Advanced Powder Technology 25 (2014) 621–624

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Synthesis of a silver nanoparticle network induced by a micro-phase separation

Chika Takai, Aya Tamura, Masayoshi Fuji *

Advanced Ceramics Research Center, Nagoya Institute of Technology, 3-101-1, Honmachi, Tajimi, Gifu 507-0033, Japan

A R T I C L E I N F O

Article history:
Received 12 March 2013
Received in revised form 2 October 2013
Accepted 5 October 2013
Available online 18 October 2013

Keywords:
Nanoparticle network
Silver nanoparticles
Micro-phase separation
Acetone
1-Octanol

A B S T R A C T

Fabrication of a silver nanoparticles (AgNPs) network by only acetone (Ace) vaporization from AgNPs/cellulose acetate (CA)/Ace/1-octanol (Oct) suspension was proposed. When Ace vaporizes from CA/Ace/Oct ternary reaction system, a micro-phase separation occurs into polar phase (CA/Ace) and non-polar phase (Oct), then CA molecules deposit as three-dimensional network. Dispersed AgNPs in the ternary system gather each other along with the flow of CA network formation and AgNPs aggregates are taken into the CA network. In Ace-rich system, CA network density increased and surface of CA strut became smooth because of well dissolved of CA. AgNPs dispersibility also increased, however, lack of continuity on AgNPs network was observed. When AgNPs amount simply increased, CA network disappeared and large AgNPs aggregates remained on CA bulk film. On the other hand, with sum volume of AgNPs/CA kept constant, continuous AgNPs network was successfully formed according to CA dense network.

1. Introduction

In order to fabricate advanced functional materials containing nanoparticles, design of nanoparticles surface and microstructure, dispersion/aggregation behavior in solvent and matrix, and ordered array of the nanoparticle (dot, line, network, etc.) in the final product is significantly important. Focused on the third process, particle array should be changed to obtain desirable functionality. For example, three-dimensional (3D) network structure is necessary to obtain electro-conductivity of final product as touch panel and electro-magnetic shielding, and so on. Such particle array has been conventionally fabricated by a photo-etching, directly printing on the substrate, woven polymeric fiber with electro-conductive particles. However, these processes are wide range and need precise nanotechnology, and have difficulty to obtain desired network structures.

In this study, we propose nanoparticles manipulation technique through a micro-phase separation. A dry cast process, as one of phase separation, typically needs ternary reaction system including polymeric substance, its good solvent with low boiling point, and its non-solvent with high boiling point [1]. When the ternary solution is casted on a substrate, the good solvent starts to vaporize first. Then the solute polymer molecules separate from its non-solvent due to decreasing of solubility in the solution. The non-solvent having rather high surface energy [2] than the polymer tends to decrease its surface area in the solution. While, the solute polymer molecules are spread and deposit away from the place where non-solvent collects, that is, polymer molecules deposit around the non-solvent pond. After the residual good solvent vaporizes and the non-solvent is removed by washing, 3D polymer network remains. For examples, when cellulose acetate (CA) as a polymer substance, acetone (Ace) as a good solvent, and 1-octanol (Oct) as a non-solvent were used, CA network forms by only Ace vaporization. In the dry cast process, polymer network structure depends on composition ratio of the ternary solution and affinities among them [3,4]. When nanoparticles are added in the ternary system, formation flow of polymer network could be a guide for nanoparticles network. As a nanoparticle, silver (Ag) nanoparticle was chosen with hope for electro-conductive materials. For AgNPs network formation, optimum composition of ternary system with AgNPs has been investigated.

2. Experimental section

In ternary reaction system, cellulose acetate (CA, cetyl content of 39.8 mass%, molecular weight of 30,000, Aldrich Chemical Company Inc.) as a polymer substance, acetone (Ace, Wako Pure Chemical Industries, Inc.) as its good solvent, and 1-octanol (Oct, Wako Pure Chemical Industries, Inc.) as its non-solvent were used. For polymer network, CA was dissolved in Ace/Oct mixed solvent under stirring until the solution becomes transparent. The

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* Corresponding author. Tel.: +81 572 24 8110; fax: +81 572 24 8109.
E-mail addresses: c_takai@crl.nitech.ac.jp (C. Takai), ayazo.tmr@crl.nitech.ac.jp (A. Tamura), fuji@nitech.ac.jp (M. Fuji).

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http://dx.doi.org/10.1016/j.apt.2013.10.002

Table 1
Composition ratios of ternary reaction systems to prepare CA network with volume of CA kept constant as 0.90 cm^3.

	CA (g)	Ace (g)	Oct (g)
(a)	1.17	10.0	5.50
(b)	1.17	20.0	5.50
(c)	1.17	30.0	5.50

Table 2
Composition ratios of ternary reaction system to prepare AgNPs network; additions of (a) 20 vol% and (b) 30 vol% AgNPs with sum volume of AgNPs/CA kept constant as 0.90 cm^3.

