_2 has smooth surface, which most probably indicated aggregation of TiO_2, whereas 3(b) has rough surface, implied dispersion of nitrogen onto the

surface of titania. The images revealed that the sample consists of agglomerates of primary particles with the crystallite size ranging from about 15-30 nm which is in good agreement with the crystallite size calculated from XRD pattern. Figure 3(b) shows the homogeneous particle size in 5N-TiO_2. Elemental mapping via EDX analysis was carried out to examine the dispersion of nitrogen in the sample. From the Figure 4, the EDX mapping image denoted that the doped nitrogen molecules were homogeneously dispersed at TiO_2 surface.

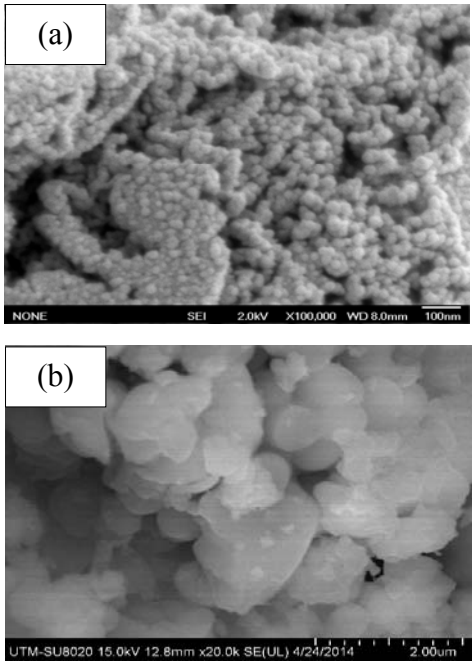

Fig. 3 FESEM images of (a) TiO_2 and (b) 5N-TiO_2

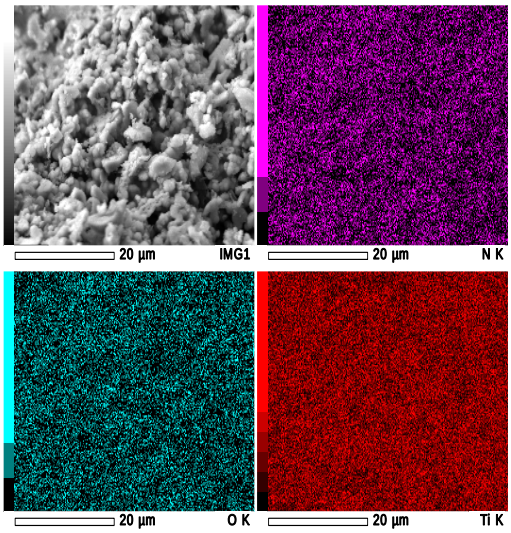

Fig. 4 EDX Mapping of 5N-TiO_2

4. CONCLUSION

The synthesis of homogeneous nitrogen doped titania nanomaterials were successfully obtained using modified sol-gel method. The crystallinity of the samples decreased with increasing of N content. Homogeneous particle size of the synthesized nanomaterials was evidenced through FESEM images. The EDX analysis confirmed the homogenous distribution of elements Ti, N and O in 5% N doped titania sample.

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