Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 135 (2015) 814–819

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Zirconium and silver co-doped TiO_2 nanoparticles as visible light catalyst for reduction of 4-nitrophenol, degradation of methyl orange and methylene blue

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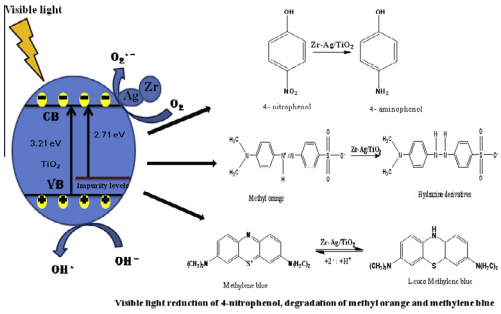
HIGHLIGHTS

- Simple sol–gel synthesis of Zr and Ag co-doped TiO_2 nanoparticles is described.
- Effective photocatalysis for the reduction of nitrophenol and degradation of dyes shown.
- Recycling of photocatalyst up to 4 cycles discussed as promising industrial application.

GRAPHICAL ABSTRACT



Visible light reduction of 4-nitrophenol, degradation of methyl orange and methylene blue

ARTICLE INFO

Article history:
Received 3 February 2014
Received in revised form 29 June 2014
Accepted 28 July 2014
Available online 7 August 2014

Keywords:
Photocatalyst
Visible light
4-Nitrophenol
Methyl orange
Methylene blue

ABSTRACT

Catalytic activity of Zr and Ag co-doped TiO_2 nanoparticles on the reduction of 4-nitrophenol, degradation of methylene blue and methyl orange was studied using sodium borohydride as reducing agent. The nanoparticles were characterized using X-ray diffraction, energy dispersive X-ray, high resolution transmission electron microscopy, selected area electron diffraction and UV–Vis spectroscopy. The rate of the reduction/degradation was found to increase with increasing amount of the photocatalyst which could be attributed to higher dispersity and small size of the nanoparticles. The catalytic activity of Zr and Ag co-doped TiO_2 nanoparticles showed no significant difference even after recycling the catalyst four times indicating a promising potential for industrial application of the prepared photocatalyst.

Introduction

Titanium dioxide (TiO_2) is a promising photocatalytic material due to its high stability, non-toxic nature & high performance in the mineralization of organic pollutants in air and water media and affordable cost [1–4]. However, photocatalytic processes with TiO_2 catalysts are mostly favoured under UV irradiation due to its large band gap (~3.2 eV). This restricts the use of TiO_2 in practical applications because of the limited availability of UV radiation (only 5% of solar light). Hence, the focus of researchers has been on introducing dopants into TiO_2 to make the material absorb radiation visible region of the electromagnetic spectrum for its use in several applications. This approach of doping metals into TiO_2 has been proved to be a very useful in making visible light sensitive catalysts [5]. Similar approach has been reported to yield good results while two different metals were doped into ZnO or TiO_2 resulting in enhanced photocatalytic activity and unique

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http://dx.doi.org/10.1016/j.saa.2014.07.070
1386-1425/

characteristics compared to doping of a single element [6–14]. 4-nitrophenol (4-NP), listed by the US EPA as a major pollutant, may induce blood disorders, eye, skin irritation, kidney and liver damage as well as poisoning of the central nervous system in humans and animals [15]. 4-NP has been used extensively as a raw material in chemical industry for manufacture of pesticides, herbicides, synthetic dyes, pharmaceuticals, for treatment of leather and in several military applications [16]. Several silver nanoparticle based catalysts have been reported for the reduction reaction of 4-NP. Naik et al. have reported the formation of Ag nanoparticles within the pores of mesoporous silica [17,18]. Zhang et al. have reported the preparation of tubular nanocomposites of Ag nanoparticles and silica with fairly uniform diameters in the range of 250–350 nm, by combining the single capillary electrospinning technique (for silica nanotubes as the supports) and an in situ reduction approach (for Ag nanoparticles) [19]. Liu et al. have modified halloysite ($Al_2Si_2O_5(OH)_4{\cdot}2H_2O$,1:1 layer aluminosilicate) nanotubes by mercaptoacetic acid, ethylene glycol to encapsulate Ag nanoparticles and utilized it for the catalytic reduction of 4-NP [20].

Textile industries discharge effluents containing fairly large amounts dyes into water, some of which are mutagenic and carcinogenic to humans [21]. These effluents are characterized by their fluctuating pH with suspended particles, high oxygen demand, non-biodegradability and resistance to oxidation [22,23]. The complex structures of these dyes and their high refractoriness to degradation poses a big challenge in their decolorisation and complete mineralization. It has, therefore, become necessary to develop new promising materials for dye removal. Methylene blue (MB) causes nausea, hypertension, haemolysis and respiratory distress. To overcome the problems posed by different conventional dye removal agents, there has been a good amount of interest in inorganic composites of nano-scale dimensions. It may be seen that doping of ZnO or TiO_2 with transition elements induces crystal defects which can also change their photocatalytic properties. By electron trapping, Zr-doping possibly conquers the recombination of electrons and positive holes [24]. Furthermore, Zr is an isoelectric impurity belonging to deep energy level doping elements [25]. Methylene Blue (MB), Methyl Orange (MO), nitrobenzene and trichloroethylene have also been used as model pollutants to determine the activity of the photocatalyst [26–29].

