

## Fabrication of Metal–Polymer Nanocomposite with Beaded Structures Using Ordered Anodic Porous Alumina Template

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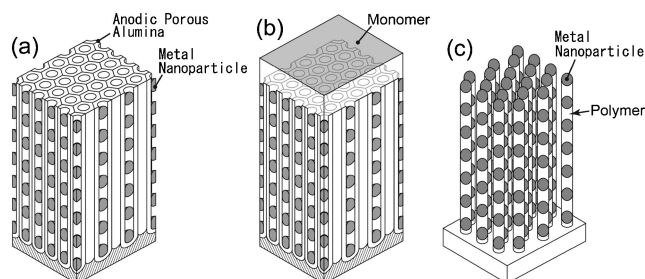
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The fabrication of nanocomposites consisting of uniform-sized metal nanoparticles arranged at uniform intervals in a fibrous polymer matrix is described. The combined process of metal deposition into periodic holes in anodic porous alumina and polymer injection into the holes yielded metal (Au, Ag)–polymer composite structures. In the obtained composition, metal nanoparticles are arranged at equal spaces in a fibrous polymer matrix.

The preparation of composite structures consisting of metal nanoparticles dispersed in a polymer matrix has attracted much interest due to the possibility for forming various types of functional devices, such as electronic, optical, and magnetic devices.<sup>1–3</sup> The performance of the obtained devices is strongly dependent on the size and uniformity of the metal particles. In addition, the arrangement of the metal particles in the polymer matrix also affects the performance of the obtained devices. The composite of metal nanoparticles and dielectrics will be applied to novel materials, such as negative index materials (NIMs). The optical properties of optics composed of NIMs will be optimized by the arrangement of nanoparticles.<sup>2</sup> A large number of processes have been reported so far for the preparation of metal–polymer nanocomposites.<sup>4–6</sup> However, a process that satisfies the requirements for preparing nanocomposite structures has not been established. In the present report, we describe the fabrication of nanocomposites consisting of uniform-sized metal particles arranged at uniform intervals in a polymer matrix. This process is based on the previously reported structure of orderly arranged metal nanoparticles in the holes of an anodic porous alumina matrix.<sup>7–9</sup> In this structure, the repetition of the formation of holes by the anodization and electrochemical deposition of metal generates a multilayered structure of metal particles in the holes of anodic porous alumina. Metal particles were arranged at regular interval by adjusting the anodization time. We found that the unfilled space in the holes can be filled with a monomer and that a composite structure consisting of metal nanoparticles with a beaded structure in a polymer matrix can be obtained after the polymerization. Although a large number of work on the preparation of nanostructures using anodic porous alumina as a template has been reported,<sup>10–12</sup> a composite structure with orderly arranged beaded metal particles has not been reported so far. An advantage of this process is the controllability of the size and arrangement of the metal nanoparticles in the polymer matrix. In addition, the process can be applied to a wide variety of composite systems consisting of metals and polymers. The composite structure obtained by the present process is expected to be used for the preparation of various functional devices typified by their functional optical properties, which originate



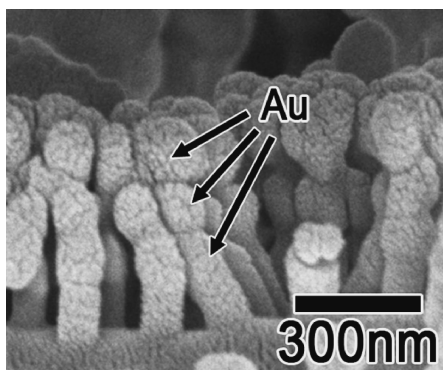
**Figure 1.** Schematic for the preparation: (a) multilayered metal nanoparticles in anodic porous alumina, (b) injection of monomer into the structure (a), and (c) fibrous polymer containing metal nanoparticles.

from the unique nanostructure of metal nanoparticles in the polymer matrix.

