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Research article

# Rapid enhanced photocatalytic degradation of dyes using novel N-doped $ZrO_2$

Hanggara Sudrajat [a], Sandhya Babel [a, *], Hiroshi Sakai [b], Satoshi Takizawa [b]

[a] School of Biochemical Engineering and Technology, Sirindhorn International Institute of Technology, Thammasat University, P. O. Box 22, Pathum Thani 12121, Thailand

[b] Department of Urban Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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ABSTRACT

A novel N-doped $ZrO_2$ (N–$ZrO_2$) photocatalyst is synthesized through thermal decomposition of zirconium hydroxide-urea complex and is characterized using various techniques, including XRD, FTIR, TGA, SEM, TEM, UV-DRS, XPS, XANES, and BET. The N–$ZrO_2$ possesses pure monoclinic structure with high crystallinity. By using the proposed facile route of synthesis, both interstitial and substitutional N doping with high dopant stability can be realized. The optical properties of the catalyst are significantly altered after N doping, giving an optical response in the visible and near infrared regions and an additional strong absorption peak in the UVA region. The N–$ZrO_2$ showed a higher photocatalytic activity than pristine $ZrO_2$ for the degradation of amaranth (AM) and methylene blue (MB) under visible or UV light irradiation, which could be attributed to the band gap narrowing, higher specific area, smaller crystalline size, and higher availability of surface hydroxyl groups. Due to its molecular structure and light absorption characteristics, MB is easier to degrade than AM. Overall removal efficiencies, including adsorption and photolysis, for AM and MB by N–$ZrO_2$ at pH 7 with initial dye concentration of 10 mg/L, catalyst concentration of 1 g/L, and visible light irradiation of 144.7 W/$m^2$ are 67.2 and 96%, respectively. Using UVA light of only 3.5 W/$m^2$ under identical experimental conditions, complete removal of MB and AM is obtained. The photocatalytically treated solution of either AM or MB is nontoxic against *Bacillus cereus*, an agriculturally important soil microorganism.



## 1. Introduction

It is estimated that up to 20% of the total world dye production is lost during the dyeing process in textile industries (Konstantinou and Albanis, 2004). As a result, a significant amount of dye wastewater has been generated. Dye wastewater can cause esthetic problems and a disturbance to the ecology of aquatic life due to reduction of sunlight penetration and inhibition of $O_2$ dissolution in water bodies. Many textile dyes, such as congo red and amaranth, are toxic and have been suspected as carcinogens and mutagens (Brown and De Vito, 1993). Some dyes with low biodegradability are found to easily pass through wastewater treatment plant due to their ability to form ionic compounds which are soluble in water (Fu and Viraraghavan, 2001). For these reasons, the treatment of dye wastewater has received increasing attention.

During the past two decades, heterogeneous photocatalysis has been considered to be a promising method for the treatment of dye wastewater due to its solar-driven and destructive process. Low-cost of catalyst material and reusability of the catalyst are the other advantages of using photocatalytic treatment. Among various materials, $ZrO_2$ is an attractive candidate for a photocatalyst. It has superb thermal and chemical stability, excellent mechanical strength, high stability towards photocorrosion, and high negative value of the conduction band potential capable of generating holes having very strong oxidation power (Zheng et al., 2009). Additionally, its large band gap (Qi et al., 2000) and suitable redox potentials in bands are very beneficial for the degradation of a wide variety of organic pollutants (Králik et al., 1998). It was reported that star-like $ZrO_2$ synthesized by hydrothermal method exhibited excellent photocatalytic activity for the degradation of methyl orange, congo red, and rhodamine B (Shu et al., 2013). Complete dye degradation was achieved within less than 2 h of UV light irradiation. $ZrO_2$ synthesized by the solution combustion method was also an effective photocatalyst for the degradation of anionic dyes, such as amido black, remazol brilliant blue R, and alizarin cyanine green, under UV light (Polisetti et al., 2011). Almost complete degradation

* Corresponding author.
*E-mail address:* sandhya@siit.tu.ac.th (S. Babel).

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of dyes was observed within 2 h. The excellent photocatalytic activity of $ZrO_2$ for the degradation of methyl orange under UV light was also reported (Sreethawong et al., 2013). It was simply synthesized by surfactant-aided sol–gel method.

To enhance the photocatalytic activity of pristine $ZrO_2$, especially under visible light irradiation, metal doping was suggested to be an effective method. It was reported that rare earth metals such as Sm and Eu greatly enhanced the photocatalytic activity of $ZrO_2$ for the degradation of methylene blue and rhodamine B under visible light irradiation (Du et al., 2013). The outstanding photocatalytic activity is due to the suitable electronic structure and increased specific surface area. However, doping with transition metals such as Cu, Pt, and Au decreased the activity of $ZrO_2$ for photodegradation of aqueous carbonate (Sayama and Arakawa, 1993). Potential toxicity of metals is also of pivotal concern when using metal dopants. Due to these facts, it might be better to employ nonmetal dopants for enhancing the photocatalytic activity of pristine $ZrO_2$. Of nonmetal dopants, N seems suitable to enhance the photocatalytic activity of wide band gap metal oxides such as $ZrO_2$ due to its lower electronegativity than that of O (Liu et al., 2010). In addition, its comparable radius to that of O may lead to a uniform distribution within the whole doped matrix (Charanpahari et al., 2013).

