Journal of Molecular Catalysis A: Chemical 412 (2016) 78–92

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

An insight toward the photocatalytic activity of S doped 1-D TiO_2 nanorods prepared via novel route: As promising platform for environmental leap

Shahzad Abu Bakar[a,b,*], Caue Ribeiro[b]

[a] Department of Chemistr—Federal University of São Carlos, Rod. Washington Luiz, km 235, CEP: 13565-905 São Carlos, SP, Brazil
[b] Embrapa CNPDIA, Rua XV de Novembro, 1452, 13560-970 São Carlos, SP, Brazil

ARTICLE INFO

Article history:
Received 12 October 2015
Received in revised form
24 November 2015
Accepted 2 December 2015
Available online 7 December 2015

Keywords:
TiO_2
Nanorods
S doping
Visible light
Photocatalysis

ABSTRACT

The photocatalytic applications of the S-doped titanium dioxide (TiO_2) are of great importance due to photon-to-carrier conversion ability of S-doping in the energy region below the band gap of pure TiO_2. Therefore, 1D (one dimensional) S-doped TiO_2 anatase nanorods were synthesized first time by facile, low temperature and template free oxidant peroxide method (OPM). The addition of thiourea as sulfur precursor favored the formation of better crystalline anatase TiO_2 and S atoms favorably crystalized the anatase structure. It was found that substitution of Ti^{4+} by S^{6+} in the lattice of S doped TiO_2 nanorods increased the number of adsorbed active groups (hydroxyl radical) at the surface of catalyst and also gave rise to the visible-light response. The formation of Ti—O—S bond favors the partial transfer of electrons from S to O atoms. It helps the electron-deficient S atoms to hold/capture electrons and thus reduce the recombination rate of photogenerated electron–hole pairs. The preferred anatase {1 0 1} facets could also act as beneficiary reservoirs to decrease the recombination probability of electron–hole pairs. Methylene blue (MB) was used as target organic molecule for evolution of photocatalytic activity by photocatalytic oxidation reaction under visible-light. The mineralization products of MB were detected using High Performance Liquid Chromatography (HPLC) and GC/MS spectroscopy that gave the pattern of possible degraded fragments from the mineralization of MB. The role of active species in the degradation process was identified with the help of Mott–Schottky measurement, addition of different scavengers and the band structure obtained from the UV–vis diffuse reflectance spectrum. It was found that holes and hydroxyl radicals played major role in the photo-degradation of MB. The fundamental mechanism for enhanced photocatalytic performance of S doped TiO_2 nanorods was discussed in detail and attributed to the S doping and morphology engineering that may improve the electron–hole pair separation efficiency for enhanced photocatalytic performance under visible-light irradiation. This work may provide an insight into the synthesis of S doped TiO_2 photocatalysts that showed good stability after four cycles and have great potential for environmental purification of organic pollutants.

1. Introduction

Rapid increase of industrial waste water discharge into streams, lakes and/or oceans is causing serious environmental problems and resulted in abnormal change to the world temperature. Research has been initiated immensely in recent years for the development of cheap, clean, renewable and environmentally friendly semiconductor photocatalytic materials [1–3]. TiO_2 has been emerged as a promising semiconductor photocatalyst for the degradation of pollutant compounds in water and accepted great deal of attention by many research groups throughout the world [1–5]. Fujishima and Honda [6] discovered water splitting on a single-crystalline TiO_2 (rutile) anode by shining UV light for the generation of hydrogen and oxygen in photoelectrochemical cell and this invention prompted the research/exploration toward TiO_2 -based semiconductor photocatalytic materials due to their chemical stability and nontoxicity for high photocatalytic activities [1,4,5].

TiO_2 has three crystalline forms, anatase, rutile and brookite, of which anatase titania (TiO_2) is considered as promising

---

* Corresponding author at: Department of Chemistry—Federal University of São Carlos, Rod. Washington Luiz, km 235, CEP: 13565-905 São Carlos, SP, Brazil. Fax: +55 1621072902.
E-mail address: shazad_158@yahoo.com (S. Abu Bakar).

