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## Template-assisted Self-assembly and Cobalt Doping of Ordered Mesoporous Titania Nanostructures\*\*

By Jin Song Yin and Zhong L. Wang\*

Ordered self-assembly of nanocrystals (Au,<sup>[1,2]</sup> Ag,<sup>[3,4]</sup> CoO,<sup>[5]</sup> CdSe,<sup>[6]</sup> Pt,<sup>[7]</sup> etc.) is scientifically interesting not only because of the unique properties of the nanocrystals,

but also because the ordered nanostructures are tunable by controlling the particle size and the length of the surface-adsorbed molecules. In order to form ordered self-assembled nanostructures, the system of solution, surfactant, and nanocrystals must cooperatively process monodisperse nanocrystals with minimum agglomeration. In most cases, however, chemically compatible systems are limited, and it may be difficult to create homogeneous nucleation of nanocrystals. Compared to the lithography method, self-assembly lacks precise control, thus ordered structures are formed at random, and may be too small for adequate characterization of their physical and chemical properties.

To increase the control of self-assembly of nanocrystals, numerous template-assisted self-assembly techniques have been explored.<sup>[8–17]</sup> It has been reported that monodisperse polystyrene (PS) particles can be synthesized by emulsion polymerization and that their ordering can be achieved easily.<sup>[18]</sup> Although nanostructured porous materials can be processed using supramolecular surfactant micelles as templates, or by the copolymerization method, the pore size is limited to < 30 nm,<sup>[13]</sup> and the systems that have been successfully synthesized are simple structures, such as silica,<sup>[8]</sup> platinum,<sup>[15]</sup> and manganese oxide.<sup>[16]</sup> For applications of ionic conductors in the fields of fuel cells, sensors, and electrodes, complex oxides with different kinds of doping are required. Owing to the interaction of different kinds of precursors, it is rather difficult to optimize the precursor, surfactant, and solution system, and in some cases it is almost impossible.

In light of recent work on the template processing method,<sup>[9,10]</sup> PS particles of smaller size were used in this paper as the template for creating an ordered anatase nanostructure with cobalt doping. The ordered structure was inherited from the PS. By choosing different sized templates, it is possible to process various porous materials with ordered pores. The nanostructure formed by this method is an ideal mesoporous material with a large interior surface area. The microstructure of the as-prepared titania nanostructures is determined using transmission electron microscopy (TEM). Cobalt doping into the mesoporous structure is reported for the first time in this system, and its structure is determined.

Porous structures were processed using the technique reported recently.<sup>[9,10]</sup> An aqueous solution, 15 wt.%, of the as-received PS (from Duke Scientific), with a mean particle size of 203 nm and a standard deviation of 2.1 %, was used as the raw material. Typically 40 mL solution was placed in a perpendicular open-end glass tube with an inner diameter of 1.5 mm. The drying process in air took about 10 h. After the template was dried, a 40 vol.% absolute alcohol solution of titanium butoxide (from Aldrich Chemicals) was added drop-by-drop. To ensure infiltration of the porous template with precursor, excess alcohol solution was added. After the precursor was dried, the glass tube was treated in an oven at 160 °C for 5 h and then at 450 °C for another 5 h. During the lower temperature annealing, the reaction

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[\*\*] This work was supported by National Science Foundation DMR-9733160

of the precursor was completed and the hollow structure was created. The high temperature annealing caused crystallization of the amorphous titania and completely burnt off the PS.

To dope cobalt into the structure, the porous titania host was infiltrated with a heptane solution of cobalt carbonyl (concentration 2.5 mg/mL). After drying in vacuo at room temperature for 5 h, the doped material was treated at 160 °C. This chemical technique allows large-scale production of the mesoporous structure. The as-prepared titania porous material was first examined using a Hitachi S800 scanning electron microscope (SEM). The phase structure and the chemical composition of the as-prepared titania porous host and the cobalt-doped titania were examined with a Hitachi HF2000 transmission electron microscope (TEM) and associated analytical techniques.

