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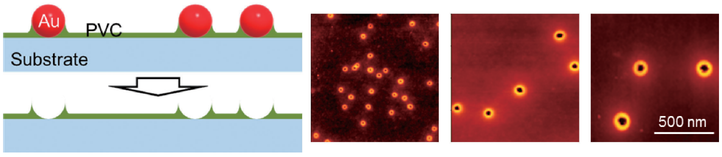

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Thin poly(vinyl chloride) films with size-controlled nanopores (40–150 nm diameter) are prepared by a new and simple method on ITO-coated glass plates and TiO_2 substrates by using monodisperse Au nanoparticles. These films are expected to be applied to nanomasks for nanoelectrode ensembles and templates for deposition of size-controlled metal nanoparticles.

Thin films with size-controlled nanopores or nanoholes have attracted much attention because of their wide variety of applications.[1–4] For example, a nanoporous film can be used as a template for nanoparticles. Size-controlled metal nanoparticles can be prepared on a substrate by spattering or evaporating metal on the template followed by its removal (lift-off method).[1,2] Electrodeposition can also be used for preparation of nanoparticles in the pores.[3] In addition, an electrode coated with a thin insulating film with nanopores or micropores serves as a nano- or microelectrode ensemble. They are studied for electrochemical analysis or applications such as advanced electrochemical capacitors, because of enhanced mass transport and current density.[4] Thin films with size-controlled nanopores are thus important. For these applications, the thin films must be stable and durable chemically and mechanically. In addition, for applications to a template for electrodeposition or a nanomask for nanoelectrode ensembles, it is preferable that the film is insulating. From these points of view, poly(vinyl chloride) (PVC) is an ideal material, because it is highly insulating, tough, flexible, and resistant to both acidic and alkaline solutions. Therefore, in this study, we develop a simple method for preparation of thin PVC films with size-controlled nanopores.

Previously reported methods for preparing nanoporous films are not necessarily easy to apply to PVC films. For example, methods of film preparation from polymer nanoparticles and a film precursor solution[5,6] are convenient but applicable only to oxide films such as titania (TiO_2) and alumina (Al_2O_3), because the polymer nanoparticles are decomposed and removed by annealing. Although polymer nanoparticles can also be removed by dissolution into organic solvents, the solvents for the polymer nanoparticles may also dissolve organic thin films such as PVC. Anode oxidation methods are also used for the preparation of nanoporous metal oxide films.[7] Electron beam lithography is a powerful method,[1,2] but the film must be electroconductive. In addition, it requires huge and expensive equipment. A track etch method,[8] which is used for production of membrane filters, also needs an expensive radiation device.

In this study, we employ monodisperse gold (Au) nanoparticles, which are chemically and thermally stable. Monodisperse Au nanoparticles with a wide variety of sizes (3–150 nm diameter) are commercially available. Here we use Au nanoparticles with 40, 100, and 150 nm diameter purchased from Tanaka Kikinzoku. Figure 1 illustrates the present method for preparing the nanoporous PVC film. In the first step (Figure 1a), Au nanoparticles are immobilized onto a solid substrate. Here we cast aqueous suspension of spherical Au nanoparticles protected with citric acid (diameter: 150 nm, pH ca. 4) (50 μL cm^{-2}) on an ITO-coated glass plate modified with (3-aminopropyl)triethoxysilane[9] and left for about 3 h in the dark. Intact Au nanoparticles were found on the substrate (ca. 10^8 particles cm^{-2}) by atomic force microscopy (AFM, Figure 2a) and scanning electron microscopy (SEM, Figure 2b). AFM measurements (NanoNavi Station/SPA400, SII Nanotechnology) were performed in a tapping mode with a silicon cantilever (SI-DF20, SII Nanotechnology). The AFM images were corrected with a Morphology Filter (SII Nanotechnology) to avoid overestimation of the particle size due to the AFM tip curvature radius (= 10 nm). If necessary, the packing and spacing of Au nanoparticles would be controlled by changing the surface charges of the nanoparticles and the substrate.[10]

