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Synthesis of mesoporous-assembled TiO₂ nanocrystals by a modified urea-aided sol-gel process and their outstanding photocatalytic H₂ production activity

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ABSTRACT

Mesoporous-assembled TiO₂ nanocrystals with very high photocatalytic H₂ production activity were synthesized through a modified sol-gel process with the aid of urea as mesopore-directing agent, heat-treated under various calcination temperatures, and assessed for their photocatalytic H₂ production activity via water splitting reaction. The resulting mesoporous-assembled TiO₂ nanocrystals were systematically characterized by N₂ adsorption–desorption analysis, surface area and pore size distribution analyses, X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The experimental results showed that the photocatalytic H₂ production activity of the synthesized mesoporous-assembled TiO₂ nanocrystal calcined at 500 °C, which possessed very narrow pore size distribution, was extraordinarily higher than that of the commercially available P-25 TiO₂ and ST-01 TiO₂ powders.

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1. Introduction

Nanostructured titanium dioxide (TiO₂), or titania, has been proven to be a promising functionalized material for a broad range of applications, particularly as the most effective photocatalyst for environmental purification [1–3] and for H₂ production via the photocatalytic water splitting process [4–9], because of its non-toxicity, inexpensiveness, and fascinating physicochemical properties. Up to now, nanocrystalline TiO₂ particles with a mesoporous structural network have been widely studied. Various processes, such as sol-gel [10], solvothermal [11], chemical vapor deposition

[12], and precipitation [13], were developed for the synthesis of nanocrystalline TiO₂ particles as advanced materials. Among these processes, sol-gel is an efficient route for the synthesis of nanocrystalline mesoporous-structured TiO₂ that has been verified to be a promising photocatalyst for H₂ production via the photocatalytic water splitting reaction, as aforementioned. The combustion of H₂ can generate a huge amount of energy with water, or water vapor, as the only harmless by-product [14–16]. Since the generated H₂ does not involve CO₂ emission, it has been strongly believed to be a sustainable energy carrier in the near future for several applications, such as environmentally friendly automobiles

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and airplanes, domestic heating, and stationary power generation [17].

Urea is a major nitrogenous end-product of human metabolism and product of petrochemical industry. It also plays a significant role in the marine nitrogen cycle, e.g. as sources both of excretion by many marine species [18] and of bacterial decomposition of nitrogenous materials [19,20]. At present, the amount of produced urea tends to considerably increase because its production and consumption rates are being continuously increased, especially in petrochemical industry and in agricultural sector. It can be applied as agricultural fertilizer, cattle-feed supplement, and as a primary reactant for polymer synthesis [21]; however, currently there seems to have a surplus quantity of urea produced, and its further value-added use is thus inevitably required. Herein, the application of urea as a mesopore-directing agent in synthesizing nanocrystalline mesoporous-structured TiO₂ was the main focus. Although there have been several reports employing other conventional mesopore-directing agents, such as di-block copolymer (e.g. AT-18, AT-25, AT-50) [22], triblock copolymer (e.g. P-123) [23], and ionic surfactant (e.g. CTAB) [24], for mesoporous-structured TiO₂ synthesis, the use of urea for such purpose offers some superior advantages to those agents, particularly the better economical viewpoint due to its less expensiveness and the requirement of less severe heat-treatment conditions when removing it from a mesoporous framework due to its smaller molecular structure.

In this work, the synthesis of mesoporous-assembled TiO₂ nanocrystals with highly enhanced photocatalytic H₂ production activity using a modified sol-gel process with the aid of urea was underlined. The purpose of this work was to investigate the influences of using urea as an efficient sol-inducing and mesopore-directing agent and calcination temperature on the characteristics of the synthesized mesoporous-assembled TiO₂ nanocrystals. The obtained mesoporous-assembled TiO₂ nanocrystals were subsequently applied for H₂ production via the photocatalytic water splitting reaction using methanol as a hole scavenger, as compared to commercially available TiO₂ powders.

