PAPER

Conducting Ag/oligothiophene complex pastes through a simple quenching/chelation method

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This paper describes a simple and environmentally friendly approach—a facile, one-pot, quenching/chelation method—for the fabrication of a silver paste in the form of Ag/oligothiophene complex composites. These Ag/oligothiophene complex composites possess excellent conductivities of 1.8×10^4 S cm^{-1} in the bulk state and 6.08×10^2 S cm^{-1} in the form of thin films. We have used X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) to characterize the microstructures of these novel Ag/oligothiophene complex composites.
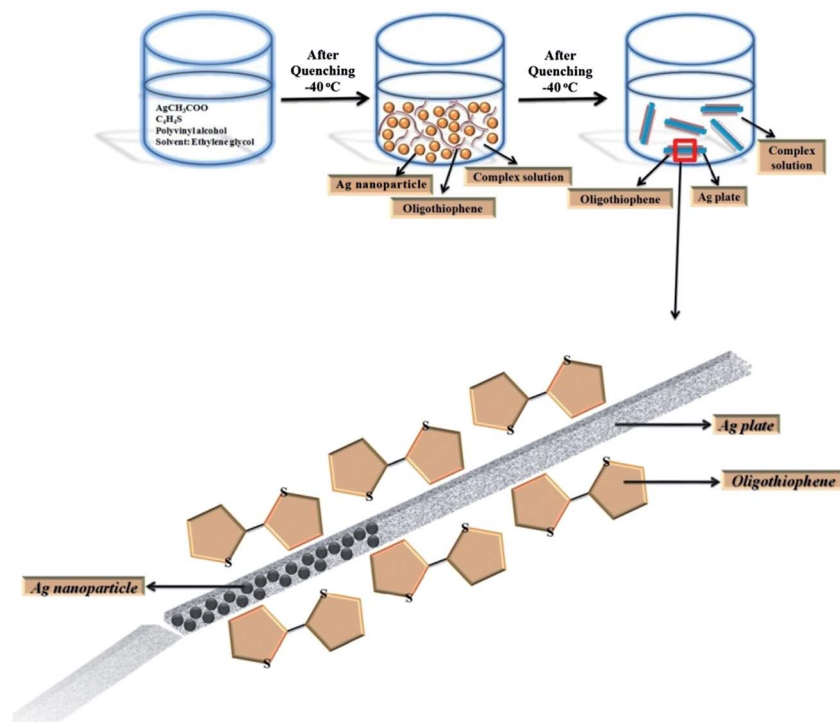
Introduction

Conducting polymers are attracting considerable attention because their electronic, magnetic, and optical properties are useful in electrochemical displays, sensors, catalysis, redox processes, capacitors, and electromagnetic shielding.[1–3] Among them, polythiophenes (PThs) and their derivatives obtained through polymerization of thiophene monomers [*e.g.*, bithiophene (2T), quarterthiophene (4T), sexithiophene (6T), and oligothiophenes] have been studied extensively because of their many applications in organic light emitting diodes (OLEDs),[4–6] organic field-effect transistors (OFETs),[7–10] chemosensors,[11,12] biosensors,[13,14] and other electronic devices.[15,16] PThs and their derivatives have been the most commonly studied electrically conducting polymers because of their excellent environmental and thermal stabilities.

In addition, a new branch of materials science—the study of nanostructures—has become quite active during the past decade because of the special characteristics of nanosized solid materials. Metal nanocomposites are particularly interesting because they display photophysical and photocatalytic aspects that are dependent upon their unique electronic and chemical properties.[17] Although noble metals, including Au and Ag, possess relatively high conductivities (10^4–10^5 S cm^{-1}) and operational stabilities, their fabrication into nanocomposites generally requires high temperatures and deposition under high vacuum. Gold nanoparticles (Au NPs) have been successfully explored as a low temperature, high conductivity alternative,[20] but the high cost of Au may negate

its merits. As a result, for this study we selected Ag as our metal of choice because of its high conductivity and lower cost and lower processing temperature compared to those of Au. In the fields of electronics and microelectronics, Ag particles are mainly used in the conductivity functional phase to formulate electronic pastes. Earlier studies of printable conductors were focused mainly on organic materials (*e.g.*, polyaniline[18] and PEDOT/PSS[19]) that possess relatively low conductivities (<3 S cm^{-1}) in addition to potential chemical, thermal, and electrical instabilities. Here, we developed a new approach using a quenching/chelation method—derived from the theories of rapid precipitation and nucleation with a metallic material under dramatic change of temperature—to generate Ag plate structures (Scheme 1). The preparation of various Ag morphologies, including particles, rods, plates, and wires, generally requires the use of organic reagents, such as poly-(vinyl pyrrolidone) (PVP) and cetyl trimethylammonium bromide (CTAB), which have relatively high degradationtemperatures and, thus, can be difficult to remove—potentially decreasing the conductive efficiencies of associated Ag pastes in photoelectric devices. On the other hand, thiophene (TP) has two lone pairs of electrons that can bind to an Ag$^+$ cation through complexation and then serve as a capping reagent to control the rodmorphology of Ag during reduction. To the best of our knowledge, no related studies have been performed for the preparation of Ag/oligothiophene complexes through a quenching/chelation method. Herein, we describe a simple and friendly one-pot procedure for the preparation of a Ag/oligothiophene complex that exhibits an excellent conductivity of 1.8×10^4 S cm^{-1} in the bulk state and 6.08×10^2 S cm^{-1} in the thin film state prior to annealing. In addition, we have found that such a Ag plate structure possessing a high aspect ratio and a fixed orientation provided a good conductive route for electrons.

