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

Authors: Chika Takai, Aya Tamura, and Masayoshi Fuji*

Authors' affiliation: Advanced Ceramics Research Center, Nagoya Institute of Technology

Affiliation address: 3-101-1, Honmachi, Tajimi, Gifu 507-0033

TEL: +81-572-24-8110, FAX: +81-572-24-8109

Authors' 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, corresponding author)

Abstract less than 200 words

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.

Keywords: nanoparticle network, silver nanoparticles, micro-phase separation, acetone, 1-octanol

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, 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.

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 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 $^{\circ}\text{C}$ for 2 hours. 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 minutes. 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 1(a), 10 vol% and 20 vol% AgNPs added in Table 1(c), 20 vol% and 30 vol% AgNPs added with sum volume of AgNPs/CA kept constant as 0.90 cm^3 as shown in Table 2(a)(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.).

Results and discussion

Firstly, formation of CA network was confirmed. Three ternary solutions were prepared with different Ace amounts as shown in Table 1(a)-(c). Figure 1(a)-(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. 1(a)), CA strut is thick and has rough surface. With increase in Ace amount (Fig. 1(b)), the CA strut surface became smooth. Further increase in Ace amount (Fig. 1(c)) made thin CA struts dense network. Based on Flory-Huggins theory, the composition of Table 1(a) 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. 1(a) 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. 1(b)). 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. 1(c)).

Fig. 2(a) and (b) shows COMPO images of samples prepared by addition of 10 vol% AgNPs in Table 1(a) 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. 2(a), the AgNPs aggregates locally appeared in the thick CA struts with around 1 μm . While in Fig. 2(b), 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 1(a), (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. 2(a)), quickly lack of Ace in the reaction system induces AgNPs aggregation. Besides, an increase in volume of solid polar phase including AgNPs/CA seems to provide thick CA struts. While Ace amount increased (Fig. 2(b)), AgNPs dispersibility in the thin CA struts were improved and also CA network structure was kept although it became slightly loose. This is because AgNPs dispersibility is already high in Ace-rich system (ie, before phase separation starts) due to good affinity between AgNPs and Ace. Furthermore, the long time phase separation prevents from AgNPs aggregation during thin CA strut formation and also provides dense CA network.

Observing carefully sample with 10 vol% AgNPs in Table 1(c) (inserted image of Fig. 2(b)), there were lots of disruptions of AgNPs network. Thus, amount of AgNPs increased up to 20 vol% in the condition of Table 1(c). Fig. 2(c) shows COMPO image of the obtained sample. Contrary to our expectation, CA network totally disappeared and AgNPs aggregations just dispersed on the smooth CA bulk surface. From these results, simply increase in AgNPs is not suitable for continuous AgNPs network formation.

A sum volume of solid polar phases (AgNPs/CA) was focused. As shown in Table 2, volume of

AgNPs increased from (a) 20 vol% to (b) 30 vol% with sum volume of AgNPs/CA kept constant as 0.90 cm^3 . Figure 3(a)(b) shows COMPO images of samples prepared with conditions of Table 2(a) and (b), respectively. Both samples showed uniform network formation. When 20 vol% AgNPs added (Fig. 3(a)), AgNPs disruptions were still observed. However, with increase in AgNPs to 30 vol% (Fig. 3(b)), AgNPs successfully connected each other. In addition, density of the obtained network seems to be similar to an original CA network shown in Fig. 1(c).

Conclusion

A simple AgNPs network fabrication has been proposed with only solvent vaporization via micro-phase separation. In order to obtain continuous AgNPs network, affinity between AgNPs and ternary reaction system, composition ratio considering surface property of AgNPs are key factors. By considering these relations, the proposed technique can be applied for other metal nanoparticles, oxides, non-oxides. In addition to network, adjustment of the ternary system provides different polymer structure such as dot, line, etc. Therefore, various nanoparticles arrays can be achieved.

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Figures

Figure 1. Formation of CA networks prepared in different conditions which corresponds to Table 1

(a), (b), and (c). Each inserted images are low magnified observations.

Figure 2. COMPO images of samples prepared by addition of (a) 10 vol% AgNPs in Table 1(a), (b) 10 vol% and (c) 20 vol% AgNPs in Table 1(c).

Figure 3. COMPO images of samples prepared by addition of (a) 20 vol% AgNPs and (b) 30 vol% AgNPs with Ag/CA volume kept constant which corresponds to Table 2(a) and (b), respectively.

Tables

Table 1. Composition ratios of ternary reaction systems to prepare CA network with volume of CA kept constant as 0.90 cm³.

	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

Polymer network

Ag nanoparticle network

Micro-phase separation-mediated metal network structure