Due to the fact that the widely used methods for the treatment of dye wastewater such as flocculation, activated sludge, membrane filtration, and adsorption are limited by their drawbacks of sludge production, membrane fouling, and adsorbent regeneration, in this research, photocatalytic treatment using a novel N-doped $ZrO_2$ (N–$ZrO_2$) as catalyst is adopted for the degradation of two textile dyes, methylene blue (MB) and amaranth (AM). Although there are some reports on the synthesis of N–$ZrO_2$ (Gutzov and Lerch, 2007; Lee et al., 2006), its use for the photocatalytic degradation of textile dyes has not been reported. The N–$ZrO_2$ is synthesized through thermal decomposition of zirconium hydroxide-urea complex. This method does not involve complicated, strictly controlled conditions, or special equipment. Urea is used as a dopant source due to its low cost and easy handling. The physicochemical properties of MB and AM are shown in Table 1.

## 2. Materials and methods

### 2.1. Materials

All chemicals were of analytical grade. Zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$), Wako), urea ($CO(NH_2)_2$, Merck), sodium hydroxide (NaOH, Wako), methylene blue ($C_{16}H_{18}ClN_3S$, Merck), amaranth ($C_{20}H_{11}N_2Na_3O_{10}S_3$, Sigma–Aldrich), and commercial zirconium dioxide ($ZrO_2$, Chameleon Reagent) were used as received without further purification. Milli-Q water was used in all the processes.

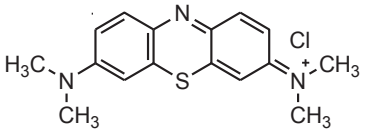
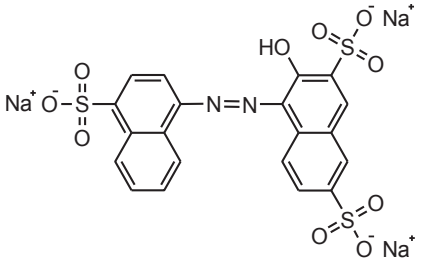
### 2.2. Synthesis

The N–$ZrO_2$ was synthesized by thermal decomposition of zirconium hydroxide-urea complex. The zirconium hydroxide was obtained through precipitation of zirconium oxychloride. About 3.22 g of zirconium oxychloride was dissolved in 20 mL of water with continuous stirring. NaOH was slowly added to the solution under continuous stirring until the pH reached 8. The obtained precipitate of zirconium hydroxide ($Zr(OH)_4$) was collected by centrifugation, repeatedly washed with water, and ground with 1.2 g of urea in an agate mortar for 30 min. The ground mixture was dried in an oven at 100 °C for 24 h and calcined at 600 °C for 3 h in a muffle furnace to form crystalline N–$ZrO_2$ with pale yellow color. This pale yellow color may be due to substitution of O by N, giving an optical response in the visible and near infrared (NIR) regions. The as-synthesized N–$ZrO_2$ was washed with water followed by ethanol prior to drying at 100 °C for 24 h. The possible formation reaction of N–$ZrO_2$ is illustrated in Scheme 1. Furthermore, pristine $ZrO_2$ was synthesized by the same method without adding urea. For the purpose of comparison, the N–$ZrO_2$ was also synthesized using a similar manner but with commercial $ZrO_2$ (c/$ZrO_2$) as starting material, denoted as c/N–$ZrO_2$. About 1.23 g of c/$ZrO_2$ was ground with 1.2 g of urea in an agate mortar for 30 min followed by calcination, washing, and drying.

### 2.3. Characterization

The infrared spectra were recorded by a Fourier transform infrared (FTIR) spectrometer (FT-IR-610, Jasco). X-ray diffraction (XRD) patterns were collected on a Bruker D8 diffractometer (Cu Kα radiation, $\lambda = 1.5406$ Å). The topological and morphological properties were observed by scanning electron microscopy (SEM) (V88-SI, Keyence) and transmission electron microscopy (TEM) (JEM 2100, Jeol), respectively. The textural properties were examined using $N_2$ adsorption–desorption isotherms at liquid nitrogen temperature of 77 K by an adsorption instrument (Belsorp 28SA, Bel). The diffuse reflectance spectra (DRS) were obtained from a UV–Vis–NIR spectrophotometer (Cary 5000, Agilent) with $BaSO_4$ as reflectance standard. The chemical state of N dopant was verified

**Table 1**
Physicochemical properties of the dyes.

| Characteristics | Dye | |
|---|---|---|
| | Methylene blue | Amaranth |
| Empirical formula | $C_{16}H_{18}ClN_3S$ | $C_{20}H_{11}N_2Na_3O_{10}S_3$ |
| $\lambda_{max}$ (nm) | 664 | 521 |
| Structure |  |  |
| Hydrogen bond donor | – | 1 |
| Hydrogen bond acceptor | 4 | 12 |