

# Ag and N co-doped TiO<sub>2</sub> nanostructured photocatalyst for printing and dyeing wastewater



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## ARTICLE INFO

### Article history:

Received 19 October 2016

Received in revised form

26 November 2016

Accepted 30 November 2016

### Keywords:

Co-doped TiO<sub>2</sub>

Nanostructured photocatalyst

Photocatalytic reaction

Continuous reactor

## ABSTRACT

Ag and N co-doped TiO<sub>2</sub> nanoparticles were synthesized by the sol–gel method. Tetrabutyl titanate was used as the precursor, AgNO<sub>3</sub> as the Ag source, and urea as the N source. When the sol was prepared, a 304 stainless steel mesh as the structured material was immersed into the solution. After calcinated at preset temperature, nanostructured photocatalysts were obtained. The photocatalysts were located at the internal shell of a continuous reactor that was designed for photocatalytic reaction. The degradation reaction of methylene blue was carried out in this reactor. The characteristics and doping dosage of the nanostructured photocatalysts were analyzed by thermogravimetric analysis, X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy, and energy dispersive X-ray spectroscopy. The degradation product samples were determined by UV–vis spectrometry. Finally, the photocatalytic efficiency was evaluated under batch and continuous reactors. The multifarious kinetic constants were determined under reaction conditions. The result illustrates that the degradation efficiency of methylene blue apparently increased.

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## 1. Introduction

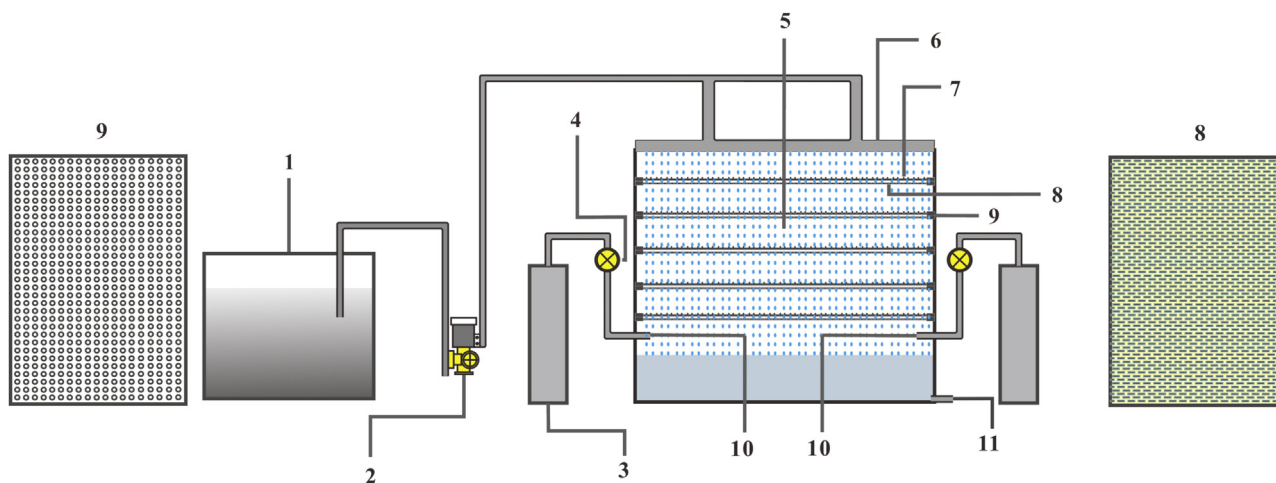
With the development of the dyeing industry, water contamination has become an important environmental issue that has attracted much attention from researchers. Printing and dyeing wastewater mainly consists of large-volume complex substances that contain many organic compounds with toxicity and poor biodegradability. These organic compounds can cause cancer and mutation in the human body via the food chain. Considerable efforts have been devoted to treating printing and dyeing wastewater to recycle water resources. Heterogeneous photocatalysis has been applied as a cost-effective treatment process to degrading printing and dyeing wastewater. Titanium dioxide (TiO<sub>2</sub>) has been widely researched for its availability, stable physical and chemical properties, low cost, and strong corrosion resistance to light [1–5]. It features high photocatalytic activity and degradation rate in controlling organic pollutants. However, TiO<sub>2</sub> possesses a high recombination rate of charge carriers and only responds to UV radiation at 387.5 nm to excite electron–hole pairs because of its

large band gap that leads to low photo quantum efficiency [6–8]. TiO<sub>2</sub> nanopowder with high surface area and binding energy easily agglomerates, which complicates its recovery from solution [9]. The present work aims to enhance the photocatalytic properties of supported TiO<sub>2</sub> nanoparticles and prepare nanostructured TiO<sub>2</sub> photocatalysts for continuous operation.

Only 3% of sunlight corresponding to UV light can be absorbed by active electron–hole pairs [10–12]. Nonmetal elements, such as N, P, S and C, have been explored as dopants for TiO<sub>2</sub> crystal to increase the utilization of sunlight [13–15]. Among these nonmetal elements, N is the most promising dopant because its similar ionic radii to O can significantly decrease the band gap as a result of the mixture of N 2p and O 2p states [16–18]. In addition, oxygen vacancies serve as an activity source of visible light, and N doping can promote the stability of TiO<sub>2</sub>. Although the range of absorbed solar light is widespread after N doping, the high recombination rate of charge carriers still restricts the application of TiO<sub>2</sub> as an efficient photocatalyst. Noble metal nanoparticles such as Ag, Au and Pt exhibit plasmonic characteristics through electron transfer [19–21]. As an excellent conductor, Ag can availably capture photogenerated electrons and promote electron–hole separation to restrain electron–hole recombination [22]. Consecutively, this electron is transferred from Ag to the conduction band of Ti and

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**Fig. 1.** Schematic of continuous photocatalytic reaction. 1-Methylene blue tank; 2-advection pump; 3-O<sub>2</sub> cylinder; 4-gas rotameter; 5-photocatalytic reactor; 6-liquid distributor; 7-nanostructured photocatalysts; 8-glass support plate; 9-fastener; 10-O<sub>2</sub> inlet; 11-product outlet.

captured by oxygen turning into O<sub>2</sub><sup>•-</sup> [23,24], which can oxidize organic molecules.