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Scheme 1 Schematic representation of a Ag paste prepared though a quenching/chelation method, based on a mechanism involving nucleation, precipitation, and chelation.

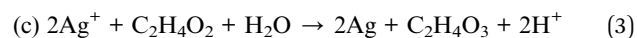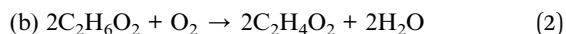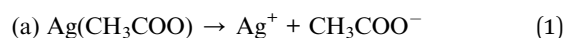# Experimental section

Materials

Reagent-grade silver acetate [Ag(CH$_3$COO)] and poly(vinyl alcohol) (PVA; molecular weight: 89 000–98 000) were obtained from Sigma-Aldrich. Ethylene glycol (C$_2$H$_6$O$_2$, EG) and the puriss. p.a. thiophene monomer (C$_4$H$_4$S; assay: ≥99%; autoignition: 395 °C; B$_P$: 84 °C) were purchased from J. T. Baker and Alfa Aesar, respectively. Anhydrous sodium hydroxide (NaOH) was obtained from Showa Chemical Industry Co., Ltd. The oligothiophenes used to assist the formation of Ag pellet morphologies were prepared based on the procedure described by Kozhevnikov et al.[21]

Preparation of the Ag/oligothiophene complex

A 250 mL two-neck flask was charged with stoichiometry of Ag(CH$_3$COO) in EG and TP monomers. After adding the diluted PVA solution with solvent deionized water at a concentration of 1–3 wt%, the mixture was stirred at 60 °C for 30 min and then rapidly quenched to −40 °C in a liquid nitrogen/acetone system. Next, the mixture was blended with NaOH at various concentrations to control the pH of mixture solution. After stirring at 60 °C for 1 h, the mixture was subjected to a second quenching. The Ag/oligothiophene complex that precipitated from the solution washed with diluted MeOH solution and solvent deionized water and centrifuged twice to remove any residual TP monomers. The bulk sample of the Ag/oligothiophene complex was prepared using a compression-molding machine operated at a pressure of 6000 psi after drying. Film samples were formed through the coating of the Ag/oligothiophene complex onto glass, silicon and polyester.

Mechanism of formation of the Ag/oligothiophene complex

Kozhevnikov et al. reported that thiophene and furan undergo oxidative coupling in the presence of palladium salts to form bithiophene and bifuran.[21] In general, Ag composites can be synthesized through a polyol process: the EG-mediated reduction of Ag salts in the presence of PVA as a surfactant.[22,23] In this study, Ag seeds were prepared at 40 °C from a mixture of AgOAc and EG, as a reducing agent, in the solvent EG:

$$\text{(a)} \quad Ag(CH_3COO) \rightarrow Ag^+ + CH_3COO^- \qquad (1)$$

$$\text{(b)} \quad 2C_2H_6O_2 + O_2 \rightarrow 2C_2H_4O_2 + 2H_2O \qquad (2)$$

$$\text{(c)} \quad 2Ag^+ + C_2H_4O_2 + H_2O \rightarrow 2Ag + C_2H_4O_3 + 2H^+ \qquad (3)$$

where (a) is ionization of AgOAc, (b) is oxidation of EG to form glyoxal, and (c) is growth of Ag seeds, respectively.
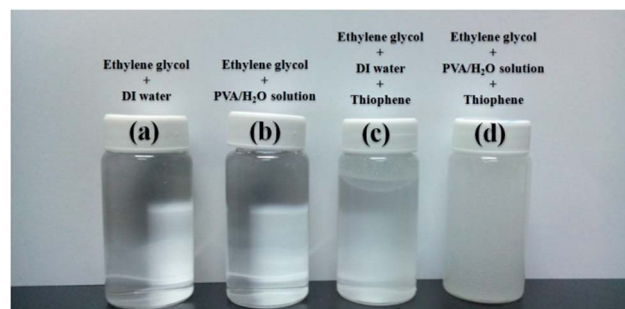

Fig. 1 Photograph of complex solutions fabricated from (A) EG/water, (B) EG/PVA, (C) EG/water/TP and (D) EG/PVA/TP.