2. Experimental

2.1. Materials

Tetraisopropyl orthotitanate (TIPT, Ti(OCH(CH₃)₂)₄) was supplied from Tokyo Chemical Industry Co., Ltd. Acetylacetone (ACA, CH₃COCH₂COCH₃) was supplied from Nacalai Tesque, Inc. Urea (NH₂CONH₂) was supplied from Wako Pure Chemical Industries, Ltd. All chemicals were analytical grade and used without further treatment. The TIPT was used as a titanium precursor. The ACA was used as a modifying agent to balance the hydrolysis and condensation rates of the titanium precursor. The urea was used as both sol-inducing agent and mesopore-directing agent. Commercially available TiO₂ powders, i.e. P-25 TiO₂ (supplied from Degussa, Nippon Aerosil Co., Ltd.) and ST-01 TiO₂ (supplied from Ishihara Co., Ltd.), were employed for comparative photocatalytic H₂ production activity testing.

2.2. Synthesis procedure

The mesoporous-assembled TiO₂ nanocrystals were synthesized via a modified sol-gel process with the aid of urea. In typical synthetic steps, a pre-determined amount of the ACA was first introduced into the TIPT with the TIPT-to-ACA molar ratio of 1:1. The mixture was then gently shaken until it was homogenized. Afterward, a 0.4 M urea aqueous solution was added to the ACA-modified TIPT mixture, where the TIPT-to-urea molar ratio was adjusted to a desired value of 4:1. The finally mixed solution was left on a magnetic stirrer and kept continuously stirring at 40 °C to accordingly obtain a transparent yellow sol solution. Then, the sol-gel transition was accomplished by placing the sol-containing solution into an oven kept at 80 °C for a week. Subsequently, the gel formed was dried overnight at 80 °C under atmospheric pressure to eliminate the solvent. The dried gel was calcined at various temperatures (i.e. 450, 500, and 550 °C) for 4 h to remove the urea molecules and to consequently produce the desired TiO₂ photocatalysts.

It should be noticed that the urea aqueous solution importantly behaves as a sol-inducing agent because the transparent yellow sol could not be obtained when using only pure water (without dissolved 0.4 M urea) as a hydrolyzing agent. In the absence of urea, the yellow precipitates formed immediately when blending the ACA-modified TIPT mixture with pure water, and such precipitates could no longer dissolve in the solution to obtain the sol even after stirring at 40 °C for several days.

2.3. Characterization techniques

The N₂ adsorption–desorption isotherms of the investigated photocatalysts were obtained by using a surface area analyzer (BEL Japan, BELSORP-18 Plus) operated at the liquid N₂ temperature of –196 °C. The Brunauer–Emmett–Teller (BET) approach was used to calculate specific surface area of the photocatalysts by using adsorption data over the relative pressure range of 0.05–0.35. The Barrett–Joyner–Halenda (BJH) approach was employed to determine pore size distribution and mean mesopore diameter by using desorption data of the isotherms. Each photocatalyst sample was degassed at 200 °C for 2 h to eliminate the moisture and volatile species adsorbed on its surface before the analysis. The crystalline phase present in the photocatalysts was investigated by using X-ray diffraction (XRD) technique. A rotating anode XRD system (Rigaku, PMG-A2) generating monochromated Cu K α radiation with a continuous scanning mode at the rate of 2°/min was used to acquire XRD patterns under operating conditions of 35 kV and 15 mA. The photocatalyst morphology and particle size were investigated by using a scanning electron microscope (SEM, JEOL, JSM-6500FE) and a transmission electron microscope (TEM, JEOL, JEM-200CX) under operating voltages of 15 kV and 200 kV, respectively.

2.4. Photocatalytic H₂ production activity testing

Photocatalytic H₂ production via the water splitting reaction was carried out in a closed gas system. A controlled amount (0.2 g) of each individual photocatalyst was suspended in

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