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Nanoporous hydrogenated TiO_2 photocatalysts generated by underwater discharge plasma treatment for solar photocatalytic applications

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ABSTRACT

In this paper, we report on the mass production, characteristics and application of a hydrogenated TiO_2 photocatalyst (H-TiO_2) with high reactivity under solar light irradiation. The H-TiO_2 photocatalyst has been prepared by simple sol-gel method/underwater discharge plasma treatment at room temperature and atmospheric pressure. The optical absorption spectrum of TiO_2 can be extended from the ultraviolet (UV) into the visible range by changing the surface properties. The crystallinity, hydrogenation and porosity of TiO_2 can be greatly enhanced within 90 s through underwater discharge plasma, using amorphous TiO_2 (as-synthesized TiO_2, a-TiO_2) as the precursor. The resultant H-TiO_2 showed high bicrystalline (anatase/brookite phases) and a large surface area (267.5 m^2/g), thus improving photocatalytic activity. We have demonstrated that H-TiO_2 showed significant photocatalytic efficiencies for degradation of reactive black 5, rhodamine B, and phenol under solar light irradiation, up to 10 times higher than those of commercial TiO_2 and a-TiO_2, leading to complete water purification. Interestingly, the H-TiO_2 photocatalyst also exhibited strong antimicrobial activities against Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* under solar light irradiation, up to 5-times greater than those of commercial TiO_2 and a-TiO_2. Given that H-TiO_2 can be mass produced and easily processed by underwater discharge plasma, we expect this plasma technology may find important environmental and medical applications.

1. Introduction

Titanium dioxide (TiO_2) has received much interest for environmental applications including photocatalytic hydrogen generation and pollutant removal, due to its strong optical absorption, chemical stability, low cost and high reactivity [1–5]. TiO_2 has large electronic bandgaps of 3.0–3.2 eV, which restrict its optical absorption mainly to the ultraviolet (UV) region, corresponding to less than 4% of natural solar energy. Therefore, the overall solar activation of TiO_2 is limited even if TiO_2 is very effective in utilizing UV light. For this reason, much effort has been devoted to improving the visible light absorption of TiO_2 over many years [6–9]. For example, studies have been conducted on the incorporation of light absorbing materials (sensitizer, quantum dots, and dyes) and the modification of TiO_2 electronic properties by the addition of external dopants (transition metals, nitrogen, sulfur, and phosphorus) [10–15]. Among these strategies, tuning TiO_2 with hydrogenation also has attracted considerable attention [16–18]. Chen et al. reported that hydrogenated TiO_2 expands the excitation wavelength range toward the visible light region, reduces recombi-

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nation centers, and increases the lifetime of holes [19]. The methods for fabricating hydrogenated TiO_2 mostly rely on the reduction of Ti^{4+} to Ti^{3+} by thermal treatment under hydrogen or reducing conditions, and high-energy electron, argon, or hydrogen plasmas that inevitably require high temperatures, a costly vacuum system, complicated multiple steps, and a long processing time [19–23]. Thus, it is desirable to develop a facile method for the fabrication of hydrogenated TiO_2.

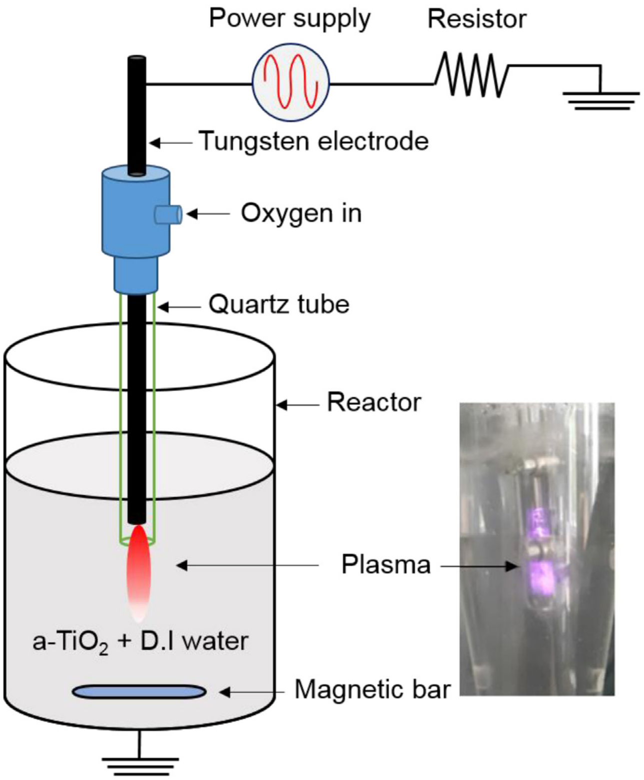
In this study, we prepared hydrogenated nanoporous TiO_2 (H-TiO_2) photocatalysts using an underwater discharge plasma system, which is a simple, fast, and mass-producible method operated at room temperature and atmospheric pressure, using underwater electrical discharges generated in a narrow capillary tube. This approach has recently received substantial attention as it can serve as a water purification tool for environmental cleanup activities and may be applicable to the elimination of airborne microorganisms [24–26]. Furthermore, a considerable number of studies have reported results involving discharges on or in water, including water treatment or decontamination [27,28], bacteria disinfection [29,30], surgical application [31], and material synthesis application [32]. These applications are enabled by numerous active plasma chemistry reactions that are not normally observed in an aqueous solution, promoted by, e.g., reactive radicals, charged particles, ultraviolet light, and shockwaves [24].