Characterization

The X-ray diffraction (XRD) data were collected using a Bruker D8 DISCOVER apparatus. A rotating copper target was employed to obtain a monochromated incident beam having a wavelength (λ) of 1.5412 Å. High-resolution field emission-scanning electron microscopy (FE-SEM) images were recorded using a JSM-7000F microscope (JEOL, Japan) operated at 30 kV. The chemical composition of the as-prepared surface was investigated using X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). The nucleation of Ag NPs and formation of Ag seeds were observed through transmission electron microscopy (TEM, JEOL 2100F) performed at an accelerating voltage of 200 kV and by variable-angle UV-Vis-NIR spectrophotometry (Hitachi U-4100). The conductivities of Ag/oligothiophene samples were calculated using a four-probe station (Hewlett–Packard).
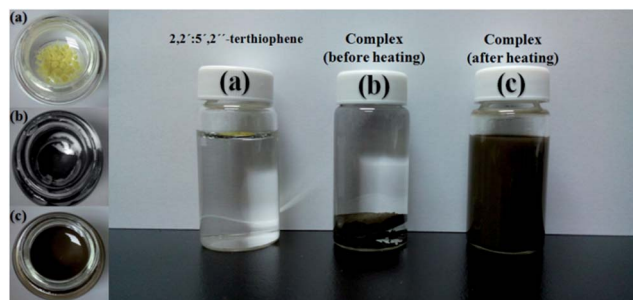

Fig. 2 Photograph of aqueous mixtures of (a) 2,2′ : 5′,2″-terthiophene and (b and c) the Ag/oligothiophene complex (b) before and (c) after heating.

Results and discussion

Preparation of the Ag/oligothiophene complex

Fig. 1(c) displays dispersions of TP in various solutions and the phase separation that generally occurred in mixtures of EG and H$_2$O; we obtained an emulsion, however, for the complex EG/PVA solution [Fig. 1(d)] fabricated after adding the PVA solution to the EG/H$_2$O mixture shown in Fig. 1(c). This emulsion formed

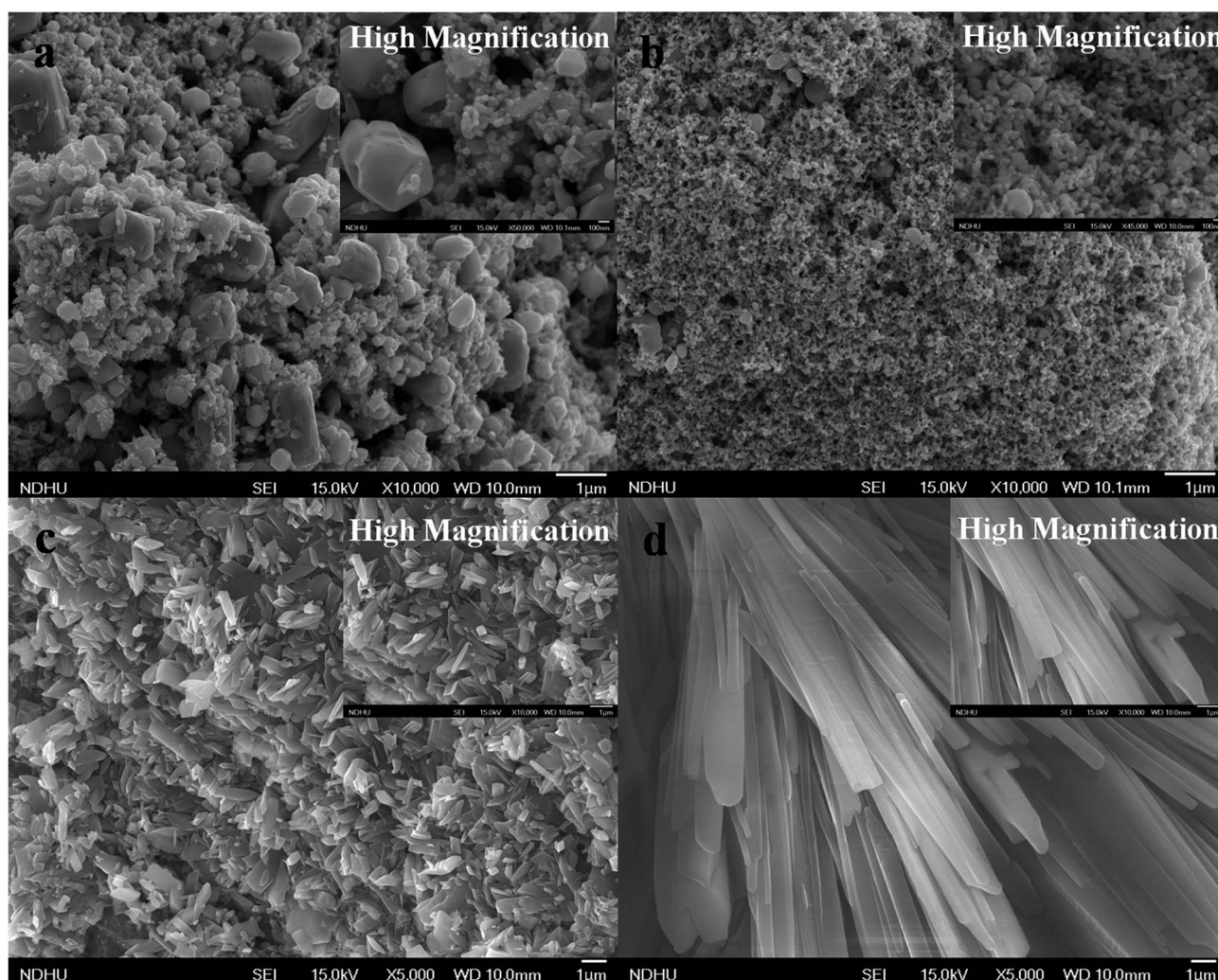**Fig. 3** Morphologies of Ag/oligothiophene complexes synthesized in the presence of NaOH at concentrations of (a) 0.5, (b) 1, (c) 3, and (d) 9 M.