Figure 1a is an SEM image of the ordered titania structure, from which the interpore distance is measured to be  $125 \pm 10$  nm. The pore size is  $95 \pm 10$  nm measured from both the SEM and TEM images (see Figs 2 and 3), smaller than the original PS spheres because of the volume contraction due to the decomposition and vaporization of the precursor during the treatment. A Fourier transform of the image clearly reveals the ordered self-assembly (Fig. 1c).

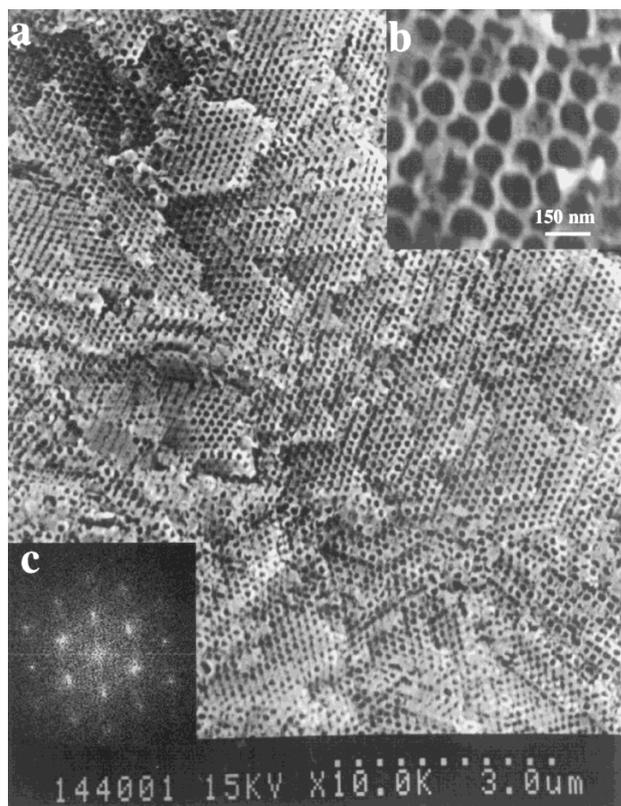


Fig. 1. a) A scanning electron microscopy image of the ordered porous nanostructure of anatase. b) An enlarged area showing the nanoporosity (diameter  $90 \pm 10$  nm) and the wall thickness of  $\approx 15$  nm. c) A Fourier transform of the SEM image clearly shows the ordered pore structure with six-fold projected symmetry (the pixel used for Fourier transform was  $512 \times 512$ ).

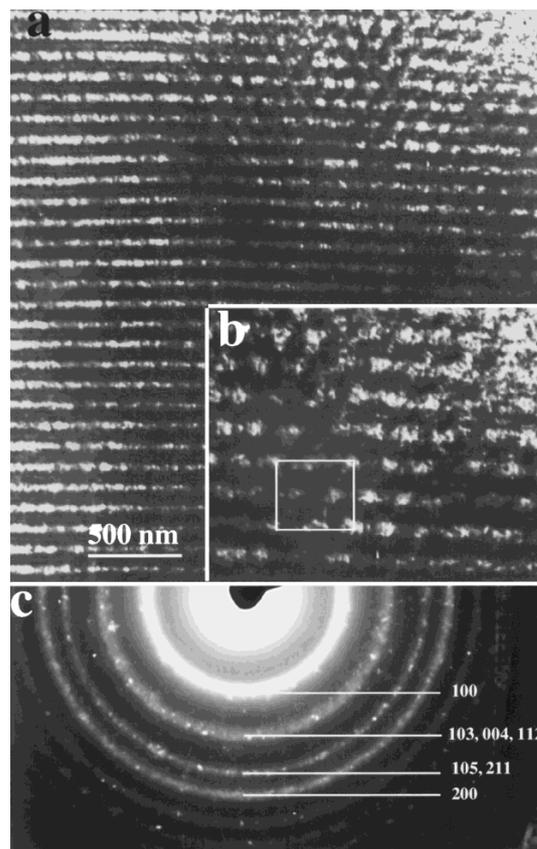


Fig. 2. a) A bright-field TEM image of the ordered pore structures. b) An enlarged area with the sketch of the projected [110] f.c.c. unit cell. c) A selected area electron diffraction pattern proves the anatase structure of titania. The rings are broadened due to the reduced size of the crystallites.