To overcome the two disadvantages, Ag and N co-doped TiO<sub>2</sub> was prepared to enhance visible light absorption and prolong charge carrier lifetime. In the present work, Ag and N co-doped TiO<sub>2</sub> was prepared by sol-gel method with AgNO<sub>3</sub> as the Ag source and urea as the N source. However, the continuous operation of a nanopowder photocatalyst is difficult in practical applications [25]. Different strategies have been employed to immobilize TiO<sub>2</sub> catalysts on different solid substrates, such as perlite granules [25], expanded graphite [26], and activated carbon [27,28], but wastewater treatment is still batch operated because of the separation of photocatalyst powder and product solution. Meanwhile, the decreased available reaction surface and suppressed product diffusion due to photocatalyst powder stacking reduce the reactive efficiency. In the present study, nanostructured photocatalysts were prepared by depositing Ag and N co-doped TiO<sub>2</sub> onto a stainless steel mesh with a dried colloid. To improve supported capacity and adhesive strength, natural zeolite powder was added to the mixed solution showing favorable combination force with stainless steel. Consequently, the stainless steel mesh loading TiO<sub>2</sub> nanoparticles was used in a continuous photocatalytic reactor to degrade methylene blue. Wastewater was sprayed passing through the stainless steel mesh from top to bottom. This technology can observably improve the quantity of wastewater treatment in unit time and can be easily applied on a large scale.

## 2. Experimental

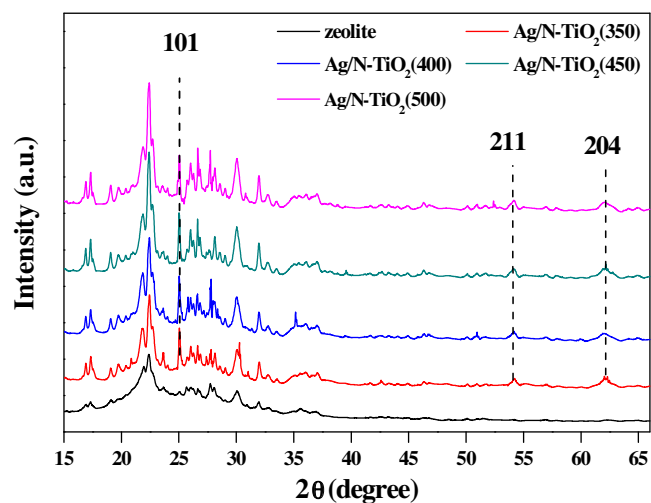
### 2.1. Nanostructured photocatalyst preparation

Nanostructured photocatalysts were prepared using the sol-gel method, with tetrabutyl titanate as the Ti precursor, AgNO<sub>3</sub> as the Ag source, and urea as the N source. All reagents were analytical grade and used without further purification. Natural zeolite minerals from Shangtianti Mine at Xinyang, Henan Province, China were manufactured into powder of 75 μm. Tetrabutyl titanate (10 mL) was dissolved in 12 mL of ethanol with magnetic stirring. HNO<sub>3</sub> was added into the solution to adjust pH and avoid the precipitation of possible byproducts. Then, the solution was left standing for 30 min until it turned pale yellow (marked as solution A). Meanwhile, different ratios of AgNO<sub>3</sub> and urea were dissolved in distilled water (marked as solution B). Solution B was slowly stirred into solution A. Then, 5 g of natural zeolite was added into the solution.

The mixed solution was stirred for 30 min under microwave, and a soliquid was obtained. The structured material used was a 304 stainless steel mesh (50 × 50 mesh, 0.203 mm diameter wire). The stainless steel mesh was cut into certain shapes as substrate and then embedded into the sol. The substrate coated with gelatin was dried at 80 °C for 2 h and then calcined for 2 h at 300 °C, 350 °C, 400 °C, 450 °C and 500 °C, respectively.

### 2.2. Photocatalyst characterization

The as-prepared gels were characterized by thermogravimetric analysis (TGA) with DSC-Q2000 (TA Instruments, USA) in air atmosphere at a flow rate of 100 mL/min and a heating rate of 10 °C/min. The TGA thermograms were employed to determine the calcination temperature at which the organic compound is finally decomposed. The specific surface areas of the photocatalysts were measured by Brunauer-Emmett-Teller analysis (BET, ASAP 2460, Micromeritics, USA) using N<sub>2</sub> adsorption-desorption isotherms at 77 K. X-ray diffraction (XRD, Bruker, λ = 0.15406 nm) was performed on a Philips X'Pro X-ray diffractometer with Cu Kα irradiation (40 kV, 40 mA). The samples were scanned from 5° to 80° under 2θ configuration with a time step of 0.01°/s. X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Fisher, USA)



**Fig. 2.** Powder XRD patterns of samples: (a) TiO<sub>2</sub>, (b) Ag/N-TiO<sub>2</sub> (350), (c) Ag/N-TiO<sub>2</sub> (450), (d) Ag/N-TiO<sub>2</sub> (500), and (e) Ag/N-TiO<sub>2</sub> (550).

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