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Photocatalytic evaluation of self-assembled porous network structure of ferric oxide film fabricated by dry deposition process

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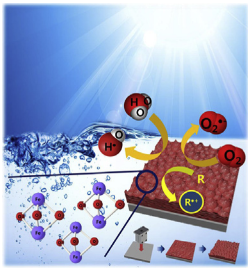
HIGHLIGHTS

- Different sizes of Fe_2O_3 agglomerates were used to form porous network structure.
- Fe_2O_3 agglomerate particles were deposited using solvent-free process.
- Self-assembled porous network microstructure formed better with small agglomerates of Fe_2O_3.
- Fabricated porous network structure showed its potential to be used for photocatalyst.

GRAPHICAL ABSTRACT



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ABSTRACT

Ferric oxide powder in the alpha phase (α-Fe_2O_3) was deposited on an aluminum oxide (Al_2O_3) substrate by a nanoparticle deposition system using the dry deposition method. X-ray diffraction (XRD) images confirmed that the phase of the deposited α-Fe_2O_3 did not change. The deposited α-Fe_2O_3 was characterized in terms of its microstructure using scanning electron microscopy (SEM). A porous network microstructure formed when small agglomerates of Fe_2O_3 (SAF) were deposited. The deposition and formation mechanism of the microstructure were investigated using SEM and three-dimensional (3D) profile analysis. First, a dense coating layer formed when the film was thinner than the particle size. After that, as the film thickness increased to over 5 μm, the porous network structure formed by excavating the surface of the coating layer as it was bombarded by particles. Rhodamine B (RhB) was degraded after 6 h of exposure to the Fe_2O_3 coating layer with SAF, which has good photocatalytic activity and a high porous network structure. The kinetic rate constants of the SAF and large agglomerates of Fe_2O_3 (LAF) were calculated to be 0.197(h^{-1}) and 0.128(h^{-1}), respectively, based on the absorbance results. Using linear sweep voltammetry, we confirmed that the photoelectric effect occurred in the coating layer by measuring the resulting current under illuminated and dark conditions.

1. Introduction

Recently, the use of fossil fuels has caused environmental problems and the depletion of energy resources. Solar energy and storage systems have been studied widely as potential replacements for fossil fuels. These technologies play an important

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role in solving current environmental problems and potentially offer an alternative energy source. The efficiency of biological photosynthetic reactions is only 1–2% in the natural world. However, using photoelectrochemical reactions, the efficiency increases by more than 5%. These reactions have byproducts such as hydrogen or methanol. Energy transformation systems based on photoelectrochemical reactions are of great interest. This photochemical reaction mainly occurs in semiconductor materials, in the following way: electrons are excited from the valence band to the conduction band, leading to the formation of an electron-hole pair. The energy of the excited electron can be transformed into light. The electron-hole pair interacts with a chemical reactant, so that an oxidation-reduction reaction occurs on the electrode surface. The band gap energy range should be close to the visible light range and the catalyst must be chemically stable, so that it has a good energy lifetime and efficiency of the energy transformation process. Moreover, electron-hole recombination should not occur before the oxidation/reduction reaction of the electron-hole pair [1,2]. In 1971, Honda reported that water was degraded to hydrogen and oxygen by titanium oxide (TiO_2) electrodes exposed to light. They proved that solar energy can be stored as chemical energy [3]. However, the band gap energy of TiO_2 ($E_g \sim 3.0$ eV) can only respond to light in the UV range so it can only convert a limited fraction of the available solar energy. Accordingly, the efficiency of the photocatalytic reaction is lower [4]. To overcome the limitation of TiO_2, various materials such as CdS ($E_g = 2.4$ eV), MoS_2 ($E_g = 1.2$ eV), WO_3 ($E_g = 2.8$ eV) and Fe_2O_3 ($E_g = 2.2$ eV) have been studied, which may induce water splitting in visible light. Among them, iron oxide is an abundant resource that exists in various forms such as FeO, α-Fe_2O_3 (hematite), γ-Fe_2O_3 and Fe_3O_4, and is used in photocatalysts. In particular, α-Fe_2O_3 is very stable and has a corundum structure. It has a 2.2 eV band gap, so can be used for applications requiring the photoelectric effect with visible light [5–7]. Usually, an α-Fe_2O_3 film is fabricated using chemical vapor deposition (CVD) [8], sputtering [9], sol-gel [10,11] or another method. However, these fabrication methods still have disadvantages with respect to deposition due to a number of factors such as a higher melting point, lower sputtering yield, dry process, and additional cost. Additionally, particle size and porosity in thin films are important factors, determining the efficiency of the catalysts in the photocatalyst reaction. Nanoparticles can enhance the surface area as reducing dimensions, improving light exposure. Particles with porous structures can improve catalysis efficiency in the same way as nanoparticles [12–15]. The formation of films with porous structures is difficult to control using a conventional deposition process. To overcome this problem, a nanoparticle deposition system (NPDS) was used. NPDS is recently developed dry deposition system in which particles are passed through a nozzle, resulting in high energies due to supersonic velocities, then sprayed onto the substrate. NPDS deposition uses kinetic energy differences between the deposition chamber and the powder feeder to induce differences in pressure. NPDS proceeds under low pressure, low cost and can be used for both metal and ceramic powders. In the case of photocatalyst film production, NPDS is a good deposition method as porous structures can be obtained [16,17].

