

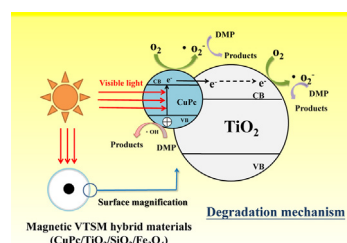
## Magnetic photocatalysts of copper phthalocyanine-sensitized titania for the photodegradation of dimethyl phthalate under visible light



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### GRAPHICAL ABSTRACT



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### ABSTRACT

In this study, magnetic hybrid photocatalysts (copper phthalocyanine/anatase/silica/magnetite, CuPc/TSM, VTSM) were synthesized, characterized, and applied to degrade the plasticizer dimethyl phthalate (DMP) under xenon-lamp irradiation. The characteristics of the VTSM hybrid materials were characterized using TEM, absorption of radiation, PL spectra, XRD, and SQUID techniques. The influence of the coating dosage of CuPc on the physicochemical characteristics of TSM composites and the photocatalytic activity of DMP was investigated along with the reusability of the VTSM hybrid materials. The best of CuPc coating dosage (1.92 wt% VTSM) was confirmed based on the PL spectra and the photocatalytic activity of DMP. An appropriate coating thickness of CuPc was proven to minimize the inhibition of exciton–exciton annihilation and to promote electron injection into the semiconductor. The degradation efficiencies of DMP by the 1.92 wt% VTSM hybrid photocatalyst for first, sixth and tenth runs were 42.4, 41.7 and 40.6%/g, respectively. The results led to the conclusions that easily controllable VTSM hybrid photocatalysts exhibited good and stable photocatalytic activity toward the degradation of DMP over ten runs and that the use of the magnetic hybrid photocatalysts for the treatment of water contaminants would result in diminished environmental impacts.

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### 1. Introduction

TiO<sub>2</sub>-type semiconductor photocatalysts have attracted considerable attention because of their good physicochemical stability and their ability to catalyze the effective elimination of organic refractory contaminants from the aquatic environment [1–5]. To effectively utilize the main part of the solar spectrum, TiO<sub>2</sub>-type

photocatalysts have been further modified to possess visible-light activity through doping with transition metals and anionic species into crystals [6], coating photosensitizers of organic dyes onto the surface [7], and the coupling of TiO<sub>2</sub>-type semiconductors with other semiconductors [8,9]. Compared with the developed methods to extend the absorption spectra of TiO<sub>2</sub>, the anchoring of photosensitizers is an effective and feasible method to prepare visible-light-active photocatalysts. Photosensitizers of porphyrins and phthalocyanines have been successfully used as photodynamic therapy agents for tumors [10,11], and the latter were reported to be more practical, more stable and more resistant to chemical degradation under irradiation [12]. Furthermore, photosensitized

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degradation efficiencies of organics by metallophthalocyanine were more effective than those by pure dye sensitizers because of greater production of  $^1\text{O}_2$  or  $^{\bullet}\text{O}_2^-$  [13], where the formation of  $^1\text{O}_2$  was reported to be the dominant step in the initial photooxidation of environmental pollutants [14]. Even though the effective absorption of visible-light irradiation by  $\text{TiO}_2$  can be improved by coating  $\text{TiO}_2$  with metallophthalocyanine, a major drawback of the system was the difficulty in achieving solid–liquid separation of the photocatalysts in the slurry photocatalytic system.

To overcome the separation problem, magnetic photocatalysts with easily, effectively and magnetically controllable characteristics have been developed and have proven to exhibit valuable advantages in environmental applications. Core–shell-type magnetic materials have been commonly used as photocatalysts; these catalysts typically consist of a ferromagnetic core, an active layer of  $\text{TiO}_2$  and a passive film between the ferromagnetic core and the active layer. The passive film is necessary to prevent the unfavorable electron–hole recombination between the magnetic core and  $\text{TiO}_2$  shell [15–17], and to effectively inhibit sintering during heat treatment [18]. Such kinds of magnetically separable photocatalysts have been proven to effectively degrade organic compounds in aqueous solutions. To effectively use the solar spectrum, magnetic photocatalysts, that are active under visible light, such as magnetic samarium-doped [19] and cerium-doped mesoporous titania [20], magnetic iodine-doped  $\text{TiO}_2$  [21], and titania-coated magnetic activated carbon [22], have been prepared. Nevertheless, few studies related to the synthesis of magnetic photocatalysts, which are associated with photosensitizers, have been reported. Because of the advantages Cu-phthalocyanine (CuPc), which includes its low cost, its ability to collect up to 50% of the solar spectrum, and its extreme resistance to chemical degradation, this metallophthalocyanine has strong potential as a photosensitizer to allow the preparation of magnetic visible-light-active photocatalysts for environmental applications.

