General process for transparent porous electrodes using metal-oxides nanoparticles

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We describe a general process, which is applicable to a wide range of materials, for transparent porous electrodes fabricated by using commercially available nanocrystalline powders. Transparent porous electrodes have potential to develop new optoelectronic devices which exchange energies between photons, electrons and molecules on large surfaces such as photoreductive/oxidative electrodes [1, 2], dye-sensitized solar cells [3–6], electrochromic [7, 8], electroluminescent devices [9], and spectroelectrochemistry [10, 11]. They consist of metal-oxide nanoparticles such as WO_3 [1, 2], TiO_2 [3–5, 9], SnO_2 [6–8, 10–13] and are synthesized mostly by means of sol-gel coating methods.

The fabrication of SnO_2 and TiO_2 transparent porous electrodes by means of sol-gel methods has been reported in the literature using precursors of metal-oxide ceramics, which were pyrolyzed into nanocrystals under pH-controlled conditions, followed by several complicated processes or under high temperature and high pressure using an autoclave: the so-called ‘hydrothermal synthesis [3, 4, 6, 9, 12, 13]. Without the pyrolysis of the precursor, only thin single films ($<0.2\ \mu$m) have been obtained, so that the coating must be repeated several times in order to increase the thickness [7, 8]. On the other hand, porous electrodes have been fabricated by using commercially available nanoparticles but the resulting electrodes were opaque [5, 14–16]. The nanoparticles prepared by hydrothermal synthesis and the commercial powders were ground and dispersed in a polymeric solution using either an ultrasonic homogenizer [3, 4, 15], a roll-mill grinder [15], or a paint shaker [14]. The resulting paste was coated on a substrate and sintered between 450 to 550 °C for 30 min, giving a transparent porous electrode. With respect to WO_3 an unstable precursor obtained by use of a cation-exchange resin from Na_2WO_4 has been coated with a polymer binder and pyrolyzed to get nanoparticles, resulting in transparent porous electrodes. A commercially available H_2WO_4 powder was not useful for the precursor [1, 2].

As noted above, each paste for transparent porous electrodes prepared by the sol-gel synthesis needs special equipments and complicated procedures that are affected by the targeting materials. In this paper we disclose a general method to fabricate transparent porous electrodes from a wide range of materials. Moreover, our process is advantageous for using only basic and inexpensive equipment: a rotary evaporator, a hot magnetic stirrer, and an oven. This method should be especially useful for many researches and industrial applications to achieve new optoelectronic devices with transparent porous electrodes.

The fabrication of transparent porous electrodes was made using inexpensive equipments available in an ordinary chemical laboratory: a rotary evaporator, a hot-magnetic stirrer, and an oven. TiO_2 (F-6, Showa Titanium; diameter: $d = 16$ nm), Sb-doped SnO_2 (SN100-P, Ishihara Sangyo; $d = 20$ nm), and WO_3 (Aldrich; $d = 30$ nm) were selected as commercially available powders. For the coating paste, HNO_3 was adsorbed on the surface of the nanoparticles by stirring the nanoparticles in 0.1 M HNO_3 aqueous solution under heating (80 °C for 8 hrs) and drying them in a rotary evaporator until the dispersion became powdery. The coating paste was prepared by mixing the aforementioned nanoparticles (0.8 g) in H_2O (4 ml), polyethylene glycol (Mw 20000, Wako Chemical) (0.24 g) and hydroxypropyl cellulose (6–10 cps, Tokyo Kasei) (0.08 g). The stirring time was controlled between 1 to 30 days, giving a coating paste which was applied on a substrate by means of a doctor-blade technique using a glass rod [3], and then sintered at 550 °C for 30 min.