The pore structure is three-dimensional, and the plane parallel to the substrate is the (111) closest packing plane. The TEM image recorded from a thin section of the structure also shows the ordered structure (Fig. 2a). The symmetry of the image demonstrates that the assembly is oriented along the [110] orientation of a face-centered cubic lattice, and the projected unit cell was plotted in the enlarged area. Chemical microanalysis using energy-dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy support the presence of titanium and oxygen in the specimen. The crystal structure was determined using electron diffraction (Fig. 2c). With reference to the diffraction standard from a gold crystal, the phase structure of the ordered nanostructure is identified to be anatase, which is the lower temperature phase of titanium oxide.

The low-magnification TEM image clearly shows the porosity of the self-assembled structure (Fig. 3a). The ordered structure of the spherical pores is also visible. A high-resolution TEM micrograph illustrates that the walls of the pores are made of fine titania nanocrystals of sizes  $\approx 8$  nm. These grains are well crystallized, but randomly oriented.

In the cobalt-doped porous structure of titania, two questions need to be addressed. First, has the cobalt been doped

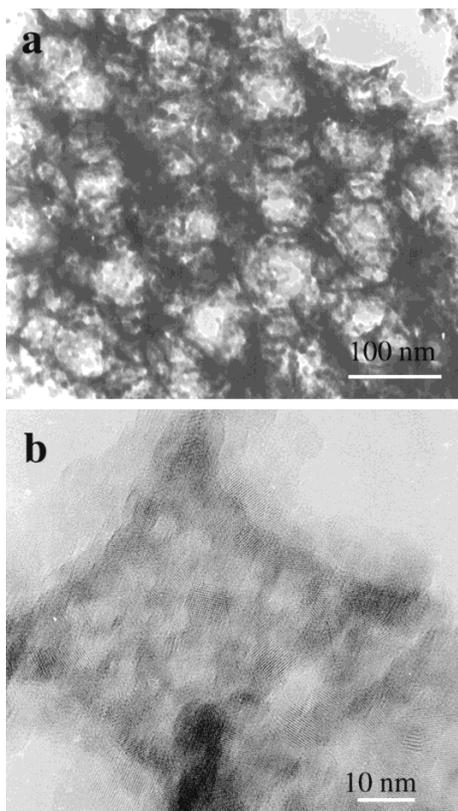


Fig. 3. a) A bright-field TEM image of the porous structure. b) A high resolution TEM image of anatase, showing the grain size of  $\approx 8$  nm.

into the porous structure? Second, what is the structure of the doped cobalt? A careful examination of the bright-field TEM image (Fig. 4a) recorded from the doped specimen shows some granular contrast on the walls of the pores. The image clearly illustrates the ordered spherical pores, but it cannot directly prove the penetration of the cobalt species into the pores. To answer this question, EDS spectra were acquired by focusing a fine electron probe of 3 nm in diameter onto the inner wall of the pore and the center of the pore, which indicated the presence of Co element, as shown in Figure 4c. The relative intensity of Co to Ti varies little between different regions of the specimen, suggesting that the Co may have formed a compound with Ti.