Dimethyl phthalate (DMP) is an endocrine-disrupting chemical and is almost ubiquitous in the environment, present in sediments, fresh water, and marine water, because of its chemical stability [23,24]. Furthermore, because of its refractory biodegradable properties, it poses a strong threat to the aquatic environment. Therefore, the effective and economical elimination of DMP from aqueous solution is currently an important environmental issue. Because of the lack of previous reports on the preparation of magnetic photocatalysts of metallophthalocyanine-sensitized titania, we here present experimental results for the physicochemical properties of magnetic visible-light-active photocatalysts (copper phthalocyanine/anatase/silica/magnetite, CuPc/TSM, VTSM) prepared with various CuPc loadings under mild conditions and evaluate the photocatalytic activity and reusability of the resulting photocatalysts under xenon-lamp irradiation using DMP as a model compound.

## 2. Materials and methods

### 2.1. Preparation of magnetically visible-light-active photocatalysts

The synthesis of magnetic visible-light-active photocatalysts (VTSM) was conducted in four sequential steps. First, magnetite ( $\text{Fe}_3\text{O}_4$ ) was prepared as a magnetic core via chemical precipitation. Second, a silica film was further coated onto the magnetite to compose a magnetic carrier ( $\text{SiO}_2/\text{Fe}_3\text{O}_4$ ) via the sol–gel route. The third step was to coat the active layer of  $\text{TiO}_2$  onto the magnetic carrier via the sol–gel route to obtain the TSM ( $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ ) composites. The last step involved the impregnation of the TSM composite in a solvent that contained CuPc and the subsequent evaporation of the suspension to obtain VTSM.

The details of the chemicals and procedures used for synthesis of TSM have been described elsewhere [17]; in this study, the water-to-titanium ratio was fixed at 130 in the admixture used in the sol–gel route to produce the  $\text{TiO}_2$  layer. The details of the synthesis of VTSM after complete preparation of the TSM composites are as follows. The suspension was prepared by mixing 5 g of TSM with 150 mL of absolute alcohol; the resulting solution was subsequently transferred to a 1-L round-bottom flask with a long extension neck. The flask was rotated at 100 rpm for 45 min under atmospheric pressure and at a constant temperature of 318.15 K using a Büchi Rotavapor (R-210, Büchi Labortechnik AG, Flawil, Switzerland). Solution A was prepared by dissolving the desired amount of CuPc (copper phthalocyanine,  $\text{C}_{32}\text{H}_{16}\text{CuN}_8$ , 95% purity, reagent grade, Acros Organics BVBA, Geel, Belgium) in 150 mL of absolute alcohol. The amount of CuPc used was adjusted to obtain a weight ratio of CuPc to TSM in the range of 0–3.45 wt%. After the ultrasonic treatment of Solution A for 30 min, a transparent blue solution was obtained, which was then slowly added to the 1-L flask that contained TSM. After being rotated at 100 rpm for 24 h at a temperature of 298.15 K, the solvent in the flask was removed via a drying procedure performed at 358.15 K in the rotary evaporator. The VTSM photocatalysts were recovered and then washed several times with double-distilled water to remove the byproducts and unreacted starting materials. The separation of the magnetic particles from aqueous solution in the heterogeneous system was performed with a simple magnet. After the washing procedure, the magnetic particles were dried overnight at a temperature of 373.15 K.

### 2.2. Characterization of physicochemical properties

Transmission electron microscopy (TEM, JEM 1400, JEOL, Tokyo, Japan) was used to gain an insight into the microstructures of various magnetic particles. The UV absorption was measured with a UV–vis–NIR spectrometer (V-630, Jasco). For the photoluminescence (PL) measurements, a DPSS 488 nm laser that emitted at 20 mW was used as the emission source with a high-resolution confocal Raman microscope (Lab RAM HR, Horoba) with a wavelength detection range of 500–900 nm. The saturation magnetism of the photocatalysts was measured using a superconducting quantum interference device (SQUID) magnetometer (model MPMS7, Quantum Design, San Diego, CA, USA). The crystal structure of the particles was characterized using a powder X-ray diffraction (XRD) analyzer (Philips X'Pert Pro MPD, Philips, The Netherlands), equipped with a Cu  $K\alpha$  radiation source ( $\lambda = 1.5418 \text{ \AA}$ ); XRD patterns were compared to those in the Joint Committee on Powder Diffraction Standards (JCPDS) database. The UV–vis irradiation intensity of the lamp (H3-12V 55W, Osram, Taiwan) was measured using a diffraction-grating spectrometer (model EPP 2000, StellarNet, Oldsmar, FL, USA).

### 2.3. Photocatalytic activity

The batch-type annular photocatalytic reactor was constructed from Pyrex glass with a diameter and height of 3.6 and 29 cm, respectively; a 55 W xenon blue halogen bulb was placed at the center of the inner quartz jacket. The irradiation intensity of the xenon lamp under various conditions was measured using a diffraction-grating spectrometer. Various initial concentrations of DMP in the range of 0–103 mg/L were prepared to compare the degradation efficiencies of DMP using various VTSM composites. The flow rate of oxygen ( $F_{\text{O}_2}$ ) was fixed at 500 mL/min with a mass flow controller (MFC, model 5850E, Brooks, Hatfield, PA, USA). Prior to illumination with the xenon lamp, the adsorption of DMP on VTSM composites was measured in the dark for a contact time of 30 min. The concentration of DMP was determined using a HPLC analyzer equipped

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