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between the PVA solution and the TP monomer can be considered as being similar to that formed from oil in water because PVA is generally regarded as a water-soluble surfactant. As a result, the Ag/oligothiophene complex could not be dispersed in the aqueous solution after removal of PVA and EG; rather, it behaved as a rubber-like material [Fig. 2(b)]. Because the Ag plate-like structure possessed a specific weight larger

than that of the water–Ag NP mixture, it tended to precipitate from the aqueous phase in the form of a rubber-like material, presumably as a result of strong π–π stacking of the oligothiophene units. Fig. 2(c) reveals that we could disperse the rubber-like Ag/oligothiophene complex in water after heating it at 60 °C for a few minutes, as a result of thermal disturbance of the regular oligothiophene chains. Accordingly, we could
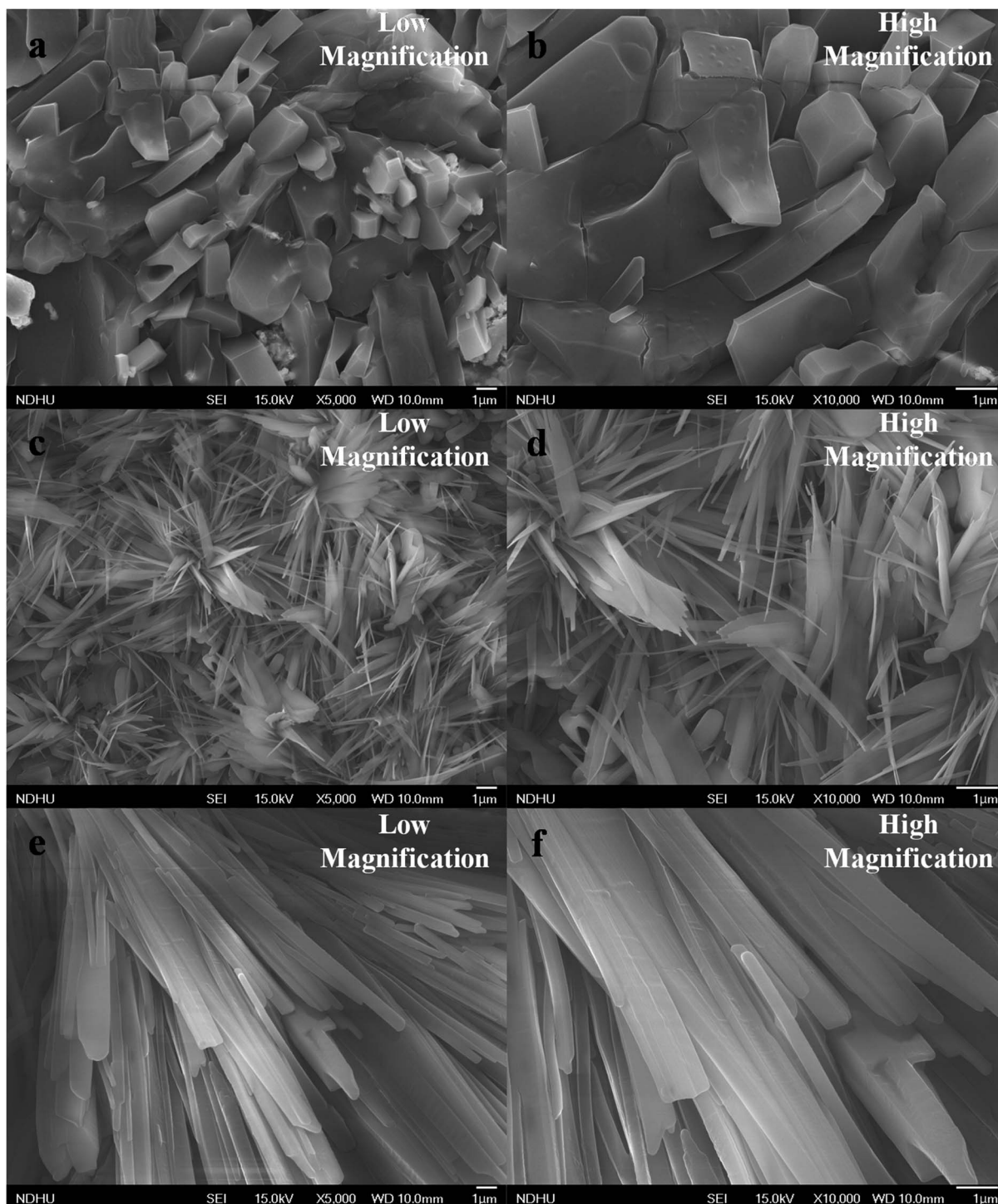

