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Preparation of core–shell microstructures using an electroless plating method

Chang-Hyun Song [a,b], Youngmin Kim [a], Byeong-Kwon Ju [b,*], Jong-Woong Kim [a,*]

[a] Display Components & Materials Research Center, Korea Electronics Technology Institute, 68 Yatap-dong, Bundang-gu, Seongnam 463-816, Korea
[b] Display and Nanosystem Laboratory, College of Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 136-713, Korea

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ABSTRACT

A simple approach for the preparation of core–shell microstructures with an anisotropic shape is proposed in which an Ag nanowire/polyurethane acrylate (AgNW/PUA) composite produced by inverted layer processing is used as a temporary template for the sequential electroless plating of a Cu metal core and Ni shell. Through careful optimization of the metallization conditions, a Cu@Ni core–shell microstructure with an anisotropic shape (i.e., an aspect ratio greater than five) is obtained, which can be easily detached from the template through simple sonication. This technique is therefore considered to be readily applicable to the fabrication of conductive fillers for use in composite structures.

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1. Introduction

Core–shell metallic structures have received much attention because of the way in which their chemical, catalytic, and electro-magnetic properties differ from those of individual materials [1–5]. For example, Ag@Ni core–shell structures are known for their unique catalytic and electro-magnetic properties that make them well suited to the fabrication of materials to shield against electromagnetic interference (EMI) [5]. These core–shell structures are typically synthesized through chemical reduction, a method which is really only suited to small-scale (i.e., nanoscale) materials because of the long processing time required [6–9]. For example, C. Li and Y. Yamauchi employed a chemical reduction method with an addition of block copolymer surfactants to make the Ag@Pt nanostructures [6]. They achieved a fabrication of physically stable core–shell structures, but the size of the products was still ranged from 30 to 50 nm in diameter. M. Shao et al. employed a redox-transmetalation method to synthesize carbon-supported Co@Pd nanoparticles, and revealed that a uniform Pd shell could be formed around Co cores by their approach, but just in nanoscale as well [7]. Although there have been other methods developed to achieve core–shell materials with different shapes, the long synthesis time and narrow processing window make these unsuitable for fabrication of the microscale core–shell structures with a specific shape.

Metallic microscale wires or rods are well suited to the fabrication of highly conductive structures, as only a relatively low density is needed to achieve percolation [10–13]; i.e., they have the potential to lower the solid content needed for a highly efficient EMI shielding film or a printable conductive paste. Yet unlike nanoscale synthesis, the simple and rapid fabrication of microscale wires and rods has been impeded by the difficulty in controlling the growth direction through the selection of a proper reducing agent alone. An electrochemical growth method reported to allow the fabrication of dendritic structures could be useful for the preparation of microscale irregular-shaped core–shell structures, but this method requires an expensive electrochemical workstation and fails to provide adequate shape control [14,15]. Thus, unfortunately, a simple and scalable method for fabrication of the microscale and anisotropically-shaped core–shell structures has not been reported so far.

This paper therefore introduces a simple, intuitive approach to the synthesis of core–shell microwires/rods through electroless plating. The main idea we adopted in this study was a use of a multiple metallization onto a free standing metal/polymer composite film with a preformed seed structure. Here we used Ag nanowires (AgNWs) for the seeding because of their high anisotropy in shape, and tried to embed them into the surface of free standing polymer by an inverted layer processing already reported in our previous study [16]. By this embedment, the nanowires were firmly fixed onto the polymer, and did not separate from it whole through the metallization process. After the final metallization, the microscale wires with core–shell structures were successfully fabricated and they could be physically detached by a simple sonication.

* Corresponding authors.
E-mail addresses: bkju@korea.ac.kr (B.-K. Ju), wyjd@keti.re.kr (J.-W. Kim).

