

Supporting Information

Tetrathiafulvalene as an Electron Acceptor for Positive Charge Induction on the Surface of Silver Nanoparticles for Facilitated Olefin Transport

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Experimental

Materials

Poly(vinyl pyrrolidone) (PVP, average M_w 630,000), tetrathiafulvalene (TTF), and silver tetrafluoroborate ($AgBF_4$) were purchased from Tokyo Chemical Industry Co. Polysulfone supports (average pore size = 0.1 μm) for the fabrication of composite membranes were obtained from Woongjin Chemicals. All chemicals were used as received without further treatment.

Sample preparation

Ag NPs were synthesized from $AgBF_4$ in the presence of PVP dissolved in an ethanol solution by heat treatment for 24 h at 75 °C; the molar ratio of $[C=O]:Ag$ was fixed at 1:1. Next, 1.0, 2.0, or 3.0 mol% of TTF to Ag was added to the Ag NPs colloid to induce a partial positive charge on the surface of the Ag NPs. The solution was then stirred vigorously for 5 h to dissolve the TTF and allow it to effectively induce positive charge. Finally, ethanol as a solvent was evaporated at high temperature with stirring until the solid content was approximately 50 wt.%.

Membrane fabrication

For the fabrication of composite membranes, the above solution was deposited on a polysulfone microsupport membrane with an RK control coater (Model 101, Control Coater RK Print-Cost instruments Ltd. UK). The mean thickness of the selective layer was approximately 10 μm . The membrane was dried in a convection oven under a stream of N_2 , and then further dried in a vacuum oven at room temperature for 2 days.

Characterization

UV-Vis absorption spectra were collected using a Jasco V-670 spectrophotometer with 1.0 nm resolution. All samples were diluted to constant concentrations, and a baseline was measured with pure ethanol. To examine the synthesized Ag NPs in the PVP/AgBF₄ solution, transmission electron microscopy (TEM) images were obtained with a JEOL JEM-3010 TEM operating at 300 kV. All TEM samples were prepared with constant concentrations by dropping the solution onto a standard TEM copper grid.

Surface charge and electron transfer between the Ag NPs and TTF were confirmed by binding energy data obtained via photoelectron spectroscopy. UV photoelectron spectroscopy (UPS, Thermo Fisher Scientific Co.) was used to measure the work function of the samples. A He I discharge lamp with a photon energy of $h\nu = 21.2$ eV was employed as the light source. Work function values for the Ag NPs were obtained from the width of the photoemission spectrum from the secondary cut-off to the Fermi edge¹. Since the Ag Fermi edge does not shift, changes in the work function can be effectively monitored by observing variations in the secondary cut-off level. The highest occupied molecular orbital (HOMO) of TTF was determined as the sum of the Fermi level of TTF and the barrier height for hole injection.²

The binding energy was measured via X-ray photoelectron spectroscopy using a VG Multilab ESCA 2000 system from Thermo Fisher Scientific Co. Mg was used as the X-ray source and the resolution was 0.05 eV. The C 1s line at 285.0 eV was utilized as a reference for determining the binding energies of both Ag and S atoms.

1. D. Kim, S. Jeong, H. Shin, Y. Xia and J. Moon, *Adv. Mater.*, 2008, **20**, 3084.
2. H. Ishii, K. Sugiyama, E. Ito and K. Seki, *Adv. Mater.*, 1999, **11**, 605.

Membrane performance (mixed gas selectivity/ ideal separation factor)

The separation performance of the composite membrane with regard to propylene/propane mixed gas was measured with a feed composition of 50/50 volume percent of propylene/propane. The composition of the flow gas was analyzed using a gas chromatograph (Hewlett-Packard G1530 A, MA) equipped with a thermal conductivity detector (TCD). The definition of mixed-gas selectivity is the molar ratio of the feed composition to that of the permeate; the gas permeance units are in GPU (where $1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3 \text{ (STP) (cm}^2 \text{ s cm Hg)}^{-1}$).

