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High-efficiency and mechano-/photo- bi-catalysis of piezoelectric-ZnO@ photoelectric-TiO_2 core-shell nanofibers for dye decomposition

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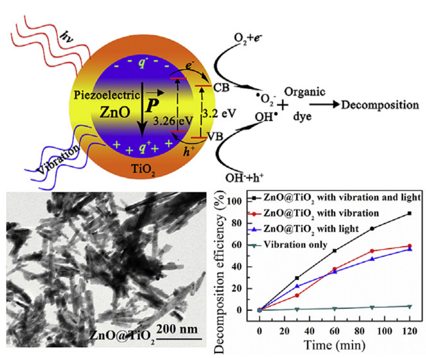
HIGHLIGHTS

- The ZnO@TiO_2 core-shell nanofibers were hydrothermally synthesized.
- A mechano-/photo- bi-catalysis of ZnO@TiO_2 was realized.
- Bi-catalysis is superior to mechano- or photo-catalysis in dye decomposition.
- ZnO@TiO_2 is potential in utilizing mechanical/solar energy to degrade dye.

GRAPHICAL ABSTRACT



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ABSTRACT

A mechano-/photo- bi-catalyst of piezoelectric-ZnO@photoelectric-TiO_2 core-shell nanofibers was hydrothermally synthesized for Methyl Orange (10 mg L^{-1}) decomposition. The mechano-/photo- bi-catalysis in ZnO@TiO_2 is superior to mechano- or photo-catalysis in decomposing Methyl Orange, which is mainly attributed to the synergy effect of the piezoelectric-ZnO core's mechano-catalysis and the thin photoelectric TiO_2 shell's photo-catalysis. The heterostructure of the piezoelectric-ZnO@photoelectric-TiO_2 core-shell interface, being helpful to reduce electron-hole pair recombination and to separate the piezoelectrically-/photoelectric ally- induced electrons and holes, may also make a great contribution to the enhanced catalysis performance. The mechano-/photo-bi-catalysis in ZnO@TiO_2 core-shell nanofibers possesses the advantages of high efficiency, non-toxicity and tractability and is potential in utilizing mechanical/solar energy to deal with dye wastewater.

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1. Introduction

Over than 0.7 million tons of organic synthetic dyes are produced and used every year (Jadhav et al., 2007; Han et al., 2009). Decomposition of dye effluents therefore becomes more and more important (Shu et al., 2004; Rauf and Ashraf., 2009). Currently, methods to decompose dyes, such as traditional physical techniques, biological treatment methods and chemical methods, have been developed. The conventional physical techniques just transfer pollutant from water to another phase, which may cause secondary load of environment (Calindo et al., 2001; Al-Momani et al., 2002). Due to the large degree of aromatics present in dye molecules and the stability of modern dyes, traditional biological treatment methods are ineffective for decolorization and decomposition (Somasiri et al., 2008; Ameen et al., 2012). Among all kinds of chemical methods, photo-catalysis, utilizing clean solar energy to decompose various organic compounds, provides a non-toxic and effective way to treat dye waste water, and is one of the most promising chemical methods (Chen et al., 2016; Zhou et al., 2016). Photo-catalysis, process mainly includes two steps as follows: In step one, generation of electrical-charge carriers under external excitation such as light, electric and thermal signals. In step two, electrical-charge carriers are reacted with water to induce actives such as hydroxyl radicals ($OH^{\bullet}$) and superoxide anions ($^{\bullet}O_2^-$) to decompose dyes (Andreozzi et al., 1999). In the past few years, photo-catalytic titanium dioxide (TiO_2) materials has been widely used for water and air purification because of its high surface activity, absence of toxicity and chemical stability (Chen et al., 2013; Fu et al., 2013; Gao et al., 2014, 2016). How to further enhance the decomposition efficiency is always the key for photo-catalysis application.

It is known to all that, in addition to solar energy, mechanical vibration is also a rich source which could be harvested easily in our living environment. It is possible to realize decomposition of dyes through utilizing mechanical vibration energy. Through applying vibration, piezoelectric or triboelectric materials, having a strong ability to transfer a mechanical signal to an electric signal, can create electron-hole pairs which further react with water to induce actives to decompose organic pollutants in theory, which is first defined by K. Domen as mechano-catalysis (Ikeda et al., 1999). It is potential in application in mechanical-forces-activating chemical reaction, such as splitting water or dye wastewater treatment (Zhang et al., 2013).