In this study, NPDS was used to spray Fe_2O_3 powder onto an aluminum oxide (Al_2O_3) substrate, with a variety of particle sizes and shapes. We obtained porous network structures on Fe_2O_3 film surfaces. We analyzed the structure of the resulting film and characterized its absorption by photoelectrical evaluation under RhB. RhB aqueous solution is highly stable to visible photoexcitation. We also assessed the photoelectric effect using linear sweep voltammetry [18].

2. Experiment

2.1. Materials preparation

Three different kinds of Fe_2O_3 power were prepared so that we could compare the effect of particle size. To obtain small size agglomerates of Fe_2O_3 (SAF) and large size agglomerates of Fe_2O_3 (LAF) particles, mill scale Fe_2O_3 nanoparticles (average size, 1 μm; theoretical density, 5.25 g/cm^3) were used as raw materials. Fe_2O_3 was mixed using bead-mill milling. First, Fe_2O_3 was milled using crushing equipment. To prevent flocculation of the oxides, the particles were mixed with methyl alcohol (CH_3OH) and milled for 10 h. Second, the methyl alcohol and Fe_2O_3 dispersion was dried. Dry conditions were obtained by injecting air into it at a pressure of 80 kPa. The mixed dispersion casting rate was 500 cc/h, the injection temperature was 30 °C and the size of the nozzle was 0.5 mm. After that, particles of each desired size of dried Fe_2O_3 aggregate powder were collected. The size distributions were 1–5 μm, which we called SAF, and 10–30 μm, which we called LAF. The microstructure of the powder and the particle size were analyzed using scanning electron microscopy (SEM) (MIRA3; Tescan, Czech Republic) (see Fig. 1).

2.2. Deposition conditions

Mill scale, SAF- and LAF-agglomerated Fe_2O_3 powders were deposited onto an Al_2O_3 substrate using NPDS. Fig. 2 shows the schematic diagram of NPDS. It consisted of an air compressor, a powder feeder, a vacuum chamber and pump, and x-, y-, z-axis translation stages. The air compressor supplies the pressure airflow that transfers particles from the powder feeder to the nozzle. The particles were sprayed into the vacuum chamber at supersonic speed at room temperature.

The deposition area was 10 mm × 10 mm, obtained using a 10 mm × 0.3 mm slit nozzle. Compressed air (0.3 MPa) was used as a carrier gas to entrain the powders. The gas flow rate was 18 L/min,

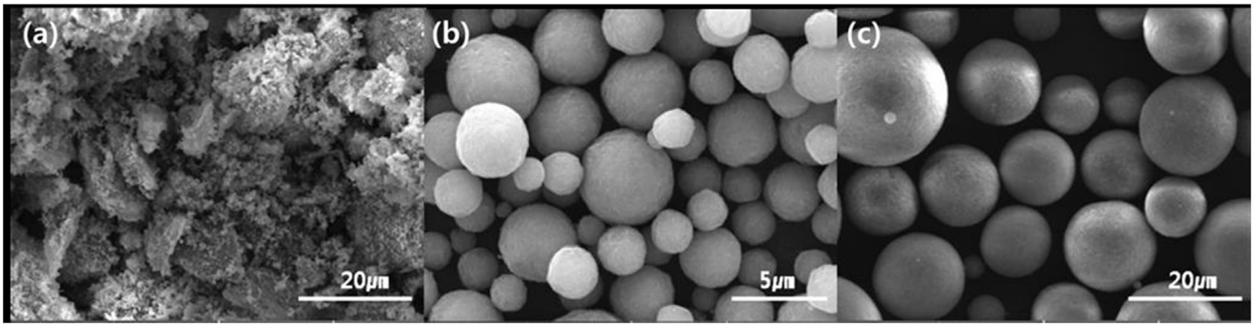

Fig. 1. Scanning electron microscopy (SEM) images of Fe_2O_3 particles: (a) mill scale, (b) small agglomerates of Fe_2O_3 (SAF), and (c) large agglomerates of Fe_2O_3 (LAF).