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Sol–gel synthesis of nanosized titanium oxide in a porous coordination polymer

Cho Rong Kim [a], Takashi Uemura [a,b,*], Susumu Kitagawa [a,c,*]

[a] Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
[b] CREST, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan
[c] Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

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ABSTRACT

Nanosized titanium oxide (TiO_2) was synthesized in the channels of a porous coordination polymer (PCP) $[La^{3+}(1,3,5\text{-benzenetrisbenzoate})]_n$ by the sol–gel reaction of titanium tetraisopropoxide. XRD, IR, UV–vis, and gas sorption measurements demonstrated that nanosized TiO_2 was formed in channels of the PCP. In this system, the resultant PCP$\supset$$TiO_2$ composite showed enhancement of the adsorption of water. Furthermore, the sorption behavior of the composite could be changed by UV irradiation.

1. Introduction

The design and synthesis of PCPs with unique structural topologies and electronic functions using the self-assembly approach of metal ions and organic ligands have been studied. Because of their regular porous structures with large surface areas, permanent porosity, and surface functionality, PCPs have emerged as an important new class of nanoporous materials with potential for many applications in storage, separation, catalysis, and chemical sensing [1–8].

The fabrication of metal and metal oxide particles accommodated in PCPs has made rapid progress because the doping of only a small amount of the materials can afford new functions to PCPs [9–14]. For example, we have previously reported the synthesis of nanosized silica in the channels of HKUST-1 ($[Cu_3(btc)_2]_n$; btc = benzene-1,3,5-tricarboxylate) which showed higher sorption amounts for a hydrophilic molecule compared to that of only the host [15–16]. Furthermore, magnetic property of a zeolitic imidazolate framework (ZIF) was exhibited by the incorporation of Fe_3O_4 particles, which allowed recovery of the PCP from a solvent suspension by applying a magnetic field [17]. For the enhancement of adsorption property for hydrogen molecules, utilization of nanocomposite consisting of Pd in PCP pores has been studied [18,19]. This methodology is useful enough to alter the properties of PCPs without changing the host structures, such as the pore size, shape, and surface.

Titanium oxide (TiO_2) is a very useful functional material due to its wide range of applications in the fields of photocatalysis, optical materials, dye-sensitized solar cells, lithium-ion batteries, and superhydrophilic materials [20–22]. These functions of TiO_2 are derived from the change of the energy transfer of TiO_2 by UV irradiation [23–25].

Recently, the use of nanoporous matrices as host media for the formation of nanosized TiO_2 has become considerable interest for specific nanosize properties and host–guest synergistic functions [26–28]. In this work, we successfully performed the synthesis of TiO_2 within one-dimensional nanochannels of $[La^{3+}(1,3,5\text{-benzenetrisbenzoate})]_n$ (**1**; pore size = 10×10 Å^2) by sol–gel polycondensation of titanium(IV) tetraisopropoxide (TTIP). The resulting material was characterized by XRD, IR, UV–vis, and SEM-EDX measurements. Alteration of the adsorption behaviors of the obtained composite by irradiation of UV light was investigated. We expect that this work will contribute to the development of PCPs for use as photosensitive materials.

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* Corresponding authors. Address: Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan. Tel.: +81 753 2733; fax: +81 753 2732 (T. Uemura). Address: Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan (S. Kitagawa).

E-mail addresses: uemura@sbchem.kyoto-u.ac.jp (T. Uemura), kitagawa@icems.kyoto-u.ac.jp (S. Kitagawa).

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2. Experimental

2.1. Materials

All reagents and chemicals used were obtained from commercial sources, unless otherwise noted. The host PCP (**1**) was prepared using the previously reported method [29].

*2.2. Sol–gel synthesis of accommodating TiO_2 within **1***

The dried host compound **1** (53 mg) was prepared by evacuation (<0.1 kPa) at 120 °C for 3 h in a Pyrex tube. Subsequently, 31 mg of titanium(IV) tetraisopropoxide (TTIP) was added to **1** suspended in 3 mL of dehydrated 2-propanol, and the resulting mixture was stirred for 10 min under nitrogen atmosphere to incorporate TTIP into the nanochannels of **1**. The solvent was then evaporated to give **1**⊃TTIP adduct (**1**⊃TTIP). **1**⊃TTIP adduct was heated at 250 °C for 24 h under exposure to water vapor to facilitate the sol–gel reaction of TTIP. Further condensation was achieved by incubating the material under vacuum at 120 °C to remove byproducts such as 2-propanol and water in the condensation process, which gave PCP-TiO_2 composite (**1**⊃TiO_2, 60 mg).

2.3. Isolation of nanosized TiO_2 from the host framework

To isolate TiO_2 particles inside **1**, the composite (60 mg) was stirred overnight in a 0.05 M aqueous solution (40 mL) of sodium ethylenediaminetetraacetate (Na-EDTA) for the complete dissolution of 1. The isolated TiO_2 (8 mg) was washed with water (5 mL × 3) and dried under a reduced pressure at room temperature.