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2. Experimental procedures

2.1. Fabrication of an AgNW/PUA composite

Polyester diol with a number-average molecular mass (Mw) of ~1000 was purchased from Songwon; methyl ethyl ketone (MEK), isophorone diisocyanate (IPDI), dibutyltin dilaurate, and 2-hydroxyethyl acrylate (HEA) were purchased from Sigma-Aldrich Chemicals; and dipentaerythritol-hexaacrylate (DPHA) and Irgacure 784 were purchased from Entis and Shinyoung Rad. Chem., respectively. All reagents were used as received without further purification. A flask charged with polyol (100 g, 100 mmol) and MEK (100 mL) was heated to 50 °C and held at that temperature until the solution turned clear, after which IPDI (33.3 g, 150.0 mmol) and dibutyltin dilaurate (cat.) were added. This mixture was then heated to 60 °C for 3 h, and after adding HEA (11.6 g, 99.9 mmol), was stirred for a further 3 h at 60 °C before cooling to room temperature [17]. The resulting solution contained 59.0% solid urethane acrylate 1 by weight and produced a stretchable film, but one that was deformed by peeling from a glass substrate. It was therefore mixed with a high-functionality DPHA cross-linker and Irgacure 184 to a ratio of 10:2:0.72 to increase the stiffness of the film produced from this precursor upon UV curing.

The procedure used to fabricate the AgNWs-polymer template was essentially the same as that outlined in a previous study [16], but was slightly modified to be compatible with the polyurethane acrylate (PUA) polymer used in this instance. In this process, a glass substrate was first cleaned sequentially with detergent, de-ionized water and isopropanol, and then placed on a Mayer rod coater. Several drops (0.3 mL) of an ink (Cambrios, USA) containing AgNWs with an average diameter of 25 nm and length of 15 μm were then applied, and a #4 Mayer rod (R.D. Specialties, Inc., USA) was immediately rolled over the top to evenly spread the ink across the glass surface. Pre-prepared Solution A was then applied using a spin coater, and after drying the samples at 50 °C for 20 min, they were cured with a UV lamp. The resulting polymer-coated glass was subsequently immersed in cold water (25 °C) to induce hygroscopic swelling of the polymer, thus allowing it to be peeled from the glass. This produced a free-standing, one-side composite film with a thickness of 100 μm.

2.2. Preparation of Cu@Ni core–shell structures

A schematic description of the fabrication procedure used is presented in Fig. 1. Here, the as-prepared AgNW-PUA composite film was cleaned with detergent, de-ionized water and isopropanol, and then immersed sequentially into each of the electroless plating solutions to form the core and shell [17,18]. Electroless plating is an auto-catalytic chemical method mainly used to deposit a layer of specific metals such as Cu, Ni and Au on a metal or polymer. This approach relies on the presence of a reducing agent which reacts with the metal ions to reduce them and deposit the metal. Fundamentals of the electroless plating method are well documented in the literature [19]. Electroless plating of up to 12 min at 85 °C in a bath containing 7 g/L of $CuSO_4$, $5H_2O$, 25 g/L of potassium sodium tartrate, 4.5 g/L of sodium hydroxide, and 9.5 g/L of formaldehyde was used to form Cu cores. For the nickel shell, the plated samples were immersed for up to 30 s in an 80 °C bath containing 25 g/L of $NiSO_4 \cdot 6H_2O$, 30 g/L of $NaH_2PO_2 \cdot H_2O$, 30 g/L of $C_6H_5Na_3O_7 \cdot 2H_2O$, and 30 g/L of Na_2CO_3. During both plating processes the solutions were vigorously stirred, with the samples being washed after each stage with flowing water for 30 s, and then immersed in an isopropanol bath. Ultra-sonication was used to separate the final core–shell structure from the template.

2.3. Evaluation of the core–shell structures

The surface morphology was measured by atomic force microscopy (AFM; XE-100TM, Park Systems, USA), while a field-emission scanning electron microscope (FESEM; JSM6700F, JEOL Ltd., Japan) equipped with an energy dispersive spectrometer (EDS) was used to investigate the microstructure and composition of the AgNW network. A cross-section of the core–shell structure was prepared by a focused ion beam (FIB, JIB-4601F, JEOL Ltd., Japan) system. The optical transmittance and reflectance was measured using a UV–visible spectrophotometer (V-560, Jasco, Japan), with the sheet resistance (R_s) measured by a 4-point probe system (MCP-T610, Mitsubishi Chemical, Japan).