The structure of the cobalt is determined by a comparison of electron diffraction patterns recorded from the host material and the one doped with cobalt. From the electron diffraction pattern, all of the diffraction rings were the same, except the ring indicated by an arrowhead (Fig. 4b). The ring clearly associated with the doping of cobalt has a  $d$ -spacing of  $0.30 \pm 0.01$  nm, and is rather diffuse, suggesting the small size of the doped cobalt species/compounds. But this  $d$ -spacing is too large for Co, CoO, or even  $\text{Co}_3\text{O}_4$ . It agrees well with the  $\{220\}$  reflection of the spinel structured  $\text{Co}_2\text{TiO}_4$ , which has a  $d$ -spacing of 0.299 nm.<sup>[19]</sup> The low-index  $\{111\}$  ring of  $\text{Co}_2\text{TiO}_4$  (with  $d = 0.4887$  nm) is likely to be shadowed by the strong central transmitted beam as well as the high diffuse scattering background

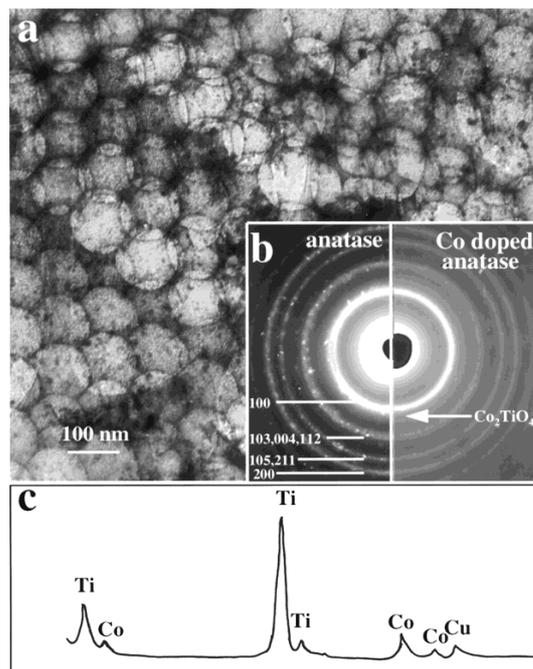


Fig. 4. a) A bright-field TEM image of the cobalt-doped anatase nanostructure, displaying the ordered structure. b) A comparison of the electron diffraction patterns between the host anatase (left-hand side) and the cobalt-doped anatase (right-hand side), where an extra ring (indicated by an arrowhead) is found in the pattern from the doped specimen, which may correspond to the  $\{220\}$  of  $\text{Co}_2\text{TiO}_4$ . c) Energy dispersive X-ray spectrum shows the doping of cobalt into titania. The Cu signal comes from the Cu grid used in TEM.

from the amorphous substrate, while the high-index reflection may be overlapping with the rings of anatase. The final compounds are dominated by  $\text{TiO}_2$  possibly with a small fraction of  $\text{Co}_2\text{TiO}_4$ , which is a result of the reaction between Co and anatase.

In summary, template-assisted ordered self-assembly of porous titania nanocrystals generates a face-centered cubically packed structure. The walls of the pores are made of anatase nanocrystals of  $\approx 8$  nm in diameter. Cobalt can be doped into the walls of the pores by solution infiltration of cobalt carbonyl. Cobalt titanium oxide may be formed on the internal surface of the ordered pore structure. This type of structure is likely to be an excellent supporting material for catalysis. The experimental results suggest that transition metal elements can be incorporated into porous titania without blocking the interconnected pores.

Received: October 9, 1998  
Final version: December 28, 1998

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## Effect of Doping Level and Morphology on the Transport Properties of Poly(4,4'-Dipentoxo-2,2'-Bithiophene)\*\*

By Nadia Camaioni,\* Giuseppe Casalbore-Miceli, Alessandro Geri, and Sergio Nicoletti