Fig. 1a, b and c depict scanning electron micrograph (SEM) images of the surface morphologies of SnO_2 films using the pastes stirred for 1, 15 and 30 days, respectively. The surface after 1 day was very rough

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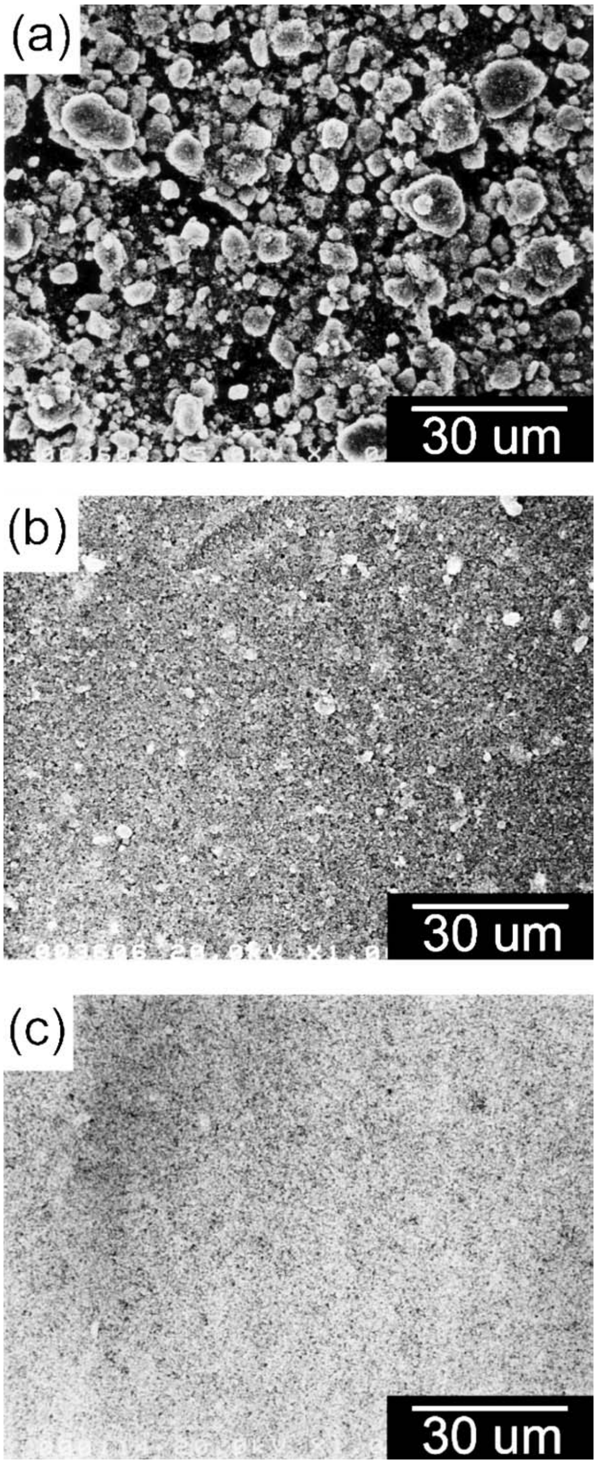

Figure 1 SEM photographs of porous SnO_2 films showing the surface morphology with the paste stirred for (a) 1 day, (b) 15 days and (c) 30 days.

and the SnO_2 particles in the film consisted of 100 micrometers order aggregates (Fig. 1a). After 15 days the surface became smooth, but micrometersize aggregates remained (Fig. 1b). After 30 days (Fig. 1c) these large aggregates disappeared and the surface became smoother with the small aggregate size of ca. 200 nm.

Fig. 2 shows the surface profiles of SnO_2 films with the paste stirred for 1 day and 30 days. The surface profile after 1 day was very rough. On the other hand, the surface after 30 days became smooth. These surface profiles are consistent with the morphologies depicted in Fig. 1a and c. Therefore, the stirring time of the paste using the magnetic tip affects the size of the aggregate of nanoparticles.

