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Solar degradation of contaminants in water: TiO_2 solar photocatalysis assisted by up-conversion luminescent materials

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ABSTRACT

Solar energy, along with other renewable resources, could potentially solve environmental problems, as demonstrated by recent developments in the use of solar energy, such as solar photocatalysis. Solar photocatalytic technology has been demonstrated to be effective for treating groundwater, drinking water, wastewater and air and soil pollution. In this study, a solar photocatalytic application for wastewater decontamination is presented. Luminescent material has been evaluated as up-conversion material for enhancing the photocatalytic activity. Wastewater decontamination by heterogeneous photocatalysis has been developed in a slurry photo-reactor, using TiO_2 as a photocatalyst. The photoactivity of TiO_2 under several sun irradiation conditions was investigated. The up-conversion luminescence agent ZBLAN, a rare-earth (Yb-Er-Tm) co-doped fluoride glass (ZrF_4– BaF_2–LaF_3–AlF_3–NaF), was incorporated to enhance the solar-driven activity of TiO_2 because this material could transform the unused near-infrared sunlight tail into UV–vis radiation available for photoreaction activation. The use of ZBLAN has demonstrated an improvement over ordinary titanium dioxide photocatalytic activity under sunlight irradiation for the photocatalytic degradation of pollutants in wastewater. Our results demonstrating the contribution of up-conversion luminescence to the improved photoactivity of titanium dioxide suggest that it can be used to develop new technologies for treating wastewater using solar light.

1. Introduction

Advanced oxidation processes (AOPs) are new technologies that are useful for removing contaminants present in both aqueous and gaseous effluents. One of these technologies is Heterogeneous Photocatalysis, which is the degradation of organic pollutants in wastewater or in contaminated air by means of a photocatalytic reaction promoted by the action of light on the surface of a semiconductor acting as a photocatalyst.

In recent years, photocatalysis research has focused on the use of semiconductor materials as photocatalysts for the removal of organic and inorganic species from aqueous or gas-phase systems in environmental clean-up, drinking water treatment, and industrial wastewater treatment. Its inertness to chemical environments and its long-term photostability make titanium dioxide (TiO_2) a useful material in many such practical applications.

TiO_2 has been extensively studied as a photocatalyst, and it has been demonstrated to be a leading semiconductor material with photocatalytic activity for the removal of environmental pollutants [1–4]. TiO_2 has been widely used as photocatalyst for environmental decontamination due to its strong oxidizing power under ultraviolet irradiation, high chemical stability, low cost, and environmental friendliness [5–11]. Additionally, TiO_2 has been regarded as a promising candidate to support the future hydrogen economy [12].

TiO_2 requires photo-excitation with light at wavelengths exceeding the band gap of the active anatase phase (3.2 eV), that is, light at wavelengths lower than 387 nm, which is in the UV range. However, the UV range in sunlight represents only 5–8% of the solar spectrum at sea level, and only a small fraction of sunlight can be used because TiO_2 as a photocatalyst absorbs only the UV spectral range [13], which limits the use of natural sunlight. This limitation results in the requirement for artificial illumination of the catalysts to degrade pollutants for water treatment or air cleaning. This limitation restricts the application of the technology to areas where abundant electricity supplies are available for artificial light implementation. Addressing the need for more

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sustainable technologies using photocatalysts that can be activated by natural sunlight is the goal of this and other research.

To significantly improve photocatalytic activity using visible light, the photocatalytic efficiency of TiO_2 has been increased using different strategies, all of which enhance photon absorption. For the purpose of extending its photocatalytic light absorption range, different methods were used, such as doping TiO_2 with heteroatoms or coupling of TiO_2 with other semiconductors with low band gaps [14–16]. In spite of the extensive efforts to dope TiO_2 with C, N, S and transition metal ions such as Ag, Au, Fe, Ru, the photocatalytic activity of TiO_2 in the visible region has remained quite low, an issue that has been addressed in recent articles that have highlighted the issues and challenges associated with the application of photocatalysis [17].

An alternative approach is the up-conversion process, which is the phenomenon whereby some materials emit light that has higher photon energy than the light source. This process is of considerable interest for photocatalytic processes because these materials can produce ultraviolet light from infrared light sources.

Up-conversion photonic processes convert photons from the near infrared range into the UV–visible range through multi-photon and energy transfer mechanisms. Materials such as rare-earth (RE) doped materials, which present efficient up-conversion luminescence, appear as one of the most promising candidates to assist the long-wavelength light harvesting of solar irradiation [18–20]. In fact, this up-conversion photonic approach has already been extensively developed to increase the efficiency of photovoltaic solar cells [21] by shifting the spectrum of solar irradiation and also to increase agricultural production by improving the sunlight conversion efficiency of the photosynthetic process. These up-conversion luminescent materials, which transform unused red and near-infrared (NIR) sunlight into available UV–vis radiation, could increase the photocatalytic activity of semiconductor materials acting as photocatalysts. Transforming the incoming infrared light into blue radiation provides extra photons for absorption by the band-gap of the photocatalytic materials used in advanced oxidation processes for water/air decontamination. Optimizing not only the photocatalyst but also the incident radiation can lead to an endless range of technological possibilities.