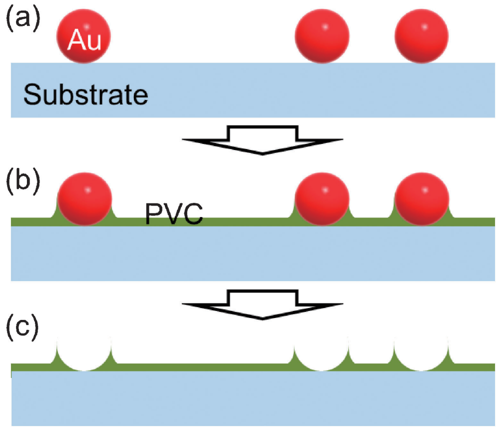

Figure 1. Preparation of a PVC film with size-controlled nanopores by using monodisperse Au nanoparticles.

In the next step (Figure 1b), thin PVC film is formed by a standard dip-coating technique (withdrawal rate was 1–2 mm s^{-1}) on the substrate with Au nanoparticles from a tetrahydrofuran (THF) solution containing 1 wt% PVC (degree of polymerization is about 1100, Wako Pure Chemical Industries). The substrate was heated at 80 °C for 30 min in order to evaporate THF. Finally, saturated aqueous solution of iodine (I_2) containing 36 mM potassium iodide (KI) was cast on the PVC-coated substrate (50 μL cm^{-2}) and left for at least 30 min. After the sample was rinsed with pure water in order to remove the ions, AFM (Figures 2c and 2d) and SEM (Figure 2e) images showed nanopores on the PVC film instead of Au nanoparticles. These results indicate that the Au nanoparticles are oxidized and dissolved by I_3^- and I^- contained in the cast solution, according to the following reaction 1.[11]

$$2Au + I_3^- + I^- = 2[AuI_2]^- \quad (1)$$

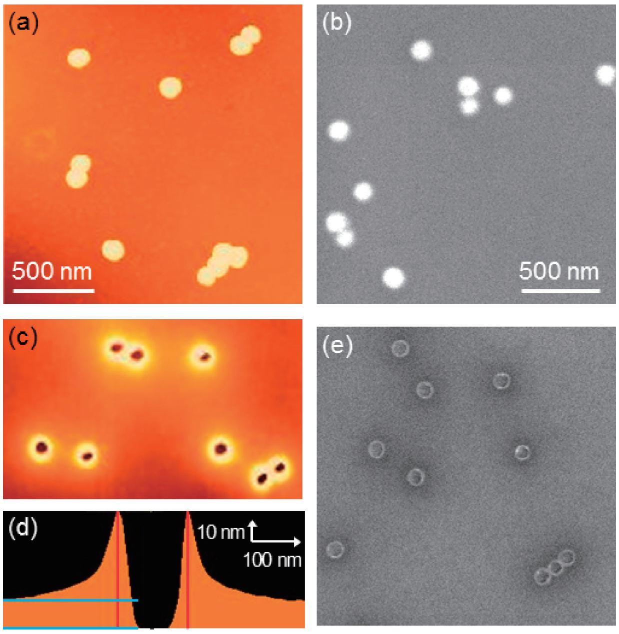

Figure 2. Typical (a, c) AFM and (b, e) SEM images of (a, b) immobilized Au nanoparticles (150 nm diameter) and (c–e) nanoporous PVC films prepared on ITO-coated glass plates. (d) A cross-sectional image of the nanopore.

The pore diameter is 151.7 ± 7.3 nm (average ± standard deviation, $n = 10$), which coincides with the diameter of the Au nanoparticles. The cross-sectional AFM image (Figure 2d) shows that the PVC film thickness is about 20 nm and that the thickness around the orifice is about 50 nm because of a meniscus formed around the nanoparticle. The thin PVC film exhibited good insulation. The AFM cantilever used with 10 nm curvature radius and 13° half-cone angle can reach the bottom of a pore of 150 nm diameter unless it is deeper than 310 nm. The surface roughness of PVC films was 5–10 nm. When the withdrawal rate for the dip-coating was as low as 0.1 $\mathrm{mm\,s^{-1}}$, PVC did not cover the substrate completely and ITO was partially exposed. On the other hand, the rate as high as 5 $\mathrm{mm\,s^{-1}}$ gave PVC films too thick without nanopores because PVC covered the Au nanoparticles completely. Tsuboi and co-workers have also prepared polymer films with nanopores by the use of 20 and 40 nm Au nanoparticles.[12] They vaporized the Au nanoparticles by pulsed laser. Their method, therefore, needs expensive laser equipment and gives polydisperse pores larger than Au nanoparticles. In contrast, the diameter of the nanopores formed in this study is in good agreement with that of Au nanoparticles.