Fig. 4 Morphologies of Ag/oligothiophene complexes synthesized under highly basic conditions ([NaOH] = 9 M) in the presence of thiophene at concentrations of (a) and (d): 1.01, (b) and (e): 1.52, and (c) and (f): 2.02 M.

repeatedly disperse the Ag/oligothiophene complex in water, with the even dispersion resulting from a balance between Ag–S chelation and the insolubility of the oligothiophene.

Microstructures of Ag/oligothiophene complexes

In general, the plate structure of Ag displays high conductivity because it provides a continuous transition route for the passage of electrons. Fig. 3(a) and (b) reveal that only particle aggregation of the Ag/oligothiophene complex occurred in media of relatively low basicity ([NaOH] = 0.5 or 1.0 M); these aggregates did not form continuous conducting routes and resulted in poor bulk conductivity (from 10^{-6} to 10^{-4} S cm^{-1}), as would be expected. In contrast, highly basic media and appropriate amounts of TP monomers allowed Ag growth and chelation to provide plate structures. After the second quenching of the Ag/oligothiophene complex at higher NaOH concentrations, the morphology of the Ag structure transformed from particles to plates [Fig. 3(c) and (d)] having widths of 0.2–0.3 μm and lengths of 2–3 μm. The formation of these Ag plates was controlled by the concentration of NaOH, the irregular structure of the oligothiophene (Fig. 3), and the quenching process. Fig. 4 reveals that the length of the Ag plate structures also increased

upon increasing the TP content in a highly basic medium ([NaOH] = 9 M). The bulk conductivities of these Ag/oligothiophene complexes were greater than 10^3 S cm^{-1} prior to annealing. Thus, optimizing the contents of NaOH and TP monomers was critical to form the Ag plate morphology. Fig. 5 displays the sheet resistances obtained after coating the Ag/oligothiophene complex onto various substrates (silicon, glass, polyester); the films of the Ag/oligothiophene complex lowered the sheet resistances of all of the substrates.