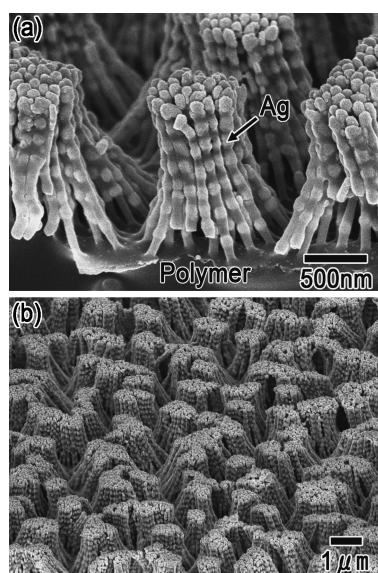
Figure 1 shows the schematic for the preparation of metal–polymer composite structures. The process consists of two main parts: the formation of multilayered metal nanoparticles in the holes of anodic porous alumina and the formation of composites by injecting a monomer into the hole and subsequent polymerization.

An Al sheet (99.99% purity) was electropolished in a mixture solution of perchloric acid and methanol. The Al sheet was then pretextured by imprinting using a metal mold with an ordered array of convexes. This process generates anodic porous alumina with an ideally ordered hole arrangement, because the pretextured pattern on Al can control the development of holes during anodization. After the anodization, metal particles were formed by electrochemical deposition using AC electrolysis. The electrolytes used for the metal deposition were 2.43 mM HAuCl<sub>4</sub> and 0.07 M H<sub>2</sub>SO<sub>4</sub> for Au, and 0.5 M AgSO<sub>4</sub> and 0.01 M H<sub>2</sub>SO<sub>4</sub> for Ag. Repeated anodization for the formation of holes and the electrochemical deposition of the metal resulted in a layered structure of metal particles in the holes of anodic porous alumina. Such anodization or electrochemical deposition proceeded by penetration of the electrolyte through the small gap between the metal particles and the walls of the porous alumina. After forming the multilayered structure of metal, a photocurable monomer (PAK-02, Toyo Gosei) was injected into the unfilled space in the holes and was polymerized by illumination from a UV source. The metal–polymer composites were obtained by resolving the residual Al and alumina matrix in 10 wt % NaOH. The obtained samples were observed by scanning electron microscopy (SEM: JSM-7200, JEOL).

Figure 2 shows a SEM image of the Au–polymer composite structure obtained by the present process. From Figure 2, it was observed that the obtained structure was composed of uniform-sized Au nanoparticles with a beaded structure in a fibrous



**Figure 2.** SEM image of Au-polymer composite.



**Figure 3.** SEM images of Ag-polymer composite: (a) high-magnification cross section and (b) low-magnification cross section.

polymer matrix. In the composite structure shown in Figure 2, each polymer fiber in the polymer matrix contains three Au particles. The Au particles are ellipsoid with major and minor axes of 120 and 80 nm, respectively. The diameter and height of each fibrous polymer are almost the same as those of the holes in the anodic porous alumina used as a template. This means that the photocurable monomer can penetrate into the entire space in each hole. Figure 2 also reveals that the Au particles are arranged at regular intervals in each polymer fiber, showing that the position of Au nanodots can be fixed by the process of injecting the monomer and the subsequent photopolymerization.

Figure 3 shows SEM images of the Ag-polymer composite. In the sample shown in Figure 3, each polymer fiber contains seven Ag nanoparticles in the matrix. The number of metal particles was determined by the number of repetitions of anodization and metal deposition. The maximum possible number of repetitions of this process (the number of nanoparticles) is greater for Ag than for Au. This is because the size

of the gap between the metal particles and the wall is larger in Ag than in Au owing to their difference in crystallinity. The high crystallinity of Ag results in larger gaps, which contribute to the well-controlled penetration of the electrolyte underneath the metal particles. From the high-magnification cross-sectional SEM image in Figure 3a, it can be confirmed that uniform-sized Ag nanoparticles are arranged at uniform intervals in the polymer matrix. The low-magnification SEM image in Figure 3b shows that the fibrous composite structure was formed over a large sample area. In the case of the Ag-polymer composite structure in Figure 3, the individual fibers aggregated with each other. This was mainly due to their high aspect ratio. The capillary force during the dehydration after removing the alumina matrix causes the aggregation of fibers. When particles come close each other, the surface plasmon will be coupled between neighboring Ag particles.

Composite structures consisting of metal (Au, Ag) nanoparticles with a beaded structure were fabricated through a combined process of the periodic metal deposition into the holes in anodic porous alumina and polymer injection into the holes followed by polymerization. In the obtained composite, the metal nanoparticles are arranged at regular intervals in the fibrous polymer matrix. The obtained composite, consisting of metal particles with a controlled period, will be used for the preparation of various types of functional optical devices, e.g., nonlinear optical or localized surface plasmonic devices.

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