*2.4. Photoirradiation of **1**⊃TiO_2*

An activated sample of **1**⊃TiO_2 in a cylindrical Pyrex glass tube was irradiated with a 500 W ultrahigh pressure mercury lamp (385–425 nm) for 12 h equipped with glass filters at 298 K.

2.5. Measurements

X-ray powder diffraction (XRPD) data were collected using a Rigaku RINT 2000 Ultima diffractometer employing CuK radiation. SEM-energy-dispersive X-ray (EDX) measurements were conducted by using a JEOL JED-2300 detector in a JEOL JSM-5600 at an accelerating voltage of 15 kV and 30 kV. The thermogravimetric (TG) analysis was carried out from room temperature to 500 °C using a Rigaku Instrument Thermo plus TG 8120 in a nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ULVAC-PHI Model 5500 spectrometer with 15 kV, 400 W Mg Ka emission as the X-ray source. The charging effect was corrected by adjusting the binding energy of the C 1s peak to be 284.6 eV. Nitrogen adsorption measurements at 77 K and solvent vapor adsorption measurements at 298 K were carried out using a Belsorp-Max and Belsorp-Aqua volumetric adsorption instruments, respectively. The samples were activated under high vacuum (<10^{-2} Pa) at 120 °C for 6 h before the sorption measurements.

3. Results and discussion

3.1. Synthesis of nanosized TiO_2 in the nanochannels of PCP

We carried out the synthesis of nanosized TiO_2 in the one-dimensional nanochannels of **1** using a sol–gel polycondensation of TTIP. The sol–gel process is based on hydrolysis and polycondensation of titanium alkoxide leading to the formation of a titanium oxide [30]. TTIP was incorporated into the channel by immersion of **1** in a 2-propanol solution of TTIP, followed by evaporation of 2-propanol (**1**⊃TTIP). **1**⊃TTIP adduct was left under H_2O atmosphere for hydrolysis of TTIP in the pore and was heated at 250 °C to initiate the polycondensation. Further condensation was achieved by evacuating the resulting material at 120 °C to provide a composite (**1**⊃TiO_2).

We checked the XRD of **1**⊃TiO_2 and found that the pattern of **1**⊃TiO_2 was almost the same as that of **1**, indicating that the framework was retained after the sol–gel reaction (Fig. 1). In the UV–vis spectroscopy results, an increase in the absorption at wavelength around 350–400 nm can be assigned to the intrinsic absorption of TiO_2, representing the existence of TiO_2 particles in the composite (Fig. 2) [31]. Quantitative analysis of **1**⊃TiO_2 showed that the number of Ti atoms per unit cell of **1** was 0.48 as determined by the SEM-EDX result. The energy dispersive X-ray analysis for elemental mapping measurements (EDX) revealed that TiO_2 particles were homogeneously dispersed in the channels of **1** (Fig. S1). Because the elemental map for **1**⊃TiO_2 showed almost the same ratio of Ti atoms in the unit of **1** at the different accelerating

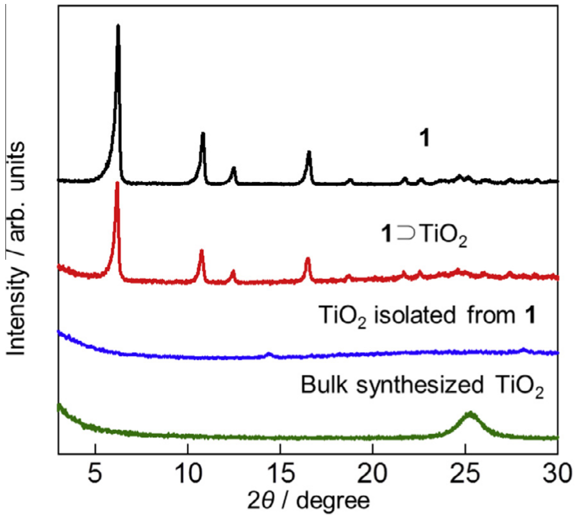

Fig. 1. XRPD of **1**, **1**⊃TiO_2, TiO_2 isolated from **1**, and bulk synthesized TiO_2.

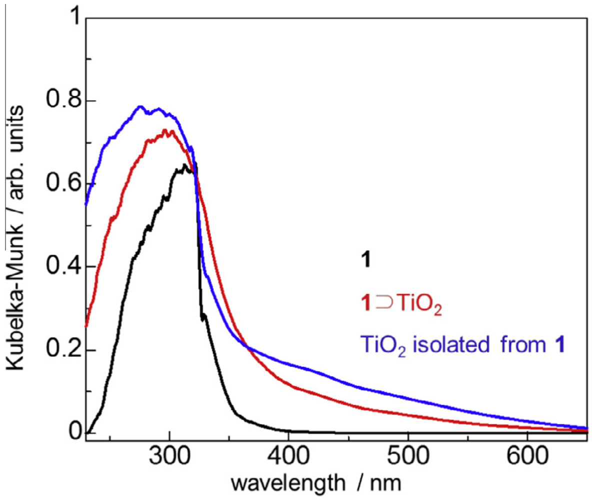

Fig. 2. UV–vis spectra of **1**, **1**⊃TiO_2, and TiO_2 isolated from **1**.