3. Results and discussion

A percolated AgNW network structure was initially coated onto glass prior to immersion in the electroless plating solutions, but its low adhesion to glass meant that it was easily detached during plating by the mix of shear and tensile stresses generated by the upward and lateral movement of the liquid [20]. This made it impossible to control the shape and composition of the microstructures formed with any real precision, and so the AgNW network was instead partially embedded in a dielectric polymer. Fig. 2a shows the surface of the AgNW/PUA composite produced after it was peeled from its initial glass substrate,

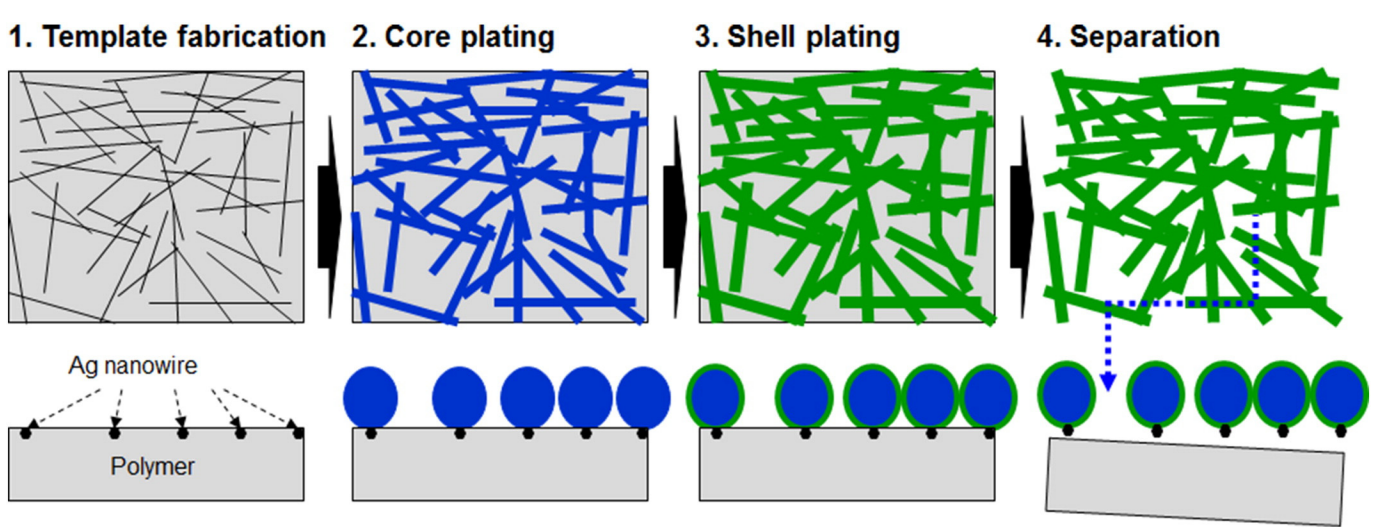

Fig. 1. Schematic showing the fabrication of core–shell microstructures.