Fig. 6(a) provides XRD analyses of the crystalline structures of the as-prepared Ag/oligothiophene complex. We assign the (111), (200), (220), (222), and (311) XRD signals to the crystallographic planes of face-centered cubic (FCC) Ag crystals. We observe that signals for the Ag composite prepared in the highly basic medium ([NaOH] > 1 M) were relatively narrower and of higher intensity. Although the Ag/oligothiophene complexes that we synthesized using an appropriate amount of TP, in the presence of a high concentration of NaOH for controlling the growth of Ag plates, exhibited characteristic Ag peaks based on a fixed orientation, they were not exactly the same as those in the Ag database, due to the polycrystalline nature of the Ag plates. Accordingly, we used X-ray photoelectron spectroscopy (XPS) to gain a better understanding of the bonding structure,
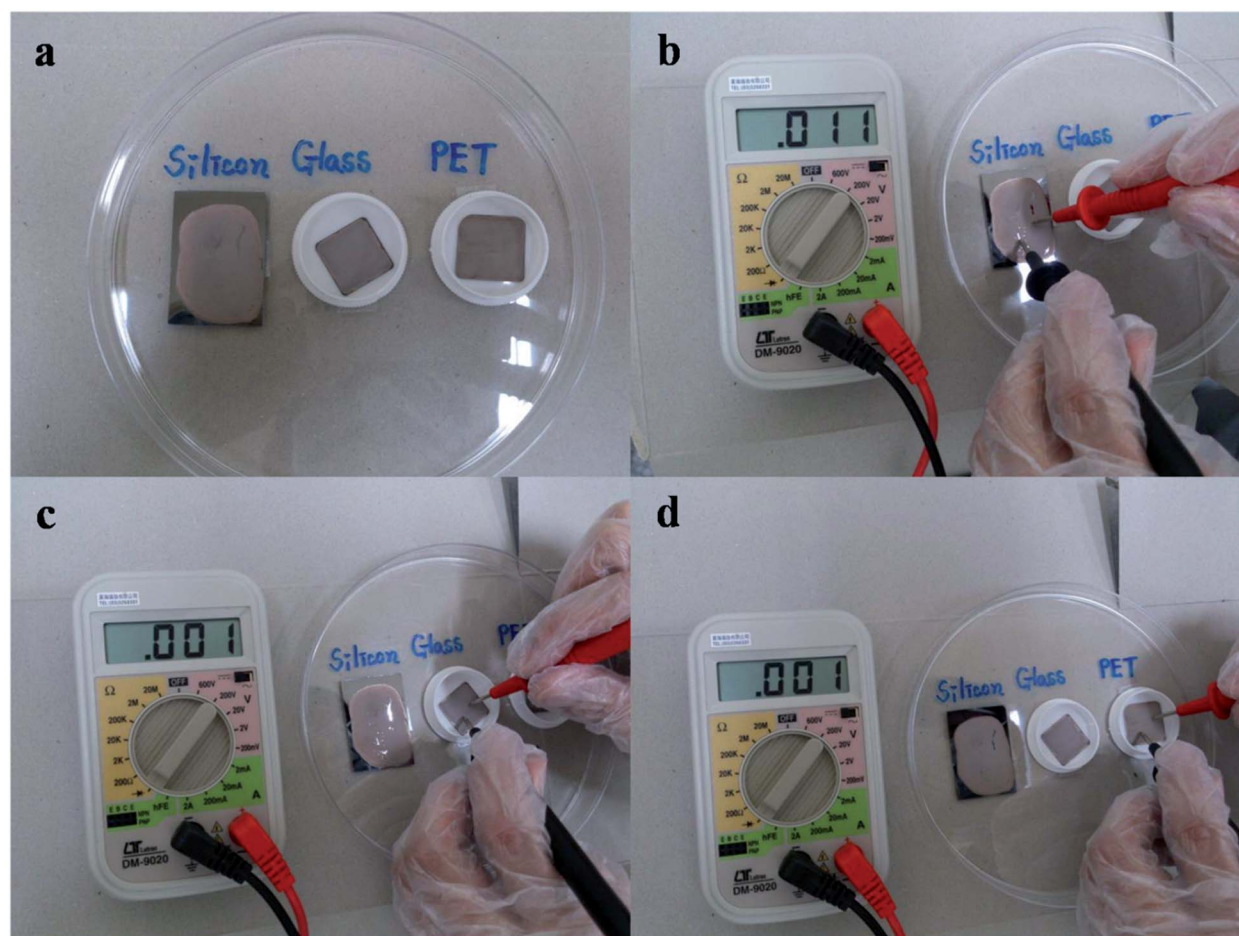

Fig. 5 (a) Ag/oligothiophene complex coated onto silicon, glass, and PET substrates; sheet conductances of the coated (b) silicon, (c) glass, and (d) PET.
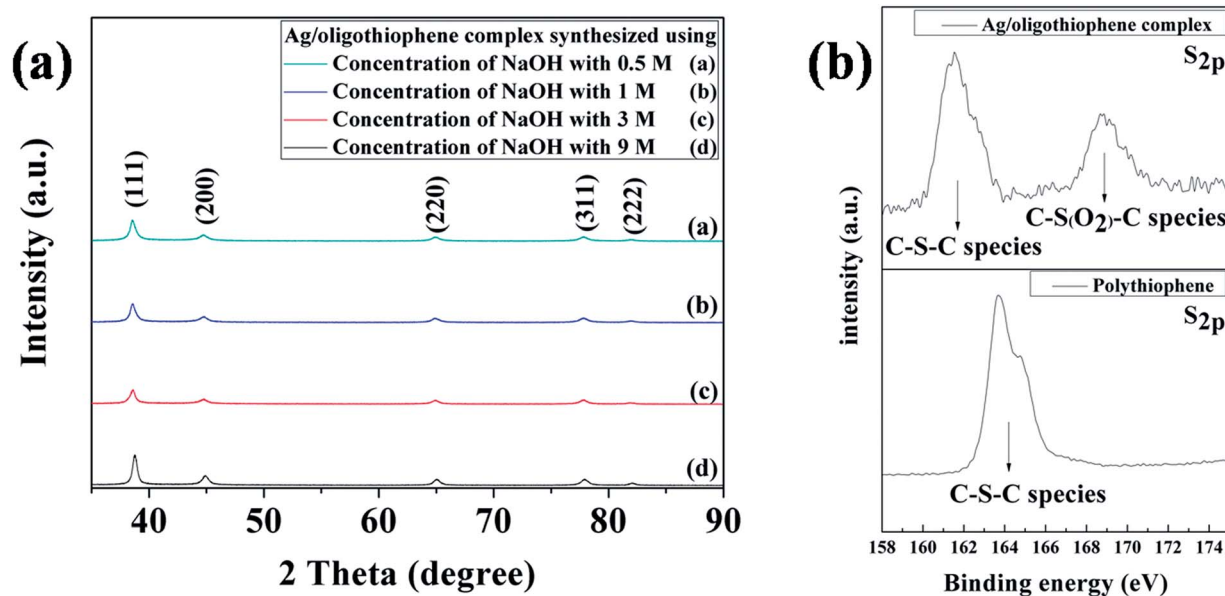
Fig. 6 (a) XRD spectra of Ag/oligothiophene complexes synthesized in the presence of various concentrations of NaOH. (b) XPS spectra (S_{2p}) of the Ag/oligothiophene complex and polythiophene.

