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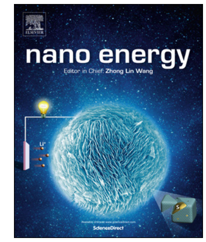

RAPID COMMUNICATION

Rice-straw-derived hybrid TiO_2-SiO_2 structures with enhanced photocatalytic properties for removal of hazardous dye in aqueous solutions

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Abstract
Rice straw, an agricultural bioresource, is utilized as a biotemplate in order to synthesize a hybrid TiO_2-SiO_2 structure, and the resulting products were used for removing hazardous methylene blue dye from aqueous solutions. Samples of the as-prepared hybrid TiO_2-SiO_2 structure are characterized by thermal gravity analysis, field emission scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, nitrogen gas adsorption/desorption measurement, and UV/vis spectroscopy. The results obtained show that the hybrid TiO_2-SiO_2 structure possesses both anatase and rutile phases, along with amorphous SiO_2. Its specific surface area is determined to be 141.1 m^2/g, and its pore size to be 3.77 nm. Light harvesting within the visible-light range is found to be enhanced by the use of this hybrid TiO_2-SiO_2 structure. Moreover, the photocatalytic activity and stability are also improved, as demonstrated by the degradation of methylene blue dye under UV irradiation.

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Introduction

Bioresource technology plays a vital role in the sustainable development of human society [1]. Biological materials derived from living organisms are defined as biomass. It represents a renewable resource for nearly half of the world's population [2]. Conventional methods for utilizing biomass consist mostly of combustion to generate heat, which although widespread in developing countries, is harmful to the global environment. Thus, new methods should be developed for utilizing biomass, leading to lesser environmental pollution.

In recent years, titanium dioxide (TiO_2) has been widely studied as a photocatalyst for water purification [3] and as a catalyst for photo-electrochemical water splitting [4]. It has also been used in pigments and semiconductors for dye-sensitized solar cells [5]. However, its relatively large band gap (3.2 eV; pure anatase crystalline) allows it to also absorb ultraviolet (UV) radiation with wavelengths of less than 387.5 nm, which represents 5% of the total solar irradiation on the surface of the Earth.

Most researchers have previously focused on improving the light harvesting and photocatalytic efficiency of TiO_2 within the visible light wavelength. One method developed is the synthesis of TiO_2 with unique mesoporous, rod, fibrous, and hollow nanostructures [6]. Recently, particular attention has been given to hollow structures, which can increase the photocatalytic activity of TiO_2 not just by creating a uniform pore-wall system with a high surface area, but also by optimizing mass transport and reducing the degradation time [7,8]. Another method of enhancing photocatalytic activity is the use of metal dopants such as Ag, Au, and Fe, or using nonmetallic elements such as N, C, and S [9]. These doping methods can be used to control the band-gap energy, or reduce the electron-hole recombination, thereby increasing the photocatalytic activity. Moreover, hybrid metal oxide photocatalytic systems such as TiO_2/SiO_2, TiO_2/Al_2O_3, and TiO_2/SnO_2 have been shown to exhibit good properties in terms of their light-harvesting ability [10].

Among the various bioresources available, the rice plant (*Oryza sativa* L.) is widely used as a food resource throughout Asia, Africa, and North and South America, with approximately 1/3 of the global population depending on the rice grain as a source of food [11]. Rice straw (RS) is the by-product of rice milling and represents a major agricultural waste, with some 620 million ton of RS produced per year in Asia alone. This unwanted RS is often simply burned by the farmer, significantly contributing to global warming [12]. Dry RS typically contains about 15% hydrated silica, depending on the geographic location [13], and its biological structure comprises tightly packed silica that increases its photocatalytic activity. Thus, this study investigates the synthesis of a hybrid TiO_2-SiO_2 structure using RS, with the intent to find a new means of recycling bioresources such as RS. In addition, the photocatalytic properties of such a structure can make a beneficial contribution to environmental protection worldwide.

RS is proposed as a non-metallic precursor for TiO_2 synthesis owing to its silicon content, which is expected to be converted to SiO_2 during calcination to produce a hybrid TiO_2-SiO_2 structure. The photocatalytic activity of TiO_2 is known to be improved by the addition of SiO_2, whose hydrophilic properties increase the available surface area of the catalyst and increase the adsorption of pollutant molecules. This improved adsorption on the surface of silica in turn improves the photocatalytic activity of a TiO_2-SiO_2 structure when compared to pure TiO_2 [14-16]. The as-prepared hybrid TiO_2-SiO_2 structure samples were characterized by thermal gravity analysis, field emission scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, nitrogen gas adsorption/desorption measurement, and UV/Vis spectroscopy. The synthesized hybrid TiO_2-SiO_2 structure was then subsequently applied to a photocatalytic reaction for methylene blue decomposition. This work therefore represents a combination of bioresource engineering and applied chemistry, serving to develop a novel method to protect the natural environment by utilizing a readily available biomass.

Experimental

Preparation of hybrid TiO_2-SiO_2 structure samples

The rice straw used (RS; *Oryza sativa*) was obtained from Naju in Jeonnam province, South Korea. It was prepared by thoroughly washing with distilled water for 24 h, and then treated with a pure ethanol solution at 60 °C for a further 24 h. In a typical synthesis, 0.4 M of titanium tetrachloride ($TiCl_4$; 99.99%, Aldrich, USA) was added to a beaker and dissolved in distilled water, with an impregnation reaction being subsequently performed at 25 °C for 6 h. The $TiCl_4$-impregnated RS samples ($TiCl_4$/RS template) were then washed with anhydrous ethanol and dried under vacuum at 80 °C for 4 h. Finally, the rice straw templates were removed by calcining the samples for 4 h at temperatures ranging from 500 to 900 °C, with a heating rate of 10 °C/min. The resulting samples were designated as TiO_2-SiO_2-500, TiO_2-SiO_2-600, TiO_2-SiO_2-700, TiO_2-SiO_2-800, and TiO_2-SiO_2-900, depending on the calcination temperature used. An additional pure sample of RS treated at 700 °C for 4 h at 10 °C/min was labeled as RS-700.

Characterization of hybrid TiO_2-SiO_2 structure samples

Thermogravimetric analysis (TGA; STARSW, Mettler Toledo, USA) was conducted in air to up to 1000 °C at a heating rate of 2 °C/min to evaluate the thermal behavior of the $TiCl_4$-impregnated RS. The surface and cross-section of the resulting hybrid TiO_2-SiO_2 structure was investigated by FE-SEM (S-4700, Hitachi, Japan), while the chemical composition of the RS samples was determined using an elemental analyzer (EA; Fisons EA 1110, Thermo Quest, USA). The surface area and pore volume of the prepared samples were measured using a nitrogen adsorption analyzer (nanoPorosity-XG, Mirae SI, South Korea), after first preheating the samples to 150 °C for 2 h to eliminate any surface contaminants (including any adsorbed water). The pore size distributions were obtained by applying the Barrett-Joyner-Halenda (BJH) equation to the nitrogen

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