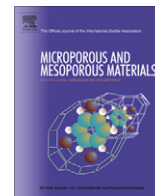




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Short Communication

Fabrication of Ag/Al(OH)₃ mesoporous nanocomposite film

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ABSTRACT

In this study, a Ag/Al(OH)₃ mesoporous nanocomposite film was fabricated for antibacterial and biomedical applications. First, a mesoporous Al(OH)₃ layer was prepared by alkali surface modification of an Al substrate. The prepared Al(OH)₃ layer was composed of flaky crystals woven within and covering the entire substrate surface so that the specific surface area was considerably enlarged because of voids of several tens of nanometers between the flakes. The substrate covered by the Al(OH)₃ layer was immersed in a solution of ethylene glycol where polyvinylpyrrolidone (PVP) and silver nitrate (AgNO₃) were dissolved for the polyol process. When the solution with the substrate was heated to 120 °C and maintained at that temperature up for 4 h, the Ag nanoparticles were nucleated and grown at the mesoporous Al(OH)₃ layer surface, as well as in the solution as colloids. It is believed that the Al(OH)₃ layer is a suitable matrix for the fabrication of mesoporous nanocomposite film.

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1. Introduction

Nanocomposite films in which metal nanoparticles were distributed in diverse matrices have been intensively studied for decades [1]. To disperse nanoparticles effectively into matrices, various kinds of porous substrates have been proposed. Because porous materials are favorable matrices for well dispersed nanoparticles [2–6], they can provide a large amount of nucleation sites for nanoparticles. The pores can act as nanoreactors for the nucleation of nanoparticles and confine their growth within the pores [2]. Considerable attention in the engineering field has been paid to disperse desirably metal nanoparticles in a matrix for potential applications with their electronic, optical, magnetic, chemical, and catalytic characteristics [7,8].

For chemical synthesis of nanoparticles or linkage to matrices, functional groups such as carboxylic acid (–COOH), carbonyl (–C=O), thiol (–SH) and hydroxyl (–OH) groups are generally utilized [9–12]. It has been reported that these functional groups can not only give rise to preferred nucleation sites but also offer coordination or linking of these groups to metal ions [12–14]. However, to enhance the chemical reactivity of metal nanoparticles, the nanoparticles must have a naked surface [15], and matrices should be exposed to the environment. Thus, the functional groups which inhibit direct reaction between the nanoparticles

and the environment should be clearly removed from the nanocomposite film surface. In the case of the aforementioned functional groups, it is difficult to eliminate those molecules without nanopartilces distortion because of the strong chemical bonds present.

In the polyol process for the synthesis of metal nanoparticles, especially of silver (Ag) nanoparticles, polyvinylpyrrolidone (PVP) [16] is usually employed for a capping agent as well as trisodium citrate [17] and polyvinylalcohol (PVA) [18]. The Ag nanoparticles have many possibilities for antibacterial and biomedical materials [19–21], hence the open structure of Ag nanoparticles in a nanocomposite film is very important for their practical applications. Therefore, a soluble capping agent used in the polyol process, like PVP, is effective at forming a nanocomposite film with an open structure using a porous matrix having a hydroxide surface.

In our previous research on mesoporous Al(OH)₃ film by alkali surface modification [22], the resultant film had a tremendous amount of surface pores and a remarkable increase in specific surface area by the presence of deposited flaky crystals. The alkali surface modification process, which allows the formation of a mesoporous surface, consists of alkali treatment and stabilization steps [22,23]. During the alkali surface modification process, Al and its naturally oxidized surface Al₂O₃ simultaneously react with the NaOH solution. The alkali treatment leads to the formation of a gelatinous layer that is a mixture of aluminate (Al(OH)₄[−]) and sodium (Na⁺) ions on the surface. In the subsequent stabilization process in boiling water, the gelatinous layer of aluminate ions transforms to aluminum hydroxide (Al(OH)₃) [22]. The porous Al(OH)₃ layer is expected to not only contain large amounts of nanoparticles but also provide new or improved nanoparticle

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functions. In the case of nanoparticles on the surface pores of porous nanocomposite film, each nanoparticle can be directly exposed to the environment where the reaction occurs. In this study, the Ag nanoparticles dispersed $\text{Al}(\text{OH})_3$ nanocomposite film was prepared by alkali surface modification and a polyol process for antibacterial and biomedical applications. The mechanism of Ag nanoparticle formation on the $\text{Al}(\text{OH})_3$ surface was discussed from the microstructural viewpoint.

2. Experimental details

Commercially pure Al (AA 1050, Al-0.4, Fe-0.25, Si) plates were used as substrates, and sodium hydroxide (NaOH, 93%, Duksan Pure Chemicals Co. Ltd.) was employed as a reagent for the alkali surface modification. Pure water was obtained by double distillation followed by filtration using a Millipore Milli-Q plus purification system with an electrical resistivity of 18.2 M Ω . Silver nitrate (AgNO_3 , 99.9%, Showa Chemicals Co. Ltd.) was used as the Ag ion source. Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, 99%, Sigma–Aldrich) and polyvinylpyrrolidone (PVP, K-15, Av. MW of 10,000, Sigma–Aldrich) were utilized to reduce Ag ions during the polyol process. All materials were used as-received without further purification.