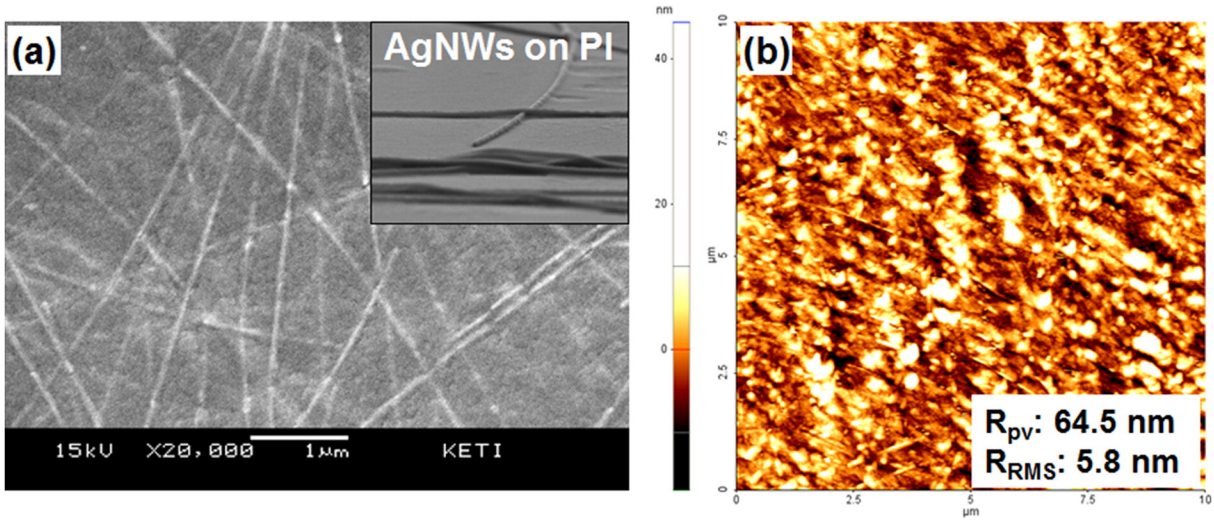

Fig. 2. (a) Surface morphology and (b) AFM topography of an AgNW-PUA composite temporary template. Inset in (a) is a tilt-view of the AgNWs on PUA.

clearly demonstrating that they were successfully embedded within the polymer. In contrast, when the nanowires are coated onto the preformed film, as shown in the inset image in Fig. 2a, they are more likely to be just placed on the polymer, not properly embedded. The AFM analysis of the surface morphology in Fig. 2b indicates that some AgNWs are fully exposed to the air, while others are buried in the polymer, based on the fact that the R_{pv} and R_{RMS} values of the same AgNWs on glass are typically greater than 100 nm and 10 nm, respectively. Measurement of R_s by a four point probe method confirmed that some AgNWs are indeed exposed, which is very different to an AgNW/colorless polyimide (cPI) composite, in which only a very small fraction of the nanowires are exposed and plasma treatment is needed to expose them [16]. This difference is possibly due to the limited wettability of the pre-polymer to the glass and AgNWs.

Onto the embedded AgNWs, Cu and Ni were sequentially deposited by electroless plating. Fig. 3a–d show the effect of varying the amount of time that the AgNW/PUA composite is immersed in the electroless Cu plating solution, with even a relatively short period of immersion (6 min) clearly producing Cu metallization along the exposed AgNWs. Moreover, the areas between the AgNWs remain very clear and free of any kind of embossed structure. Increasing the period of immersion to 8 min increased the size of the metal structure while keeping the PUA areas clear; however, a further increase in time to 10 min resulted in the formation of particulate Cu on the PUA areas. Increasing the immersion time beyond this only resulted in the composite surface becoming overly metallized, and so an immersion time of 10 min is considered to provide the best balance between forming stable wire/rod structures while avoiding unnecessary metallization. Fig. 3e–h show the samples metallized with Cu for 10 min after Ni plating for relatively short periods of time to ensure that only a thin capping layer was formed on the surface of the Cu cores. As shown in Fig. 3f and g, only 15–20 s of immersion was needed to change the morphology of both the Cu wires and PUA, which indicates that both surfaces were metallized by a thin coating of Ni that is shown in more detail in Fig. 3h. Unfortunately, any further increase in the immersion time caused unwanted interconnections to be created between the plated core–shell structures that made it impossible to obtain the desired structure, and so the Ni plating time was kept to 20 s.

