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Fast photocatalytic degradation of bisphenol A by Ag_3PO_4/TiO_2 composites under solar radiation

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ABSTRACT

In this work, the photocatalytic degradation of bisphenol A (BPA) was investigated. Silver orthophosphate (Ag_3PO_4) and its composites with P25 TiO_2 (Ag_3PO_4/TiO_2) at various molar ratios were prepared and used as the photocatalyst, while radiation was provided by a solar simulator. The physicochemical and optical properties of the synthesized samples were investigated employing the BET method, X-ray diffraction (XRD), UV–vis diffuse reflectance spectroscopy (DRS) and scanning electron microscopy (SEM/EDS). High performance liquid chromatography (HPLC) was employed to monitor changes in BPA concentration.

Pure Ag_3PO_4 and its composites with TiO_2 were found to be highly responsive in the visible spectral region owing to the narrow band gap of silver orthophosphate (2.33 eV). Optimal photocatalytic performance for the title reaction was observed for the Ag_3PO_4/TiO_2 photocatalyst with a molar ratio 75:25. This material resulted in complete degradation of 220 μg/L BPA in pure water with an apparent rate constant of 0.91 min^{-1}, which was much higher than that obtained with pure Ag_3PO_4 (0.43 min^{-1}) or P25 TiO_2 (0.27 min^{-1}). Reaction rates were found to increase with increasing catalyst concentration in the range 50–500 mg/L and decreasing BPA concentration in the range 2200–440 μg/L. The rate was affected negatively by the water matrix in the order pure water > drinking water > wastewater. However, spiking pure water with bicarbonate or humic acid had no measurable effect on BPA degradation.

The catalysts partially lost their activity upon repeated use for 5 consecutive runs, *i.e.* the rate decreased by 80% and 65% for Ag_3PO_4 and Ag_3PO_4/TiO_2, respectively, due to irreversible reduction of silver orthophosphate by photogenerated electrons.

1. Introduction

Heterogeneous photocatalysis induced by sunlight can offer a green technology for the decontamination of water from organic micro-pollutants. TiO_2 is undoubtedly the most popular and extensively investigated photocatalyst due to its relatively high activity, low cost, elevated chemical and photochemical stability and availability. Nonetheless, TiO_2 photocatalysis suffers a serious drawback that may restrict its use in large-scale applications, namely its wide bandgap energy (3.0–3.2 eV) which overlaps only in the UV region of the electromagnetic spectrum [1]. Two strategies can be adopted to achieve catalysts that would be responsive in the visible: (i) to reduce the wide bandgap of *e.g.* TiO_2 through doping, and (ii) search for new semiconductors capable of absorbing visible light [1,2].

In their pioneering work published in 2010 [3], Yi et al. discussed the enhanced photooxidative activity of Ag_3PO_4 for water splitting and the photodegradation of methylene blue under visible light reporting rates several times greater than those of $BiVO_4$, WO_3 and $TiO_{2-x}N_x$ catalysts. More importantly, this novel photocatalyst could achieve a quantum efficiency of up to 90% at wavelengths in the range of 400–480 nm, thus implying a very low electron-hole recombination rate. This can be ascribed to (i) a large dispersion of the conduction band, which facilitates the separation of charge carriers, (ii) the high concentrations of silver vacancies in the catalyst lattice, and (iii) the role of the phosphate anion, which possesses a large electron cloud, to attract holes and repel electrons [1,2].

A drawback associated with the use of silver orthophosphate as photocatalyst is its insufficient long-term stability since it is photochemically decomposed in the absence of a sacrificial agent [1]. This can be overcome by covering the surface of Ag_3PO_4 with metallic silver nanoparticles which create localized surface plasmon resonance effects [4], thus hindering the reducibility of silver ion in the catalyst lattice. Another strategy to improve catalyst activity and

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stability is the synthesis of Ag_3PO_4/TiO_2 composites [5–8], where improved performance is attributed to the more efficient charge separation and the higher specific surface area of the composite, compared to pristine Ag_3PO_4.

Notably, the photocatalytic testing of Ag_3PO_4 and Ag_3PO_4-based catalysts has nearly exclusively been performed with organic dyes as the probe molecules [5–7,9–11], while some studies have evaluated the bactericidal ability of the catalysts [7,9,10]. Persistent micro-pollutants, such as endocrine disruptors (ED), have gained considerable attention in recent years as priority pollutants due to their continuous release in the water cycle and their suspected adverse effects on living organisms. Bisphenol A (BPA) has been widely used as raw material in the manufacturing of numerous chemical products, such as polycarbonate plastics and epoxy resins. Due to its wide usage and its estrogenic effects, BPA can be regarded as a representative compound, among various endocrine disruptors, which are responsible for reproductive damages to aquatic organisms [12].

To the best of our knowledge, this is the first report on the use of Ag_3PO_4/TiO_2 composites for the degradation of emerging micro-pollutants under solar radiation. Several composites were prepared and characterized and their activity was appraised for the degradation of BPA. Emphasis was given on the effect of various operating conditions (BPA and catalyst concentration, water matrix) on degradation kinetics. Moreover, photocatalyst stability upon repeated use was assessed following kinetics and characterizing the material before and after its use.

