



Investigation of the influence of vanadium, iron and nickel dopants on the morphology, and crystal structure and photocatalytic properties of titanium dioxide based nanopowders



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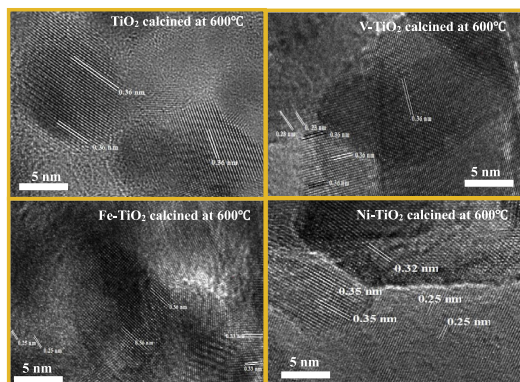
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GRAPHICAL ABSTRACT

High resolution TEM of pure and doped titania photocatalysts.



ARTICLE INFO

Article history:

Received 31 January 2016

Revised 18 April 2016

Accepted 19 April 2016

Available online 22 April 2016

Keywords:

Sol-gel process

TiOCl₂

Calcination

Heterogeneous photocatalysis

ABSTRACT

Photoactive V, Fe and Ni doped TiO₂ (M-TiO₂) nanopowders were synthesized by a modified two-step sol-gel process in the absence of additives. Titanium oxychloride, which is a rarely-used TiO₂ precursor was used to yield M-TiO₂ photocatalysts with preferential photochemical performance in the presence of natural solar irradiation. The obtained samples were calcined at different calcination temperatures ranging from 450 to 800 °C to evaluate the influence of the sintering on the physicochemical properties. The properties of the obtained samples were examined by XRF, XRD, Raman spectroscopy, UV–visible DRS, XPS, nitrogen gas physisorption studies, SEM-EDAX and HRTEM analyses. Structural characterization of the samples revealed the incorporation of these transition metal element into TiO₂. It was also depicted that the morphology, crystal structure, optical and photochemical properties of the obtained samples were largely dependent on the calcination temperature and the type of dopant used during the preparation process. The photochemical performance of the samples was investigated in the photodegradation of methylene blue in the presence of natural sunlight. The experimental results indicated that the VT600 sample possessed the highest activity due to its superior properties. This study provides a systematic preparation and selection of the precursor, dopant and calcination temperature that are suitable for

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the formation of TiO₂-based heterogeneous photocatalysts with appealing morphology, crystal structure, optical and photochemical properties for myriad of applications.

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1. Introduction

Metal oxides semiconductors such as TiO₂, ZnO, WO₃, In₂O₃ and SnO₂ have attracted much attention due to their wide applications in solar cells, heterogeneous photocatalysis, hydrogen gas production through photocatalytic water splitting and sensor technologies. Of the metal oxide semiconductors that have been investigated, TiO₂-based materials have shown remarkable performances due to their unique thermal, electrochemical and optical properties [1–8]. This has significantly prompted many researchers to design versatile preparation approaches to facilitate large-scale production of TiO₂-based materials [9–11]. TiO₂ occurs in three different polymorphic structures: anatase, brookite or rutile phases. These polymorphs can be prepared readily from TiO₂ sources and typically the metastable anatase and brookite transforms into the thermodynamically stable rutile upon calcination at high temperatures [12–15].

The wide band gap of TiO₂ ($E_g \sim 3.0\text{--}3.3$ eV) and the rapid recombination of its photogenerated electron–hole pairs hamper the performance of TiO₂ in some applications especially in those that require visible light excitation [13–17]. Various research investigations [13–19] have proposed that TiO₂ material with a mixture of titania phases exhibits improved quantum efficiency compared to single phase material. Thus, the photochemical performance of the former is thought to be superior to that of the latter. So far, various preparation methods have been suggested that allow for the preparation of metal oxide semiconductors with promising properties for numerous applications. These include co-precipitation, ball milling, spray pyrolysis, hydrothermal, sol-gel, chemical vapor deposition techniques and others [7,8,20–25]. However, the sol-gel process has undoubtedly attracted much attention due to its simplicity, cost-effectiveness and ability to form homogeneous and pure final products at ambient conditions [12,18]. Therefore, the formulation of simplified and convenient sol-gel synthetic routes to prepare metal oxide semiconductors from less expensive precursors will considerably enhance the large-scale production and commercialization of these potential materials.