order, and charge location in the oligothiophene. Fig. 6(b) reveals that the S_{2p} peak for the thioether C–S–C unit of pure polythiophene was located in the region 163–165 eV; on the other hand, the Ag/oligothiophene complex provided two peaks at 162–164 and 167–170 eV for the C–S–C and C–S(O_2)–C units, respectively. Thus, the position of the signal for the C–S–C units
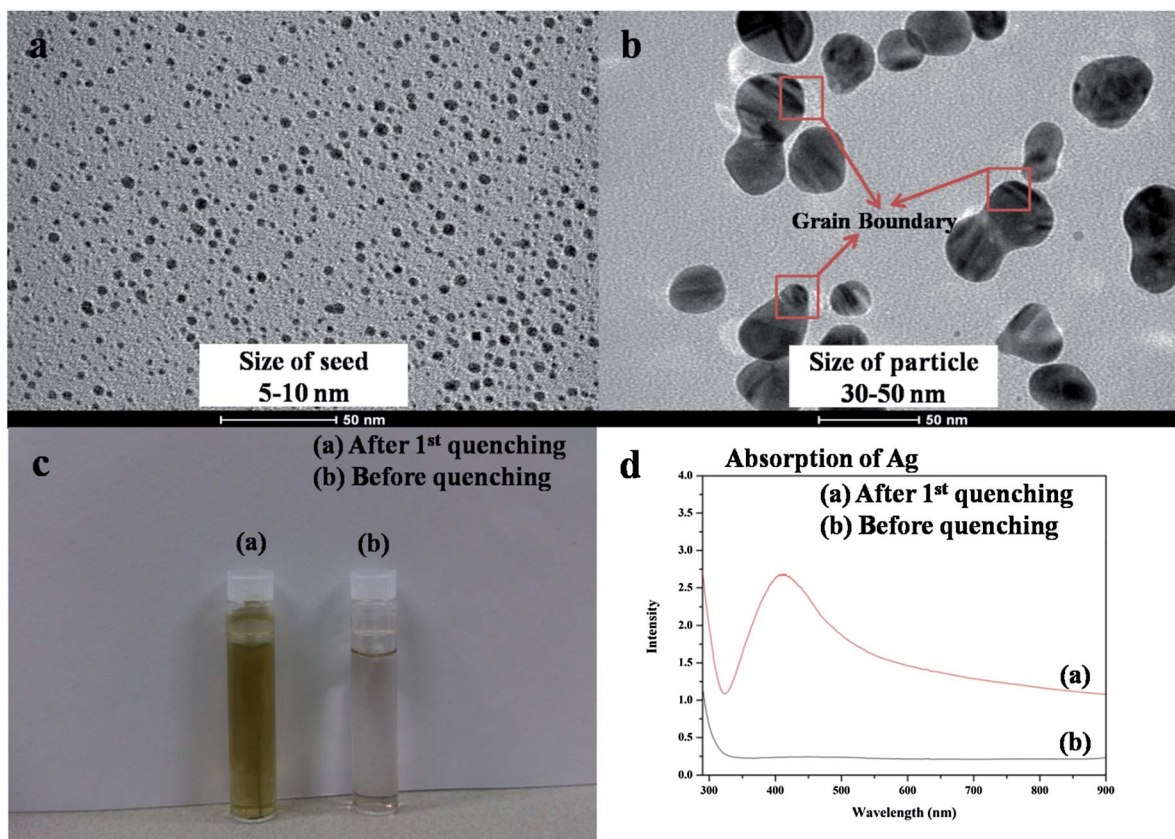

Fig. 7 TEM images of the morphologies of (a) Ag seeds and (b) Ag NPs. (c) Photograph of the Ag seeds and NPs dispersed in DI water. (d) UV-Vis absorption spectra of the samples in (c).

of the Ag/oligothiophene complex had shifted to a lower binding energy relative to that for the pure oligothiophene, presumably because of the influence of Ag–S chelation.