2. Materials and methods

2.1. Materials

BPA ($C_{15}H_{16}O_2$, CAS number 80-05-7) was purchased from Sigma-Aldrich and used as received. Evonik P25 titania (TiO_2, CAS number 13463-67-7), silver nitrate ($AgNO_3$, CAS number 7761-88-8) and monosodium phosphate (NaH_2PO_4, CAS number 7558-80-7), used for catalyst synthesis, were purchased from Sigma-Aldrich.

Most of the experiments were carried out in ultrapure water (UPW, pH = 6) taken from a water purification system (EASYpure RF-Barnstead/Thermolyne, USA). Commercially available bottled water (pH = 7.5, 0.4 mS/cm conductivity containing 211 mg/L bicarbonate, 10 mg/L chloride, 15 mg/L sulfate, 5 mg/L nitrate and 78 mg/L of various metal ions) was employed for experiments in drinking water (DW) matrix. Humic acid (CAS number 1415-93-6) and bicarbonate (CAS no: 144-55-8) added in UPW were purchased from Sigma-Aldrich. Secondary treated wastewater (WW) was taken from the university campus treatment plant (pH = 8, COD = 21 mg/L).

2.2. Catalyst preparation

Ag_3PO_4/TiO_2 composites were synthesized employing a simple method described in detail elsewhere [5]. In brief, an appropriate amount of P25 TiO_2 (*e.g.*, 1.60 g for the sample containing 75% TiO_2) was dispersed in 50 mL distilled water and sonicated for 15 min. After sonication, 3.06 g of $AgNO_3$ were added and the solution was left under stirring for 15 min. Then, 1.91 g of NaH_2PO_4 dissolved in 50 mL distilled water, were dropwise added into the solution, which was stirred for 240 min at room temperature. The as prepared Ag_3PO_4/TiO_2 composites were filtered off, washed with water and ethanol and dried in an oven at 60 °C for 12 h. Pure Ag_3PO_4 was prepared using the same method but in the absence of TiO_2.

Composites with different molar ratios of Ag_3PO_4 to TiO_2 were prepared by varying the amount of P25 TiO_2 in the starting solution, while keeping constant the content of Ag_3PO_4. The photocatalysts thus prepared are denoted in the following as $Ag_3PO_4/TiO_2(x{:}y)$, where $x{:}y$ is the molar ratio of Ag_3PO_4 to TiO_2.

2.3. Catalyst characterization

2.3.1. Specific surface area

The specific surface area (SSA) of the synthesized samples was determined according to the Brunauer-Emmett-Teler (BET) method with the use of a Micromeritics (Gemini III 2375) instrument, employing nitrogen physisorption at the temperature of liquid nitrogen (−196 °C). Prior to each measurement, the sample was outgased under dynamic vacuum for 2 h.

2.3.2. X-ray diffraction (XRD) measurements

The X-ray diffraction (XRD) patterns of the photocatalyst powders were obtained using a Philips P (PW 1830/40) instrument employing Cu K_a source (λ = 1.5406 Å) operated at 40 kV and 40 mA. Data were collected in the 2θ range of 15°–80°. Phase identification was based on JCPDS cards.

The primary crystallite size of nanocrystals was estimated by means of the Scherrer's formula [13]:

$$d = \frac{0.9\lambda}{B\cos\theta} \tag{1}$$

where λ is the X-ray wavelength corresponding to Cu K_a radiation (0.15406 nm), θ is the diffraction angle and B is the line broadening (in radians) at half of its maximum.

2.3.3. Diffuse reflectance spectroscopy (DRS)

The diffuse reflectance spectra were recorded on a UV–vis spectrophotometer (Varian Cary 3) equipped with an integration sphere, using $BaSO_4$ as a reference. The catalyst powder was loaded into a quartz cell and spectra were obtained at room temperature in the wavelength range of 200–800 nm. The DR measurements were converted into the equivalent absorption coefficient by applying the transformation based on the Kubelka-Munk function:

$$F(R_\infty) = \frac{K(\lambda)}{S(\lambda)} = \frac{(1-R_\infty)^2}{2R_\infty} \tag{2}$$

where K and S are the absorption and scattering coefficients, respectively, and $R_\infty = R/R_{\mathrm{ref}}$ is the reflectance. The optical band gap of the semiconductor was evaluated based on the following expression [14]:

$$(\alpha h\nu)^{1/n} = B(h\nu - E_{bg}) \tag{3}$$

where a is the absorption coefficient, $h\nu$ is the incident photon energy, E_{bg} is the band gap energy, B is a constant related to the effective masses of charge carriers associated with valance and conduction bands, and n is a factor that depends on the kind of optical transition induced by photon absorption ($n = 1/2$ for direct transition and $n = 2$ for indirect transition). Band gap energy (absorption threshold) was estimated assuming that $F(R)$ values are proportional to the optical absorption coefficients. Thus, the values of E_{bg} were obtained from the plot of $[F(R)h\nu]^{1/\mathrm{n}}$ *vs.* $h\nu$ (Tauc plot) in the region of high absorption and the extrapolation of the linear region to the horizontal axis, at zero $F(R)$ [15,16].

2.3.4. Scanning electron microscopy

Scanning electron microscopy (SEM) images were obtained by using a JEOL 6300 scanning electron microscope equipped with an Energy Dispersive Spectrometer (EDS) for the determination of the chemical composition and element distribution of the samples.

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