Table 1 shows the effect that electroless plating has on the optical and electrical characteristics of the AgNW/PUA composite, with the transmittance (85.13%) and R_s of (565.7 Ω/sq) remaining relatively unchanged during the first 6 min of Cu plating due to the metallization

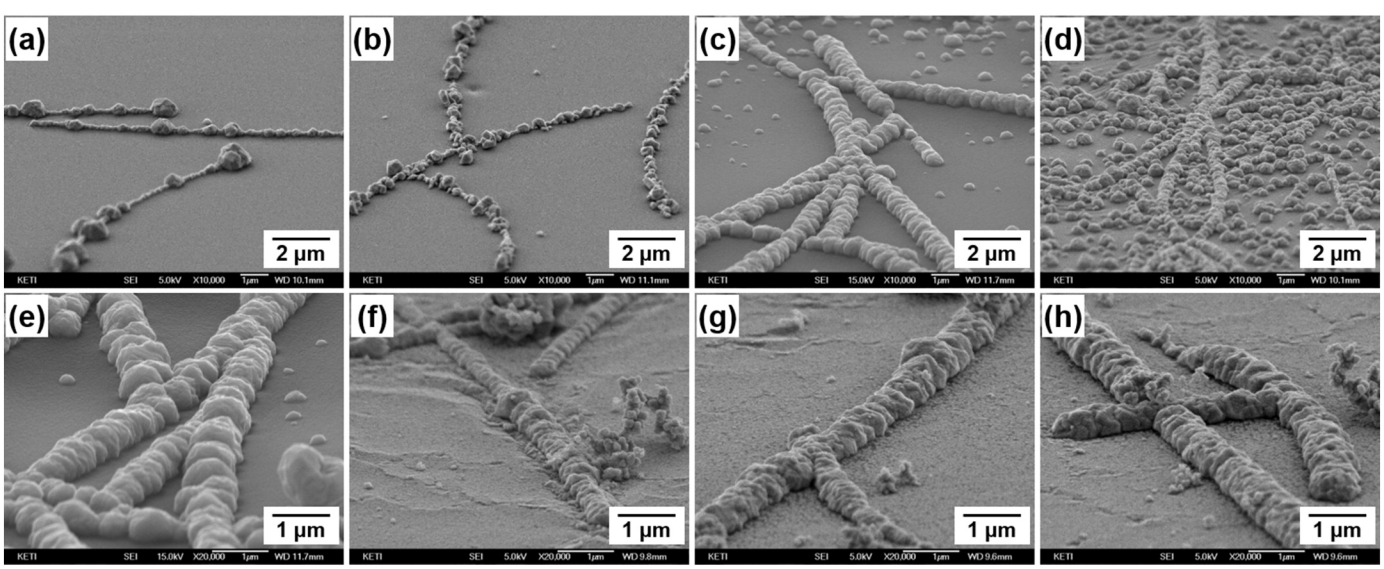

Fig. 3. Tilt-views of samples after (a) 6, (b) 8, (c) 10, and (d) 12 min of Cu plating, and of sample (c) after (e) 10, (f) 15, (g) 20, and (h) 30 s of Ni plating.

Table 1
Optical and electrical properties of samples with various Cu and Ni plating times.

Plating time (min)	Copper			Plating time (s)	Nickel (copper plating: 10 min)		
	Transmittance (at 550 nm, %)	Reflectance (at 550 nm, %)	Sheet resistance (ohm/sq)		Transmittance (at 550 nm, %)	Reflectance (at 550 nm, %)	Sheet resistance (ohm/sq)
0	85.13	8.51	565.7	10	35.12	18.39	12.3
6	78.67	12.69	431.3	15	22.54	23.72	5.6
8	73.28	14.24	278.6	20	16.15	30.74	0.9
10	41.01	16.63	15.6	30	8.09	33.46	0.9
12	14.71	28.89	1.4				

being largely random and lacking in long-range connectivity. The situation was much the same after 8 min, but an increase in long-range connection after 10 min caused a rapid drop in the transmittance and R_s. Interestingly, further immersion for 2 min produced a further significant drop in R_s, but at this point the composite was no longer transparent due to excess Cu deposition. Subsequent Ni plating had the effect of causing a rapid decrease in transmittance, which is most likely the result of Ni metallization on the PUA. The R_s stabilized after 20 s of Ni plating, and although this did not decrease with further immersion, the continued decrease in transmittance and increase in reflectance suggests that metallization was still occurring.