Mechano-catalysis on basis of triboelectric effect designed by K. Domen is on the basis of the electric charges induced through mechanical friction force of a stir bar and only exists in few materials (Cu_2O, NiO, Co_3O_4 and Fe_3O_4) (Ikeda et al., 1999). The triboelectric mechano-catalytic efficiency is very low (<4.3%) (Hara et al., 2000), which limits its practical application. The piezoelectric effect with an energy conversion efficiency of >35% (Luo et al., 2007; Feng et al., 2008; Jia et al., 2008), is promising to be used to design a novel mechano-catalysis. It has been reported that lead-based $Pb(Zr_{0.52}Ti_{0.48})O_3$ fibers or multiferroic $BiFeO_3$ nanosheets can mechano-catalytically decompose dye wastewater via piezoelectric effect (Lin et al., 2014; You et al., 2017).

Recently, some lead-free piezoelectric nanofibers, have been widely reported (Jung et al., 2011; Fei et al., 2015; Wang et al., 2015). In 2015, Wang et al. reported $BaTiO_3$ fibers could possess good local piezoelectric response with a piezoelectric coefficient of ~40 p.m./V through using piezoresponse force microscope. Fei et al. reported $BiFeO_3$ Nanofibers exhibit an excellent ferroelectric and piezoelectric property. ZnO nanofibers, one of the most popular piezoelectric nanofiber materials, have been reported to possess an excellent piezoelectric performance with a 3 V voltage and 300 mA current output after being bent through conductive atomic force microscope's probe tip (Wang and Song, 2006). Therefore, ZnO nanofibers can be theoretically used to decompose dyes and has potential application in mechanical-force-activated chemical reactions such as mechanically-splitting water into hydrogen and oxygen gases (Zhang et al., 2013).

In theory, it is possible to design mechano-/photo- bi-catalytic core-shell nanofibers structure of piezoelectric-ZnO@photo-electric-TiO_2 system by combining the photo-catalytic effect of TiO_2 materials and the piezoelectric effect of ZnO to further enhance the dye decomposition efficiency and promote the photo-catalysis application.

In this study, we synthesized ZnO@TiO_2 core-shell nanofibers via a hydrothermal method. The nanofibers are composed of ZnO in the core and thin layers of TiO_2 on the surface. The mechano-/photo-bi-catalysis in ZnO@TiO_2 is superior to mechano- or photo-catalysis in decomposing Methyl Orange. The mechano-/photo-bi-catalysis of ZnO@TiO_2 nanofibers possesses the advantages of high efficiency, non-toxicity and tractability and is potential in utilizing popular vibration energy and solar irradiation energy in nature to deal with dye wastewater.

2. Materials and methods

2.1. Materials preparation

The piezoelectric ZnO nanofibers were synthesized according to a hydrothermal reaction scheme (Li et al., 2008). For the typical procedure, hexamethylenetetramine ($C_6H_{12}N_4$, Sinopharm Chemical Reagent Co., Ltd, > 99.8%) and zinc nitrate hexahydrate ($Zn(NO_3)_2\cdot 6H_2O$, Sinopharm Chemical Reagent Co., Ltd, > 99.9%) precursor solutions were mixed together (1:1 M ratio) by vigorous stirring for ~ 30 min. Then the solution was transferred into a Teflon-lined stainless steel autoclave and heated at 120 °C for 11 h. After that, the white ZnO nanorods were collected from the solution by centrifuge and fully rinsed with deionized water and ethanol. Finally, the ZnO nanofibers were dried in an oven at 60 °C for 24 h.

The ZnO@TiO_2 core-shell nanofibers were synthesized via a hydrothermal reaction scheme. 0.1 g as-prepared ZnO nanofibers and 1 mL tetrabutyl titanate (Sinopharm Chemical Reagent Co., Ltd, > 99.9%) were added into 40 mL anhydrous ethanol. Then the solution were well dispersed by vigorous stirring for about 10 min. After that, 0.5 mL ammonia with a 28% mass concentration (Sinopharm Chemical Reagent Co., Ltd) was added to the solution. Then the obtained solution was sealed with vigorous stirring for 24 h. The products were collected from the solution by centrifuge and fully rinsed with deionized water and ethanol. Finally, the products were dried at 60 °C for 8 h and the final products were obtained after calcination at 500 °C in static air for 2 h with a heating rate of 5 $°C\cdot min^{-1}$.

2.2. Characterization

The X-ray diffraction (XRD) patterns of hydrothermally-synthesized ZnO and ZnO@TiO_2 nanofibers were recorded by Philips PW3040/60 X-ray powder diffractometer (the Netherlands) equipped with a Scintag Pad V diffractometer system and Cu Kα radiation ($\lambda = 1.54178$ Å). The morphological observation was done by employing a Hitachi H-7650 a transmission electron microscope (TEM) (Japan). The measurements of the dye decomposition concentrations were carried out by using Hitachi U-3900 UV–vis spectrophotometer (Japan) at $\lambda_{max} = 484$ nm and a calibration curve.

The mechano-/photo- bi-catalytic decomposition experiments