In this paper, we present a suitable candidate for highly efficient UV–vis up-conversion emissions: a RE co-doped (Yb-Er-Tm) fluoride glass (ZrF_4– BaF_2–LaF_3–AlF_3–NaF) (ZBLAN) under near-infrared excitation at 980 nm to enhance solar-driven activity of an efficient commercial photocatalyst such as TiO_2.

Several TiO_2 photocatalytic studies using artificial light have been reported in the literature [22–27], but little research has been performed using natural sunlight, which is a source of energy that represents the most economic and sustainable alternative for treating wastewater effluents or air decontamination by photocatalysis.

The aim of this work is to evaluate the performance of TiO_2 as a photocatalyst for wastewater decontamination using sunlight. Additionally, RE-doped ZBLAN was incorporated in the reaction process scheme to enhance the solar-driven photocatalytic activity of TiO_2 because RE-doped ZBLAN crystals could transform the unused red and near-infrared sunlight tail into available UV–vis radiation and increase the activity of the photocatalyst. The photocatalytic activity of TiO_2 under sunlight and the effect of the addition of RE-doped ZBLAN to the photoreactor were investigated under different solar radiation conditions.

2. Experimental section

The photocatalytic activity of TiO_2 (Degussa P25) under sunlight was evaluated using Methylene Blue (MB) as a wastewater pollutant molecule model. TiO_2 Degussa P25 is a commercial photocatalyst with high photocatalytic activity and is a mixture of anatase and rutile (80:20). ZBLAN crystals used in this study were synthesized with the following composition (in molar percentage): 51.7 ZrF_4-20.7 BaF_2-4.5 LaF_3-3.4 AlF_3-19.7 NaF. ZBLAN crystals were doped with rare earth (RE) constituting RE doped ZBLAN crystals where LaF_3 was completely substituted by YbF_3, ErF_3 and TmF_3 to obtain Yb^{3+}-Er^{3+}-Tm^{3+} co-doped ZBLAN with 3.5 mol% Yb^{3+}, 0.5 mol% Er^{3+} and 0.5 mol% Tm^{3+}. The glass was prepared as reported in detail in a previous paper [28].

The photocatalytic oxidation of the pollutant in wastewater was carried out using both artificial UV/visible light and natural sunlight. Photo-oxidation experiments under artificial light were carried out in the laboratory, using a visible Xe-lamp (Hamamatsu L2274, 150W) and a UV Hg-lamp (Heraeus TQ-150, 150W). The reaction was performed in a cylindrical quartz Heraeus UV reactor system (250 mL). Photocatalyst particles and ZBLAN crystals inside the reactor were dispersed in wastewater by magnetic stirring forming a slurry-type photo-reactor with UV and visible lamps positioned coaxially inside the reaction vessel; the reaction temperature was kept constant at 20 °C.

Experiments under sunlight were conducted in stirred photoreactors (50 mL) with parabolic sunlight irradiation concentrators to collect direct and diffuse solar radiation. Quartz reactors were used to maximize the incident radiation intensity. The concentration factor for experiments developed under solar irradiation was 1.5. This factor was calculated as the ratio of the aperture area of the reflector to the area of the receiver. This quantity approximates the factor by which the radiative flux density (W/m^2) is increased in the surface of the receiver, compared to the incoming solar radiation. The concentration ratio is commonly expressed as a number of “suns”; for instance, our collector that increased the radiative flux density 1.5 times is said to have a concentration ratio of 1.5 suns. The photocatalytic reactions took place in open spaces where it was possible to completely gather the solar radiation. Two Atmospheric Research Centres were used for these locations: IARC (Institute of Atmosferic Reasearch Center) and IAO (Izaña Atmosferic Observatory), which are at 52 and 2367 m above sea level, respectively. These locations allowed for exact measures of the solar irradiation during the photocatalytic experiments. The intensity of solar radiation was measured using a Kipp & Zonen CMP-21 pyranometer. The study of the photo-degradation of the pollutant was executed on sunny days, from March to May between sunrise and sunset with solar zenith angles (SZA) in the 67–40° and 43–14° range.

Reaction variables were maintained constant in both reaction systems: wastewater (50 mg L^{-1} of MB as pollutant model molecule) and photocatalyst (TiO_2 Degussa 0.5 g L^{-1}) were introduced into the reactor and continuously stirred and aerated to provide oxygen. RE-doped ZBLAN (0.26 g L^{-1}) was added when studies of the up-conversion phenomenon were performed. Aliquots of wastewater were taken during the photoreaction to evaluate the photocatalytic activity for the decontamination process. The MB concentration in wastewater was determined using a UV–vis spectrophotometer (Varian Model Cary 50) at the maximum wavelength peak (λ=663 nm). The optical absorption spectrum of RE-doped ZBLAN was measured by an ultraviolet-visible-infrared spectrophotometer (Perkin-Elmer Lambda 9) with a resolution of 0.5 nm.

3. Results and discussion

The use of heterogeneous solar photocatalysis for wastewater treatment is gaining interest. In fact, the use of solar energy in the treatment of urban and industrial effluents could be an effective,