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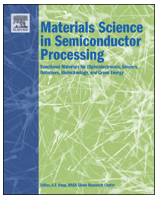

Photocatalytic degradation of organic dye using titanium dioxide modified with metal and non-metal deposition

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ABSTRACT

In this study, photocatalytic degradation of methyl orange (MO) as an example of organic dye was investigated using different wt% Pd-loaded and N-doped P-25 titanium dioxide (TiO_2) nanoparticles, as example of metal and nonmetal-doped TiO_2, respectively. The Pd-loaded and N-doped TiO_2 photocatalysts were prepared by post-incorporation method using K_2PdCl_4 and urea, respectively, as precursors. A variety of surface analysis techniques were used for characterization of surface and functional group while using ultraviolet/visible (UV–vis) analysis for monitoring photocatalytic degradation of MO. Kinetic parameters were obtained using Langmuir-Hinshelwood model to determine the degradation rate constants. It was found that the metal-loaded titanium dioxide degraded MO in water at a higher rate than did non-metal-loaded titanium dioxide fabricated by using the post-synthesis method. Also, the pure P25-TiO_2 degraded MO more than N-doped TiO_2 because of decreased surface area by particle agglomeration after being made by the post-incorporation method.

1. Introduction

Water security is one of the major challenges of the 21st century. In order to conserve water resource from contamination, conventional water treatment technologies such as precipitation, adsorption, filtration, or stripping do not destroy pollutants but rather transfer them from one phase to another [1]. Therefore, advanced oxidation processes (AOPs) or advanced reduction processes (ARPs) combined with those conventional methods are gaining growing attention as effective water treatment processes because they can destroy pollutants and convert them to innocuous compounds [2,3]. Among AOPs, use of heterogeneous semiconductor photocatalysis (SP) is an attractive tool because of its high stability in biological and chemical environment, cost effectiveness, tangible redox potential, and efficient performance [4].

TiO_2 has been widely used in many applications in the energy and environment fields because of its stability, low cost, non-toxicity, feasible surface modification, and non-corrosivity [5–7]. For example, TiO_2 semiconductor has been used for water and air purification [8], hydrogen production through water splitting [9], gas sensors [10], and smart materials [11]. However, its use in practical applications is hindered by its high band gap energy (E_g =3.2 eV) which allows the absorption of light only in the UV range, thus limiting the use of visible light and incurring high cost of operation. Also, the fast recombination of photogenerated electron–hole pairs leads to low quantum efficiency [12,13]. To overcome the limitations, several approaches have been employed including bulk doping or surface modification with organics (polymers, dyes), inorganics (metal, non-metal, semiconductor) [14], or carbon nanotubes materials [15].

Metal and nonmetal-doped TiO_2 have been extensively used to remove a wide range of contaminants in air and water using sunlight [12]. Transition and noble metals are common modifiers enhancing the transfer of charge carriers of photoactive TiO_2 to contaminants [16,17]. Nonmetals such as boron [18], nitrogen [19], fluorine [20], and carbon [21] have also been used to modify TiO_2 in order to enhance its photocatalytic activity in the visible light range, but amongst them nitrogen has been found to be the most favorable dopant due to its stability and atomic size that is comparable to oxygen in TiO_2 [12]. In addition to doping with metals and nonmetals, catalyst synthesis method was found to enhance

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Table 1
Apparent rate constant for metal and non-metal-doped TiO_2

Metal/non-metal-doped TiO_2	Experimental conditions and method	Substrate	Rate constant, degradation time	Ref.
Pd	Sol–gel method for synthesis of TiO_2 nanoparticles Pd/TiO_2 using impregnation method with $PdCl_2$ Molar ratio ($Pd:TiO_2=0.03$) 500 ml of 50 ppm substrate Catalyst used = 0.25 g	Methyl blue	40×10^4 min^{-1}	[23]
Gd	Gd/TiO_2 by sol–gel method using tetra-n-butyl titanate and $Gd(NO_3)_3 \cdot 5H_2O$ Catalyst Concentration = 1 g dm^{-3} Initial concentration of substrate = 1.2×10^{-4} M pH = 6.5	NO_2^-	9.1×10^6 M min^{-1}	[34]
Sm	Sm/TiO_2 by sol–gel method using tetra-n-butyl titanate and $Sm(NO_3)_3 \cdot 5H_2O$ Catalyst Concentration = 1 g dm^{-3} Initial concentration of substrate = 1.2×10^{-4} M pH = 6.5	NO_2^-	2.2×10^6 M min^{-1}	[34]
Ag	Nano-size Ag/TiO_2 by sol–gel method involving a reduction agent. Titanium tetraisopropoxide, silver nitrate as precursors for titania and silver and sodium citrate tribasic dehydrate as a reduction agent Catalyst used = 1 mmol Catalyst concentration = 1 mg/L 500 ml of 50 mg/L substrate Calcination temperature = 300 °C	p-Nitrophenol	2.9×10^{-2} min^{-1}	[35]
V	Cooled water hydrolysis Titanium butoxide and VCl_3 as precursors for titania and vanadium V/Ti ratio = 0.035 Catalyst used = 0.05 g Initial concentration of substrate = 1.3×10^{-5} M	Crystal violet	3.07×10^{-7} M h^{-1}	[36]
Au	Au/TiO_2 using Photoreduction method P25 TiO_2 mixed with tetrachloroauric acid, a gold precursor, and methanol, a hole scavenger Catalyst used = 0.2 g 165 ml of 12 mg/L substrate 0.5% Au–TiO_2 prepared	Methylene blue	0.052 min^{-1}	[24]
Pt	TiO_2 by sol–gel method with $Ti(O–Bu)_4$ as Ti precursor Pt–TiO_2 by photoreduction process using hexachloroplatinic acid as a Pt precursor Catalyst used = 0.2 g 0.75% Pt/TiO_2 photocatalyst 165 ml of 15 mg/L MB and 165 ml of 20 mg/L MO	MB and MO	0.1042 min^{-1} for MB 0.0988 min^{-1} for MO	[37]
Zn	TiO_2 nanotube using hydrothermal chemical process with TiO_2 anatase powder. Zinc acetylacetonate as a Zn precursor. Zn–TiO_2 by mixing TiO_2 and Zn precursor with stirring for 6 h. Calcined at 400 °C for 1 h Catalyst used = 0.2 g 100 ml of 20 mg/L substrate	MO	Degraded 65% MO in 3 h	[38]
N	Oxidation of TiN at 450 °C for 2 h in air Nanoparticle catalyst used = 0.20 g Substrate concentration = 150 mg/m^3	Toluene	10.5×10^3 min^{-1}	[29]
N	Incipient wet impregnation method TiO_2 Degussa P25 mixed with urea Calcined at 773 K for 3 h Catalyst used = 0.2 g/100 ml 600 ml of 1.0×10^{-2} M substrate pH = 5.9 0.50% N–TiO_2	4-Nitrophenol	18.388×10^3 min^{-1}	[25]
N	TiO_2 nanotube using hydrothermal process with TiO_2 rutile powder Guanidine carbonate as N precursor N–TiO_2 by mixing TiO_2 and n precursor with stirring for 24 h Calcined at 350°C for 1 h	Methylene blue	Degrade 95.1% in 7 h under artificial solar light	[32]