Recovery of the catalyst is an important step in heterogeneous catalysis and to facilitate this, metal nanoparticles are usually dispersed onto solid matrices while preparing the heterogeneous catalysts. The supporting matrices used include carbon nanotubes, silica, titania, ceria and alumina [30–32]. Shi et al. [33,34] have synthesized stable gold nanoparticles using natural materials such as tannin or collagen. However, TiO_2 is still one of the most favorable supports for metal nanoparticles due to its thermal and chemical stability, non-toxic nature and relatively low cost. The present study reports the synthesis of Zr and Ag co-doped TiO_2 nanoparticles and their application as photocatalyst for the reduction of 4-NP, degradation of MB and MO using $NaBH_4$ as the reducing agent.

Materials and methods

Materials

Titanium (IV) isopropoxide from Sigma Aldrich, commercial azo dyes methylene blue, methyl orange, 4-nitrophenol and sodium borohydride ($NaBH_4$) from SD-Fine chemicals, hydrazine hydrate and zirconyl nitrate [$ZrO(NO_3)_2$] from SRL chemicals, tween 20 from Himedia were used in the present study. Milli-Q water was used in all the experiments.

Synthesis of Zr and Ag co-doped TiO_2 nanoparticles

A mixture of 5 mL of titanium (IV) isopropoxide in 50 mL isopropanol was added drop wise to 200 mL of distilled water maintained at pH 1.5 while the solution was continuously stirred. To this solution, required amount of aqueous solutions of $AgNO_3$ and $ZrO(NO_3)_2$ (0.2–0.8 mol%) were added drop wise and stirring continued for an additional 45 min. Then, a small aliquot of distilled water and 0.05 M hydrazine hydrate were added to it followed by 5 mL of tween 20 (capping agent to prevent agglomeration of particles) and the stirring was continued for an additional 30 min. The resultant sol was sonicated at 80 MHz for 90 min and then dried at 100 °C in a hot air oven for 24 h to get the dry gel. The gel was then calcinated at 450 °C to obtain required nanoparticle powder.

Characterization of co-doped TiO_2 nanoparticles

Powder XRD pattern was recorded using X-ray BRUKER D8 Advance X-ray diffractometer with Cu Kα source (λ = 1.5406 Å). The crystalline phase of the nanoparticles was identified by comparing the major peak positions with standard JCPDS files. JEOL JEM 2100 high resolution transmission electron microscope (HRTEM) was used for imaging, SAED pattern and energy dispersive X-ray with an accelerating voltage of 200 kV at different magnifications. Diffuse reflectance spectra were recorded using JASCO V-670 UV–Vis spectrophotometer. Specific surface area of the sample was arrived at through nitrogen adsorption at 77 K using BET, Micromeritics ASAP2020 V4.01 (V4.01 H).

Catalysis

Reduction of 4-NP, degradation of MB and MO catalyzed by Zr and Ag co-doped TiO_2 nanoparticles was carried out at room temperature (30 °C). The reduction process was initiated by adding the 0.01 g doped nanoparticles to a solution containing 50 mL of 4-NP (0.1 mmol L^{-1}) and 5 mL of freshly prepared 0.05 M $NABH_4$ in a beaker while constantly stirring. The resultant suspension was irradiated with a 200 W Philips tungsten filament lamp (λ > 400 nm) which was placed at a distance of 5 cm from the suspension.

The catalytic degradation of MB and MO was carried out by adding1 mL of 0.01 M $NABH_4$ solution to 30 mL of 10^{-3} M MB and MO solutions respectively while stirring. After 5 min, 0.01 g of catalyst powder was added and the stirring continued. The kinetics of degradation of dyes was studied by taking a small aliquot of the sample and measuring the absorbance at specific λ_{max} at regular time intervals. Degradation was visualized by the disappearance of color of the dye solutions. In the case of MB, the blue color which was initially seen in an oxidizing environment turned colorless in the presence of reducing agent ($NaBH_4$) indicating the degradation of MB to leuco MB (LMB) [35].

The catalytic activity was verified by varying the amount of catalyst (0.01, 0.05 and 0.1 g) while monitoring the degradation processes through absorbance measurements on the UV–Vis spectrophotometer.

Results and discussion

Optical properties

Fig. 1(a) shows the UV–Vis absorption spectra of pure TiO_2, Ag doped TiO_2 & Zr and Ag co-doped TiO_2. A definite band edge in the UV region at 300–350 nm seen in the spectra which could be assigned to photo excitation from valence band to conduction