In recent years there has been considerable interest in the study of conductive polymers because their optical and electrical properties can be modified by chemical or electrochemical doping.<sup>[1-3]</sup> In particular, the electrical conductivity can be varied over a large range from insulator to a good conductor; however, knowledge of the electrical conductivity is not sufficient for understanding the transport properties of these materials. The transport properties are related to two physical quantities: the carrier mobility and the carrier concentration. The carrier mobility of polymer materials is usually calculated from the drain current characteristics of field-effect transistors (see, e.g., the paper by Garnier<sup>[4]</sup>) or, in some cases, can be evaluated from the conductivity and the doping level.<sup>[5]</sup> Electrochemical doping, unlike chemical doping, allows a precise tuning and determination of the doping level by measuring the amount of charge exchanged during the doping process. However, the concentration of the effective mobile carriers may sig-

nificantly differ from the density of the doping carriers. Therefore, the carrier concentration requires a direct measurement, which can be achieved only by simultaneously measuring the conductivity and the Hall coefficient ( $R_H$ ) of the material.

In this communication, a study of the carrier concentration and mobility as a function of doping in poly(4,4'-dipentoxo-2,2'-bithiophene) (polyET2) is reported. The polymer was prepared and doped by electrochemical techniques using tetrabutylammonium tetrafluoroborate (TBAF) as the supporting electrolyte. The results are compared with those previously obtained<sup>[6]</sup> for the same polymer synthesized and doped, using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The carrier concentration and mobility were obtained using the Hall effect technique.

$R_H$  was found to be negative in many of the tested films, as in the case of polyET2 prepared using TBAP as the supporting electrolyte.<sup>[6]</sup> The so-called sign anomaly of  $R_H$  is well known for non-crystalline materials, both inorganic<sup>[7-9]</sup> and organic.<sup>[10-12]</sup>

Figure 1 shows the X-ray diffraction patterns of polyET2 prepared with both TBAF (polyET2f) and TBAP (polyET2p). The two materials are clearly made up of amorphous and semicrystal phases, but with different compositions. In fact, the X-ray pattern of polyET2f presents, at  $4.6^\circ$ , a stronger and narrower reflection (with the relative higher-order peaks) than that of polyET2p, indicating a more regular structure. The other sharp peaks overlapped with the polymer patterns are mainly due to small amounts of included electrolyte.<sup>[13]</sup> Further evidence of the different morphologies of the two polymers comes from their voltammetric patterns (Fig. 2). The voltammetry of polyET2f shows two well-structured redox systems, whereas that of polyET2p is characterized by only one large, capacitive redox system.<sup>[13]</sup> The more ordered structure of polyET2f could require a higher energy for its modification and, consequently, could make this material less sensitive to the environmental conditions. This hypothesis is also supported by the fact that, although all the polymer films were doped

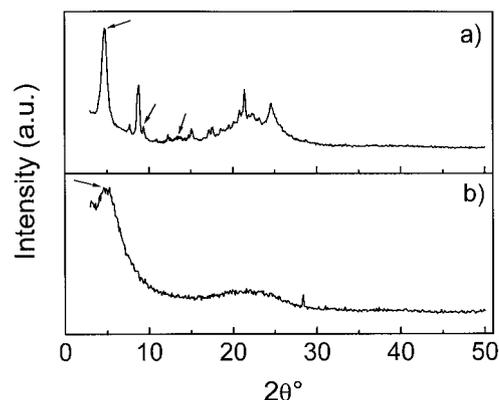


Fig. 1. X-ray diffraction patterns of a) polyET2f and b) polyET2p. The arrows indicate the positions of the reflections.

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[\*\*] The authors thank Dr. M. C. Gallazzi, at Dipartimento di Ingegneria Chimica e Chimica Industriale G. Natta (Milano), for supplying the monomer. Acknowledgments are also due to Mr. L. Ventura and Mr. M. Cristani, at Istituto FRAE (Bologna), for their technical support. The X-ray measurements were performed at Centro (Bologna) by Dr. A. Fichera. This work was supported by the National Research Council of Italy within the program Progetto Finalizzato Materiali speciali per tecnologie avanzate II.