The commercially pure Al (AA 1050) substrates were mechanically fine polished. A simple alkali surface modification process [22–24] composed of alkali treatment and stabilization was applied. The alkali treatment was performed in a 5×10^{-3} M NaOH solution (pH 14) at 80 °C for one minute. The alkali treated Al substrate was immediately immersed in boiling water for 30 min to stabilize the surface layer after the alkali treatment. For the measurement of pore size distribution by Brunauer–Emmett–Teller

(BET) method, cylindrical porous Al body whose dimension was 10 mm in diameter and 10 mm in length having 45% porosity was fabricated by powder metallurgical process, in which alkali surface modification was performed on the porous Al body.

The polyol solution was prepared with ethylene glycol as a solvent, PVP, and AgNO_3 . At the initial stage, PVP (1×10^{-4} M) and AgNO_3 (2×10^{-4} M) were dissolved into ethylene glycol and then both were stirred at room temperature until complete dissolution. Then, the system was heated to 120 °C, held at said temperature up to 4 h, and then rapidly cooled in a water bath. For synthesis and *in situ* dispersion of Ag nanoparticles on the substrate, each the alkali surface-modified substrate was immersed in the solution for synthesizing Ag nanoparticles using the polyol process. After the process, each Ag nanoparticles dispersed substrate was rinsed with distilled water and was ultrasonically cleaned with ethanol for 3 min.

The surface morphology of the substrate was observed by a field emission scanning electron microscope (FE-SEM, JEOL 6701F, JEOL) with energy dispersive spectroscopy (EDS). The chemical state of the surface layer was analyzed by X-ray photoelectron spectroscopy (XPS, VG Multilab ESCA 2000, Thermo Fisher Scientific) using a monochromatized Al K α X-ray source ($h\nu = 1486.6$ eV). The charge-up shifts of the XPS peaks were calibrated by adjusting the C 1 s peak position to 284.5 eV. For the cross-sectional nano-composite film observation, transmission electron microscopy (TEM, TECNAI G2, FEI) was performed with a high accelerating voltage of 200 kV. The TEM samples were prepared to observe the cross-sectional morphologies and selected area diffraction (SAD) patterns using a dual-beam focused ion beam (FIB, FEI Nova 600 Nanolab, FEI).

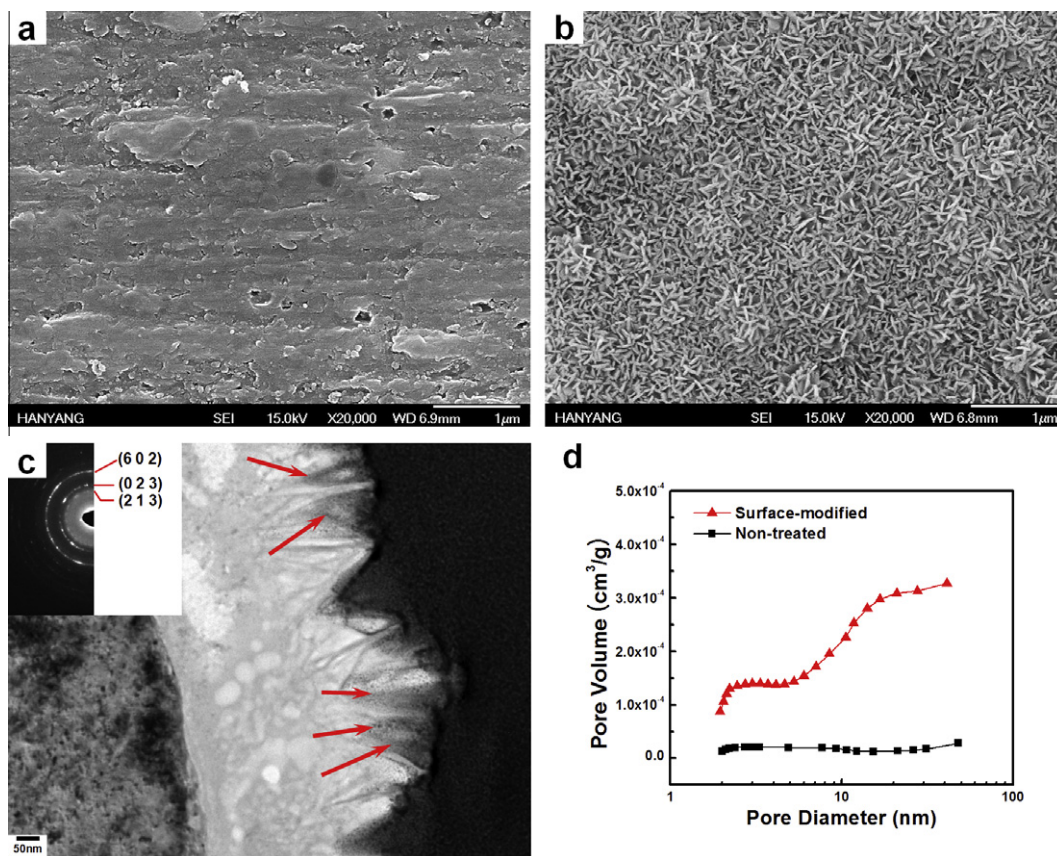


Fig. 1. SEM micrographs of (a) a polished Al substrate, (b) an alkali surface-modified substrate, (c) cross-sectional microstructure of surface-modified layer, and (d) BET results of non-treated and surface-modified specimen.

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