TEM images revealed the particle sizes of the Ag seeds and the grown Ag NPs. The Ag seeds prepared through EG-mediated reduction of AgOAc had an average diameter of 10 nm (Fig. 7(a)); the grown Ag NPs had an average diameter of 40 nm and featured grain boundaries (Fig. 7(b)). These Ag NPs were formed after polymerization of oligothiophene during the first quenching and redox steps. Moreover, the photograph in Fig. 7(c) compares the complex solutions before and after the first quenching and removal of the excess TP monomers and PVA. The non-quenched complex solution consisted of Ag seeds and the water solvent; it did not form an evenly dispersed solution after standing for two days. We suspect that this behavior arose from the removal of the surfactant PVA, which was unable to assist the even dispersion of the Ag seeds. A uniformly dispersed solution of Ag NPs appeared in the quenching complex solution because of their chelation to the oligothiophene, even though the surfactant PVA had been removed (see Fig. 2). The UV-Vis spectra in Fig. 7(d) reveal that the Ag seeds and NPs absorbed in the same wavelength ($\lambda_{\max} = 410$ nm), but their intensities were obviously different because of the uneven dispersion of Ag seeds in the complex solution. Fig. 3 presents SEM images of the Ag/oligothiophene complexes synthesized in the presence of NaOH at various concentrations. According to the thermal dynamic function, Fick's law,

$$\log\left(D^2 - \frac{D_0{}^2}{t}\right) = -\left(\frac{Q}{2.3RT}\right) + \log K_0 \qquad (4)$$

where D is the diffusivity, t is the time, and Q is the activation energy, the driving force for the diffusion of Ag NPs decreases upon decreasing the temperature and results in large Ag plates with stacking along the fixed growth orientation. In addition, the procedure that we used for quenching led to rapid precipitation of several grain boundaries in the Ag particles.

Electrical conductivity of the Ag/oligothiophene complex

We used the four-probe method to test the electrical conductivity of the Ag/oligothiophene complex composite. Here, we measured the conductivity of the Ag/oligothiophene complex in its bulk and film states prior to annealing. Table 1 reveals that the bulk conductivity of the Ag/oligothiophene complex was 0.82–1.80×10^4 S cm^{-1} after drying at 60 °C for 2 h. This conductivity is less than that of bulk Ag metal because of the presence of the grain boundaries. On the other hand, the conductivity of the film prepared from the Ag/oligothiophene complex was 5.49–6.08×10^2 S cm^{-1}. Although we prepared these Ag/oligothiophene complex films at various thicknesses, the phenomena of phase separation and aggregation did not occur (Fig. 8) because of chelation between the Ag plate and the oligothiophene. In addition, the conductivity of the Ag/oligothiophene complex in its film form increased to 10^3–10^4 S cm^{-1} after annealing at 100 °C for 30 min.

Conclusions

We have applied a new quenching/chelation method to prepare a novel Ag paste. EG plays an important role during the formation of this Ag paste, providing many active sites for nucleation, growth, and chelation. We expect that this approach could be extended to the preparation of other novel metallic nanomaterials, such as those based on indium tin oxide (ITO), Au, and Cu.

Acknowledgements

Table 1 Conductivity of Ag/oligothiophene complex samples, measured using a 4-4-probe station

Sample type	Thickness (mm)	Resistance (Ω cm)	Conductivity (S cm^{-1})
Film 1	0.008 (8 µm)	0.502	5.49×10^2 S cm^{-1}
Film 2	0.025 (25 µm)	0.145	6.08×10^2 S cm^{-1}
Bulk 1	1.273	2.167×10^{-4}	0.82×10^4 S cm^{-1}
Bulk 2	2.038	6.017×10^{-5}	1.80×10^4 S cm^{-1}
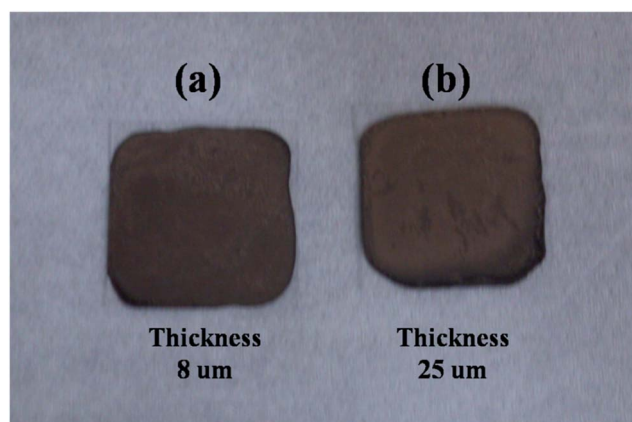
Fig. 8 Photograph of film samples of Ag/oligothiophene complexes prepared at thicknesses of 8 and 25 µm.

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