Fig. 4a shows a top-view of the Cu@Ni core–shell structure created on the AgNW/PUA composite template under optimized conditions (10 min of Cu plating and 20 s of Ni plating), with a line profile of the height of the core–shells formed. This structure was designed so that the AgNWs would be sparsely distributed, providing sufficient gap between each nanowire to ensure that they would not become interconnected. The SEM image in Fig. 4b shows a cross-section of the Cu@Ni core–shell structure fabricated on an exposed AgNW, which clearly demonstrates that metallization proceeded from AgNW side of the template. Although it is difficult to distinguish between Cu and Ni in this image, the EDS data in Fig. 4c–d indicate that Cu@Ni core–shell structures were successfully obtained by this simple sequential approach.

Fig. 5 shows these core–shell structures after they were peeled from the template and dried, revealing them to be around 2–2.5 μm in width and more than 10 μm in length, which results in an aspect ratio of greater than 5 and an anisotropy to their shape that makes them ideal for use as a conductive filler in metal-polymer composites. The interconnection seen between these structures is the result of the original form of the AgNW network, and should prove beneficial to creating

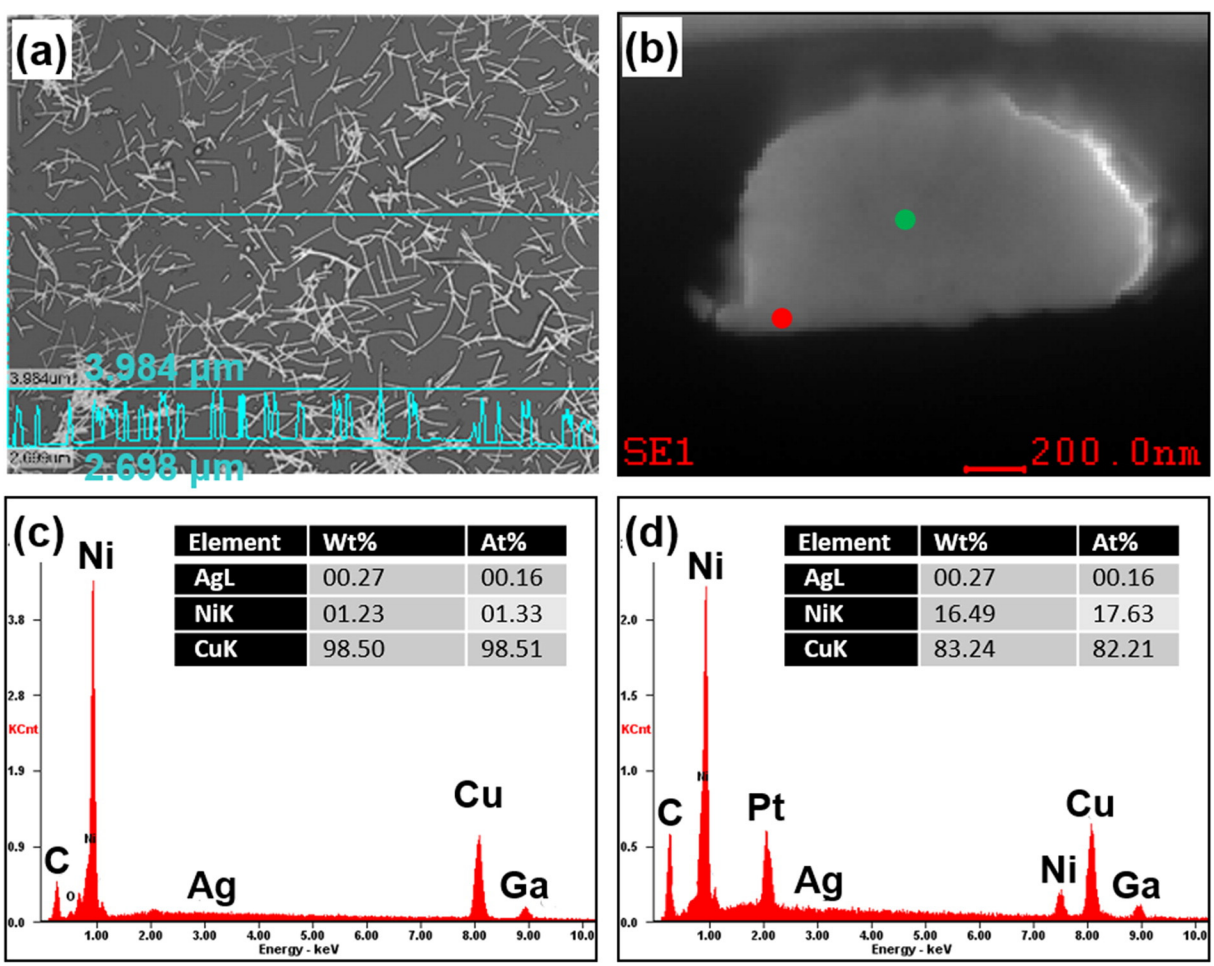

Fig. 4. (a) Surface profile of a sample plated with Cu (10 min) and Ni (20 s). (b) Cross-sectional view of a Cu@Ni core–shell microstructure. EDS peaks and compositions for the (c) green and (d) red points in (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

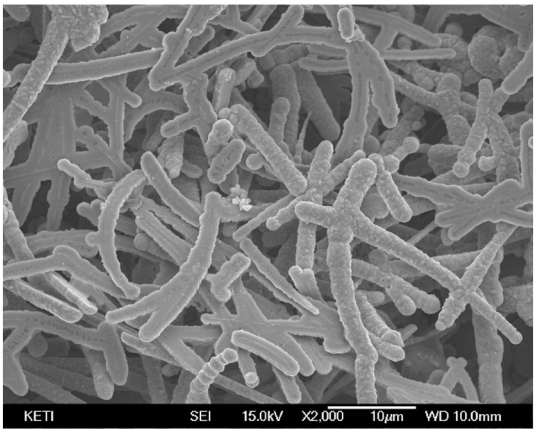

Fig. 5. Fabricated Cu@Ni core–shell microstructure.

three-dimensional conductive pathways in a composite structure. Another thing to note is that the composition of the core and shell produced by this method is solely dependent on the plating solutions selected. Thus, if we consider the fact that there are many solutions already available for electroless metallization, then this simple approach has incredible potential from an engineering