http://dx.doi.org/10.1016/j.molcata.2015.12.002
1381-1169/

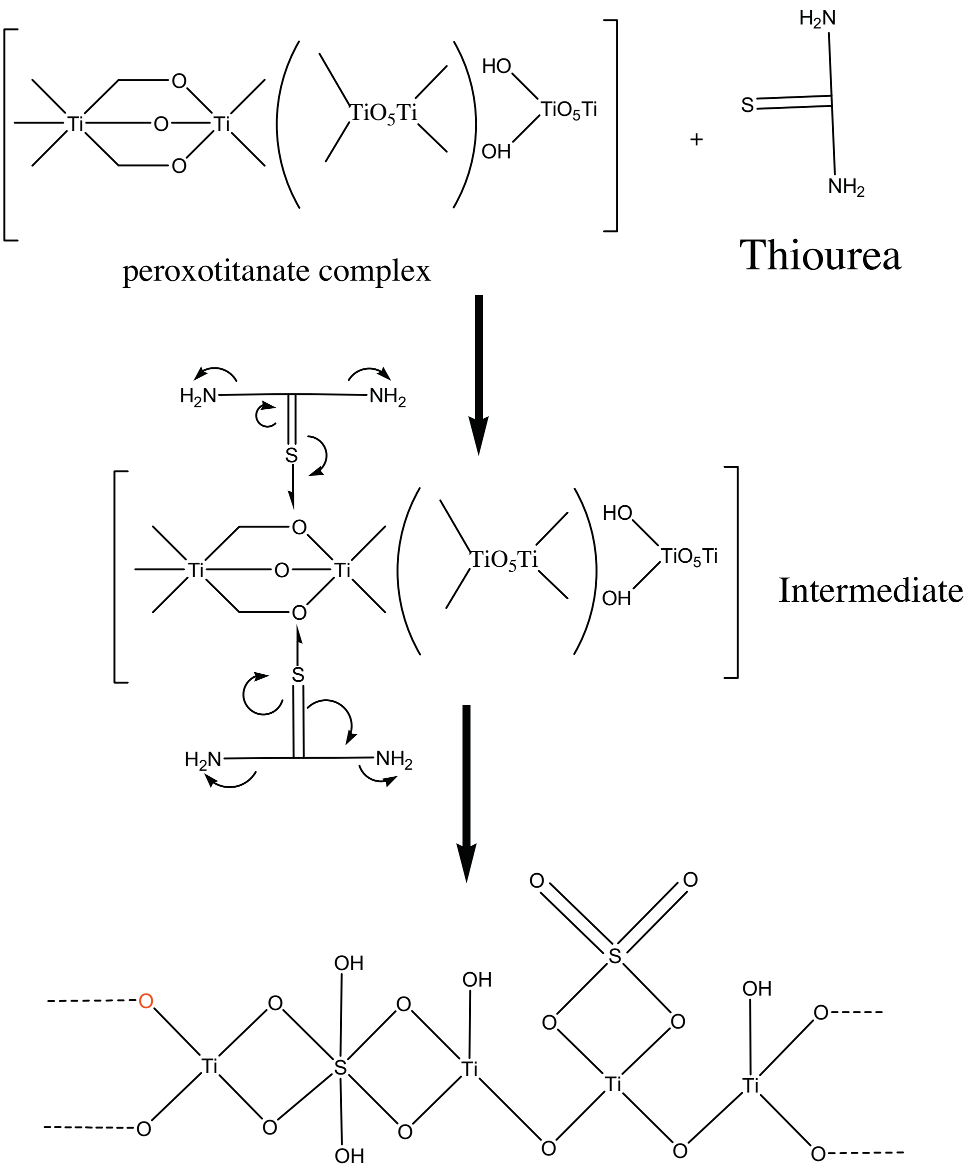

Fig. 1. Proposed mechanism for the sulfur doping into TiO_2.

solar-driven photocatalyst for the generation of hydrogen and water cleaning [4,5]. Rutile phase has narrow band gap (3.0 eV) than anatase (3.2 eV) but has much lower photocatalytic activity [7]. Therefore, much effort has been made on anatase by molding its microstructure (size, crystallinity, morphology and facets) to improve its photocatalytic activity in the ultraviolet and visible-light region via tuning its band structure (with oxygen vacancies, element doping, etc.,) near the conduction band minimum (lower energy empty state) and valence band maximum (highest energy filled states) [1–3]. These approaches may also work for rutile TiO_2 to utilize UV light ($\leq$388 nm), which makes up only 4–5% of the incoming whole solar spectrum. From the viewpoint of solar energy utilization, an efficient strategy to enhance the photoactivity of photocatalyst by tuning its light absorption capability into the visible region ($\lambda > 400$ nm) is indispensable [8].

Wide-bandgap anatase TiO_2 was reported to have better solar absorption and visible-light-driven photocatalytic activity with the doping of transition-metal ions [9,10], coupling metallic oxides [11,12], depositing some noble metals [13,14], and/or non-metal elements (e.g., N, S, and C) [15–21] into TiO_2 lattice to narrow its band gap. However, thermal instability and/or an increase in carrier recombination centers in the cation doped TiO_2 photocatalyst reduced its photocatalytic activity even in the UV region [22]. Therefore, recently non-metal element doping has attracted much attention due to higher potential energy of their atomic orbitals (e.g., N2p, S3p, and C2p) than that of O2p atomic orbital in TiO_2. Thus, formation of new valence bands instead of pure O2p atomic orbital results in decrease of band gap energy without affecting the conduction band level [16,17,22]. Although, number of research work has been reported by several research groups for the preparation of nitrogen doped and carbon-doped TiO_2 photocatalysts which showed beneficial effects of the doped elements on photocatalytic properties [22]. However, the photocatalytic activity of non-metal elements doped TiO_2 is still very low and needs to improve, including S-doped TiO_2. Hence, the current photocatalytic activity of TiO_2 remains insufficient. Herein, we reports the combination of element doping and TiO_2 nanorice structure for enhancing photocatalytic activity of TiO_2 under visible-light photocatalysis. The presence of large amount of stable Ti^{3+} and oxygen vacancy (VO) in the S doped TiO_2 during the dopants introduction enhanced the visible and infrared light absorption of the material. In this study, we have investigated the possible enhancement of the