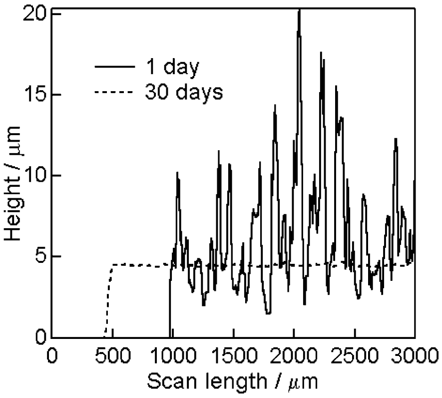

Figure 2 Surface profiles of SnO_2 films from the paste stirred for 1 day and 30 days.

In order to reduce the size of aggregates, powerful apparatus like an ultrasonic homogenizer, a paint shaker, or a roll-mill grinder have been used [3, 4, 14, 15]. In this research, only a magnetic stirrer was used. The effectiveness in reducing the aggregate size can arise at the interface between the stirring magnetic tip and the bottom of the sample vessel: the stirring magnetic tip has enough power to generate hydrogen from water, the so-called 'mechano-catalysis' [17].

Fig. 3a shows transmittance spectra of porous SnO_2 films in the visible-spectral region ($\lambda = 400$–700 nm) as a function of the stirring days. The transmittance after 1 day was low in the whole spectral range, because

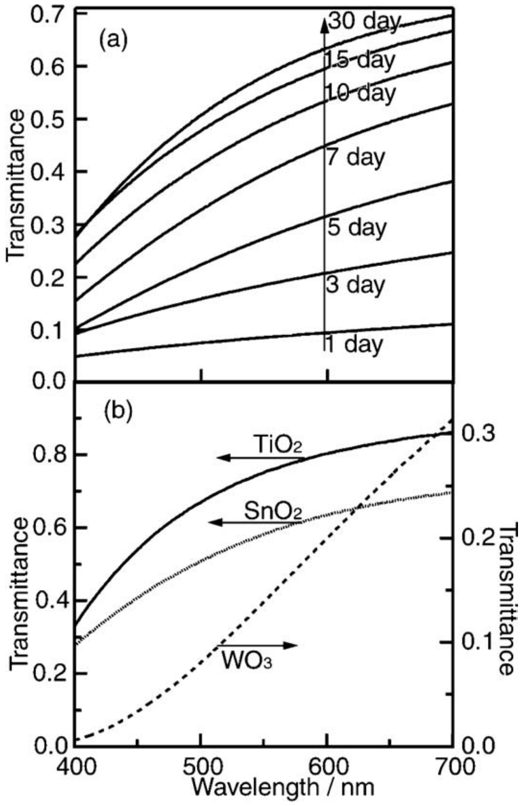

Figure 3 (a) Variation of visible-region transmission spectra of porous SnO_2 films with the stirring time of SnO_2 paste. (b) Visible-region transmittance spectra of porous TiO_2, SnO_2 and WO_3. Each paste was stirred for 30 days using a magnetic stirrer.

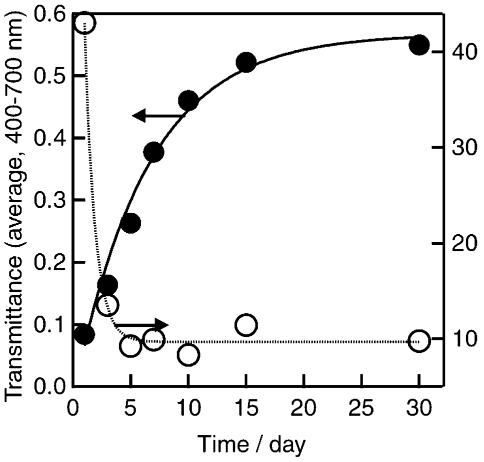

Figure 4 Variations of average transmittance (400–700 nm) and sheet resistance of porous SnO_2 films with the stirring time of SnO_2 paste.