	AgNps (g)	CA (g)	Ace (g)	Oct (g)
(a)	0.72	0.94	30.0	5.50
(b)	0.82	0.82	30.0	5.50

compositions of the solution were listed in Table 1, where volume of CA is 0.9 cm^3. The solution was coated on a glass substrate by a doctor blade (DP-50, Tsugawa Seiki Seisakusyo Ltd.) with coating speed of 1.0 m/s and wet thickness of 20 μm. The samples were dried in the air at relative humidity range of 40% and 60% at 25 °C for 2 h. For Ag network, Ag nanoparticles (AgNPs, 41.0 nm diameter, Nisshin Engineering Inc.) were used. Firstly, the above ternary solution was prepared, and then AgNPs were dispersed in there using an ultrasonication (Power sonic Model 50, Power sonics Inc.) for 10 min. The suspensions were coated on a glass substrate and dried in the same way. The composition ratios of prepared samples were 10 vol% AgNPs added in Table 1a, 10 vol% and 20 vol% AgNPs added in Table 1c, 20 vol% and 30 vol% AgNPs added with sum volume of AgNPs/CA kept constant as 0.90 cm^3 as shown in Table 2a and b.

Formation of the CA and Ag network were confirmed by a scanning electron microscope (SEM, JSM-7000F, JEOL Ltd.) and existence of AgNPs was confirmed by a COMPO image of SEM. AgNPs dispersibility was characterized by a laser diffraction scattering (Microtrac MT-3000, Nikkiso Co., Ltd.).

3. Results and discussion

Firstly, formation of CA network was confirmed. Three ternary solutions were prepared with different Ace amounts as shown in Table 1a–c. Fig. 1a–c shows SEM images of the obtained samples with inserted low magnified observations. In the all conditions, CA network formed. When Ace amount is small (Fig. 1a), CA strut is thick and has rough surface. With increase in Ace amount (Fig. 1b), the CA strut surface became smooth. Further increase in Ace amount (Fig. 1c) made thin CA struts dense network. Based on Flory–Huggins theory, the composition of Table 1a belongs to binodal area [5]. This composition has low solubility for CA molecules, therefore CA molecules seems to already deposit before Ace vaporizes. The rough surface seen in Fig. 1a could be caused by "the already-deposited-CA". With increase in Ace amount, bundle of CA molecules becomes to be unwoven and it can be spread in the reaction system. That is why the deposited CA strut showed smooth surface (Fig. 1b). With further increase in Ace amount, retention time of Ace in the reaction system becomes long. The further spread CA molecules slowly separate from Oct which resulted in dense network with thin CA strut (Fig. 1c).

Fig. 2a and b shows COMPO images of samples prepared by addition of 10 vol% AgNPs in Table 1a and c, respectively. In these images, deposits in the form of lines and networks with light gray color are deposited CA and particulates with light color are AgNPs. In Fig. 2a, the AgNPs aggregates locally appeared in the thick CA struts with around 1 μm. While in Fig. 2b, CA struts formed 3D network structure and AgNPs evenly dispersed in each CA struts.

Aggregation size of AgNPs in CA/Ace solutions corresponding to Table 1a, b and c was measured by laser diffraction method. The results were (a) 403 nm, (b) 237 nm, and (c) 182 nm, respectively. With increase in Ace amount in the suspension, dispersibility of AgNPs increased. It seems that surface of AgNPs is relative polar and have good affinity with CA/Ace solution. In the ternary system with AgNPs, when Ace starts to vaporize, AgNPs also move along with flow of CA separation from Oct. Because of good affinity between AgNPs and CA/Ace, AgNPs can be taken into the deposited CA struts. When Ace amount is small (Fig. 2a), quickly lack of

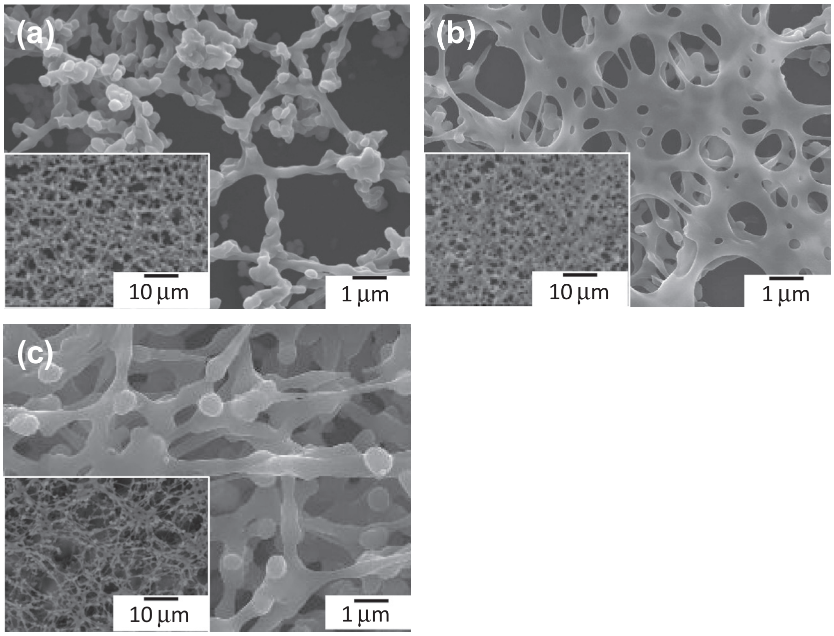

Fig. 1. Formation of CA networks prepared in different conditions which corresponds to Table 1a, b and c. Each inserted images are low magnified observations.