Meanwhile, there are promising strategies than can be used to extend the optical absorption of TiO₂ into the visible region while simultaneously reducing the recombination behavior of the photogenerated charge carriers during photocatalysis. These include non-metal doping (N, S, C or F); noble metal and transition metal deposition (Au, Ag, Fe, Co, Pt, V or Ni); and the formation of oxygen-rich TiO₂ [8,16,17,20–26]. TiO₂ photocatalysts doped with transition metals and rare earth elements such as Cu, W, Ce, Ni, Eu, La, Nb, Y, V and Fe have been widely investigated. Various studies [17,26,27] have shown that transition metal doped TiO₂-based materials exhibit high photocatalytic performance under visible light irradiation. It has also been deduced that the presence of these species can affect phase transition, morphology and optical properties of the yielded materials. Nevertheless, in most reports, commercial TiO₂ or highly pure metal alkoxide precursors such as tetrabutyl orthotitanate or titanium isopropoxide are utilized as titania sources. Additionally, additives such as tri-block copolymer, polyethylene glycol and cetyltrimethylammonium bromide are used to act as structure-directing agents [21,24,27,28]. This causes the production of TiO₂ based materials to be more expensive and tedious; therefore, the large-scale production and commercialization of heterogeneous photocatalysts is adversely hampered.

In our previous study [20] we found that doping TiO₂ with vanadium has three substantial effects on the mesostructure of the obtained photocatalysts: (1) it reduces the aggregation behavior of the primary particles of the obtained photocatalysts; (2) it facilitates the formation of photocatalysts with a mixture of brookite, anatase and rutile phases; and moreover, (3) it remarkably extends the optical absorption of the obtained products to the visible region. These three outcomes are crucial for the production of final products that possess enhanced photocatalytic performance in the presence of natural solar irradiation. Therefore, it is prudent to carry out a study to compare the morphology, crystal structure, optical properties and photocatalytic performance of Fe, V and Ni doped TiO₂ photocatalysts that are obtained from simple and convenient preparation methods. The ionic radii of V⁵⁺ (0.063 nm), Fe³⁺ (0.065 nm) and Ni²⁺ (0.069 nm) are very close to that of Ti⁴⁺ (0.068 nm) and therefore, they can easily be doped into TiO₂ to yield visible light-active (VLA) materials with desirable properties for heterogeneous photocatalysis [29].

The present study compares the morphology, crystal structure and photocatalytic properties of sol-gel based V, Fe and Ni doped TiO₂ photocatalysts in the absence of additives. A controllable, reproducible and cost-effective sol-gel process was used to synthesize photoactive V, Fe and Ni doped TiO₂ heterogeneous photocatalysts. The sol-gel process proposed in the present study involves peptization of the preformed TiO₂ gel using an acidic solution of metal ions precursors which allows the formation of porous products with a homogeneous dispersion of primary particles in the absence of additives. The photochemical performance of the formed photocatalysts was evaluated in the degradation of methylene in the presence of natural solar irradiation. To the best of our knowledge, only a few reports [24,26] have investigated the influence of transition metals on the mesostructure of TiO₂-based materials. None of these has provided a systematic comparison using the preparation method and titania precursor proposed in the present study. Moreover, the photochemical performances of the obtained photocatalysts were evaluated in the photodecolorization of a methylene blue solution in the presence of solar irradiation to substantiate their practical reliability in degrading non-biodegradable toxic organic contaminants.

2. Experimental part

2.1. Materials

All of the chemical reagents used in this study were purchased from commercial sources and used without further purification. TiOCl₂ (25 wt%) was purchased from Kukdong Chemicals Co. Ltd, South Korea while ammonium hydroxide solution (28%) was bought from Dae-Jung Chemical and Metal Co. Ltd, South Korea. Iron (III) nitrate nonahydrate (98+%), methylene blue hydrate and HNO₃ (60%) were acquired from Sigma-Aldrich. Vanadium pentoxide (99%) was procured from Junsei Chemical Co. Ltd, Japan and nickel (II) nitrate hexahydrate (98%) was acquired from Dusan Pharmaceutical Co. Ltd, South Korea.

2.2. Synthesis process

Photoactive V, Fe or Ni doped TiO₂ photocatalysts were synthesized through two-step modified sol-gel synthetic approach in the

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