of the light scattering due to the large aggregates in the film (Fig. 1a). The transmittance of the porous SnO_2 films was increased with the stirring time and the decrease of the size of the aggregates. Finally, the transmittance at 700 nm and that of the total average became 70 and 55%, respectively. Fig. 3b shows the transmittance spectra of porous TiO_2, SnO_2 and WO_3 electrodes using their pastes stirred for 30 days. The transmittance of porous electrodes decreased in the order $TiO_2 > SnO_2 > WO_3$. These characteristics arise from the varying diameters of the nanoparticles. Large particles in porous films scatters the visible light more effectively than small ones [5]. One more reason for the small transmittance of WO_3 is that the visible light shorter than 440 nm is absorbed by WO_3 (energy band gap, 2.4 eV).

Fig. 4 shows the time dependence of the average transmittance in visible-light region ($\lambda = 400$–700 nm, Fig. 3a) and the sheet resistance of the porous SnO_2 electrodes. The transmittance of SnO_2 gradually increased with the stirring time and became stable after 15 days, but the slight increase of the transmittance from 15 days to 30 days was observed, due to the decrease of the micrometer-ordered aggregates in Fig. 1b. The sheet resistance of the porous SnO_2 films decreased rapidly to $10\,k\Omega_{\square}$ after 5 days after which it remained constant. In spite of the presence of the large aggregates in the film produced after 5 days stirring, each SnO_2 particle appeared to be electrically connected to each other.

A transparent porous SnO_2 electrode stirred for 30 days was characterized by means of electrochemical measurements. Fig. 5 shows the cyclic voltammograms for an aqueous $K_4Fe(CN)_6$ solution using the porous SnO_2 electrode and a flat SnO_2 electrode. The porous SnO_2 electrode had a larger charge and diffusion current than those of the flat SnO_2 electrode. These increases depend on the porosity and surface area of the porous SnO_2 electrode [7, 8, 11]. Nitrogen-adsorption measurements revealed that the surface area and pore volume of the film were 84.9 $m^2\,g^{-1}$ (5 point BET) and 0.224 cc g^{-1} (BJH method cumulative desorption pore volume), respectively. Knowing the average weight and thickness of samples, 0.605 mg cm^{-2} and 4.13 μm, respectively, the roughness factor (r.f.) and the void fraction were determined. They are 514 and 32.8 %, respectively.

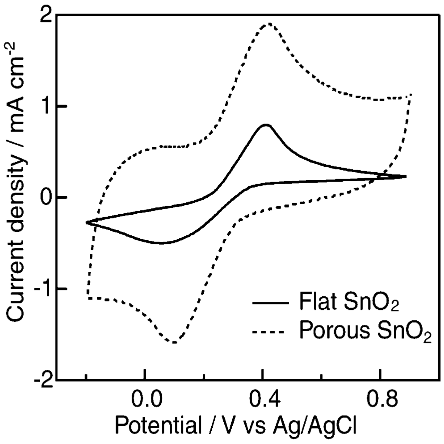

Figure 5 Cyclic voltammograms using a porous SnO_2 electrode (porous SnO_2 using the paste stirred for 30 days on F-doped SnO_2, Nippon Sheet Glass) and a flat SnO_2 electrode (F-doped SnO_2, Nippon Sheet Glass) as working electrodes. Counter electrode: Pt, Reference electrode, Ag/AgCl, 5 mM $K_4Fe(CN)_6$, N_2 gas was bubbled for 15 min. Potential sweep: 200 mV $s.^{-1}$

In conclusion, transparent porous electrodes of SnO_2, TiO_2 and WO_3 were fabricated from the commercially available powders by uses of a hot-stirrer, an evaporator, and an oven. This fabricating method is easy and uses only inexpensive equipment which can be applied also for other metal-oxide-nanoparticle powders, provided that the nanoparticles are insoluble in a nitric acid solution. The knowledge gained through this work will be useful for many applications and investigations of optoelectronic devices that exchange energies of light, electron, and molecule, which like dye-sensitized solar cells, are electrochromic and electroluminescent devices.

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