Discharge in and on water can initiate a variety of plasma-chemical effects, and a number of primary and secondary species can be formed by these discharges in the gas phase and at the gas-water interface [31]. In view of this, we specially designed the underwater plasma electrode system to sustain a stable discharge with an oxygen gas flow in water. We hypothesized that the plasma electrode system could synthesize the highly crystalline H-TiO_2 from amorphous TiO_2 (a-TiO_2), incorporating atomic hydrogen and hydroxyl molecules produced from water dissociation into its surface. Simultaneously, reactive oxygen species could oxidize carbon species present on the TiO_2 surface, thereby increasing its specific surface area. As a result, the high crystallinity (anatase/rutile bicrystalline) and large responsive surface area obtained via the underwater plasma process contribute to a ten-fold increase in the H-TiO_2 photocatalytic efficiency for degradation of organic compounds in water, and a five-fold increase in efficiency for sterilization of Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* compared to other commercial TiO_2 (P25) and a-TiO_2 photocatalysts.

2. Experimental

2.1. Fabrication of H-TiO_2 photocatalysts

Nanoporous hydrogenated TiO_2 (H-TiO_2) photocatalysts were fabricated via a combination of a simple sol-gel process and underwater discharge plasma treatment. All the reagents for the synthesis of H-TiO_2 photocatalysts were prepared without further purification. First, a solution containing 5 mol titanium(IV) butoxide (170 g, $Ti(OC(CH_3)_3)_4$, Sigma-Aldrich, USA) and 0.5 mol hexadecyltrimethylammonium bromide (18.2 g, CTAB, $C_{16}H_{33}N(CH_3)_3Br$, Sigma-Aldrich, USA) in 100 ml deionized water was used to prepare TiO_2 nanoparticles. The particles in the solution were then well dispersed by stirring for 30 min and allowing to stand for 4 h. The precipitate obtained from the cloudy solution was separated and washed several times with deionized water and dried at room temperature. The amorphous TiO_2 (a-TiO_2) were synthesized according to our previous literature report [33]. From this process, 123.1 g of a-TiO_2 could be obtained and the yield was estimated to be 71.4%. The yield of the sol-gel reaction was calculated on the basis of initial raw materials weight taken and weight of end product fabricated after the treatment.



Scheme. 1. Schematic presentation of experimental set-up for synthesis of hydrogenated nanoporous TiO_2 (H-TiO_2) photocatalysts.

Scheme 1 shows the schematic presentation of experimental set-up for the synthesis of H-TiO_2. The dried a-TiO_2 nanoparticles (15 g, as-synthesized TiO_2) were dispersed with deionized water (400 ml). The suspension was then treated with the underwater discharge plasma in a vessel. As shown in Scheme 1, the plasma treatment system (manufactured by NPAC Co., Korea) consists of a power supply operated at 20 kHz, a plasma electrode system with a gas injection channel, and a reactor. In the plasma electrode system, the tungsten electrode with a diameter of 9.5 mm was tightly inserted into a quartz tube with an inner diameter of 10 mm. The distance between the ends of the tungsten electrode and the quartz tube was approximately 10 mm. Oxygen gas at the flow rate of one liter per minute was introduced into the narrow gap formed between the metal electrode and the dielectric tube. The inset of Scheme 1 shows the discharge plasma image during operation. The applied plasma power was approximately 90 W at the discharge voltage of 13 kV. During plasma treatment, the vessel was constantly stirred by a magnetic bar. The underwater plasma treatment time was controlled within the 0–7 min range. We labelled the resulting nanoporous hydrogenated TiO_2 (H-TiO_2) treated for 1.5 min, 3 min, 5 min, and 7 min, as H-TiO_2-1.5, H-TiO_2-3, H-TiO_2-5, and H-TiO_2-7, respectively.

2.2. Characterization of H-TiO_2 hybrid photocatalysts

The morphology and size distribution of the H-TiO_2 samples were characterized by FE-SEM (Hitachi; S-4700, Japan) and HR-TEM (JEOL JEM 2200, Japan). For the analyses, samples were placed on the surface of a copper grid and dried under ambient conditions. Surface properties including the respective Brunauer-Emmett-Teller (BET) surface areas, pore volumes, and pore diameters of the H-TiO_2 samples were estimated using a BET analyzer (Micromerit-