We also prepared nanoporous films on a TiO_2 substrate in the same way. We have found plasmon-induced charge separation, which takes place at the interface between plasmonic metal (Au, Ag, or Cu) nanoparticles and a semiconductor such as TiO_2.[13–19] The charge separation can be applied to photovoltaics,[15,16] photocatalysis,[16] photochromism,[13,14,19] and others.[18,19] Coating TiO_2 with a thin insulating film with size-controlled nanopores would allow deposition of size-controlled metal nanoparticles and thereby materials and devices with sharp spectra. A TiO_2 film was prepared on a Pyrex glass plate from a ethanolic titanium alkoxide solution (NDH-510C, Nippon Soda) by dip-coating (withdrawal rate was 2 $\mathrm{mm\,s^{-1}}$), followed by calcination at 500 °C for 1 h. The colloidal solution of Au nanoparticles (150 nm diameter) was cast on the TiO_2 film and left for 30 min in the dark. Figure 3a shows an AFM image of the Au nanoparticles immobilized on TiO_2. Since the TiO_2 surface is charged positively due to partial protonation ($\text{–}OH_2^+$), negatively charged Au nanoparticles protected by deprotonated citric acid ($\text{–}COO^-$) are electrostatically adsorbed onto the TiO_2 surface in the solution at about pH 4. Subsequently, a PVC film was formed and Au nanoparticles were dissolved as described above. As a consequence, a PVC film with nanopores was formed on the TiO_2 substrate (Figure 3b).

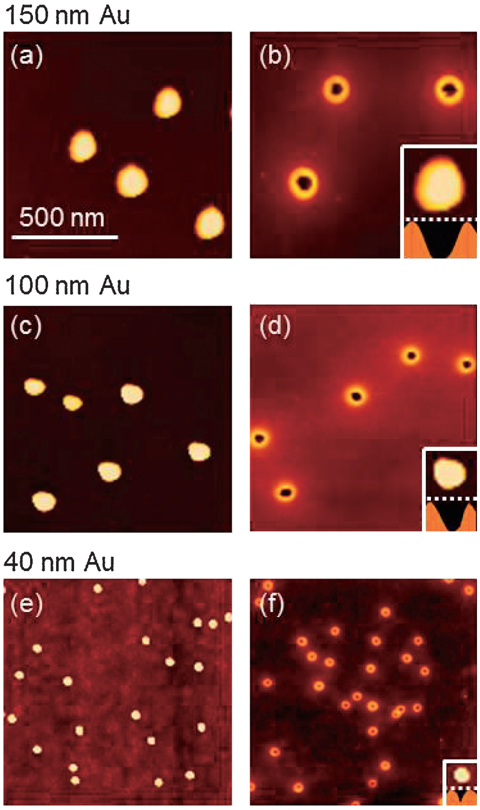

Figure 3. Typical AFM images of (a, c, e) immobilized Au nanoparticles (150, 100, and 40 nm diameter, respectively) and (b, d, f) nanoporous PVC films prepared on TiO_2-coated glass plates. Inset images are typical AFM images of Au nanospheres and cross-sectional images of the nanopores.

We also used Au nanoparticles of 40 and 100 nm diameter. As a result, thin PVC films with nanopores of corresponding size were obtained (Figures 3c–3f). In the cases of 40, 100, and 150 nm Au nanoparticles, the pore diameters were 40.4 ± 2.6, 101.7 ± 3.3, and 150.5 ± 5.2 nm, respectively ($n = 10$).

In summary, we developed a new and simple method for preparation of thin PVC films with size-controlled nanopores by using commercially available monodisperse Au nanoparticles and a conventional method for etching Au with iodine.

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