perspective. Furthermore, the number of shell layers can be varied through multiple immersions, meaning that metallic structures with three- or even four-fold piles of shells could potentially be achieved using this simple method. If we consider that the electroless plating is a generally accepted industrial method to form a metal layer, this approach is very competitive when compared to the common chemical synthetic methods [6–9]. Especially, the processing window to control the size and shape of the fabricated products is relatively large in comparison to a common chemical synthetic method. We needed to control only three parameters such as time, temperature and pH of the solutions. It must be reminded that the extremely narrow processing window in a normal synthetic approach by reduction often makes it hard to be adopted for a large scale fabrication. To the best of our knowledge, this is the first achievement of realizing low-cost and simple fabrication of microscale and anisotropic (in shape) core–shell structures.

4. Conclusion

Metallic core–shell microstructures with an anisotropic shape have been successfully achieved using a simple method that uses a template created by partially embedding silver nanowires into the surface of a soft polymer, followed by sequential electroless plating. This not only allows control over the composition of the core and shell by varying the plating solution, but repeated immersions can be used to create a desired number of shells. In this case, optimization of the conditions produced a Cu@Ni core–shell structure with an anisotropy determined by the shape of the exposed AgNWs on the original template. If they are used as a conductive filler in a composite structure, this structure is expected to be beneficial in lowering the percolation threshold. This newly developed method is therefore believed to provide an effective means of overcoming the major challenges that have previously been faced in preparing core–shell microstructures with an anisotropic shape.

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