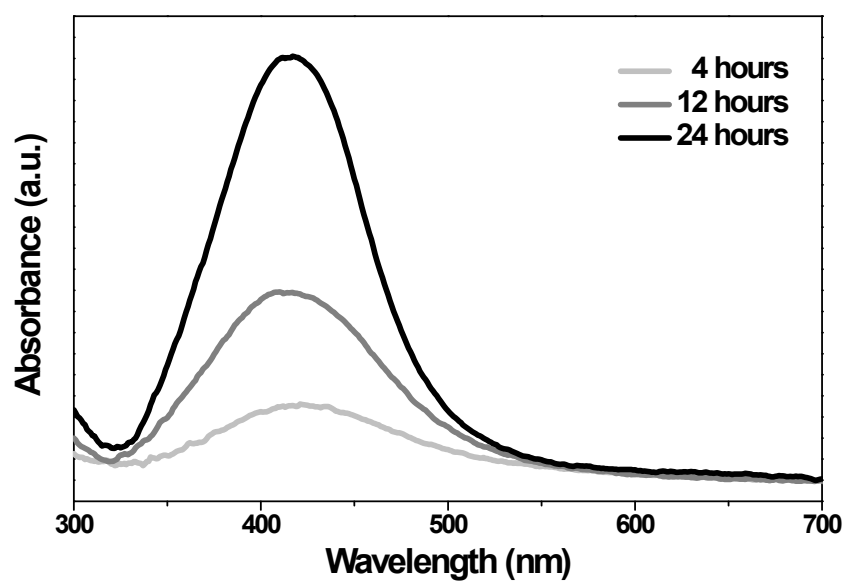


Fig. S1 UV-Vis absorption spectra of synthesized Ag NPs with PVP ($M_w = 630,000$) as a function of time.

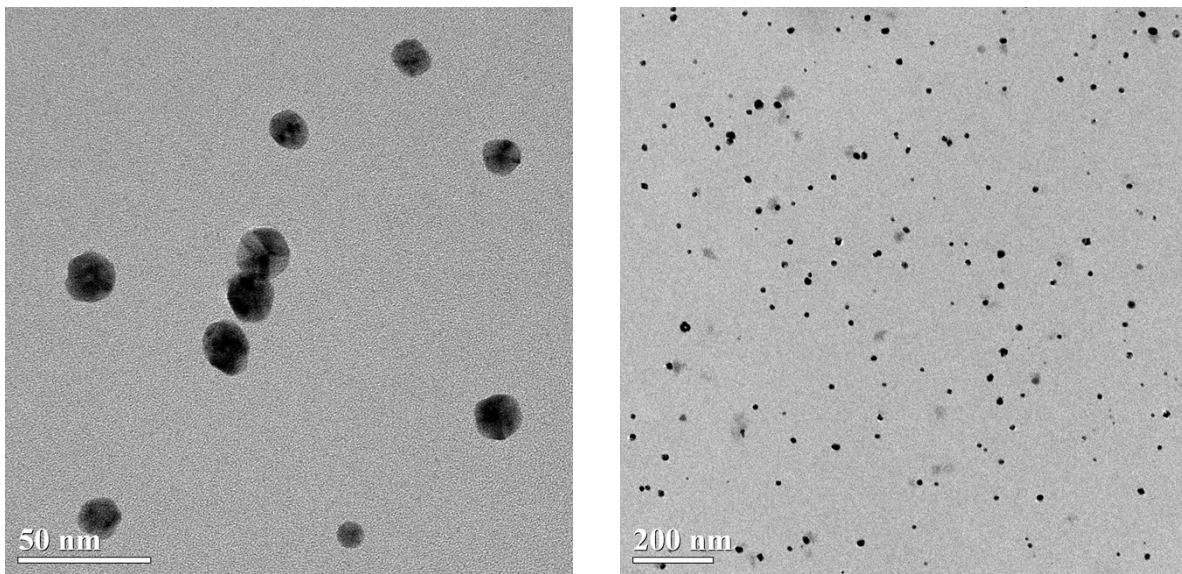


Fig. S2 TEM images of the synthesized Ag NPs dispersed in PVP ($M_w = 630,000$).

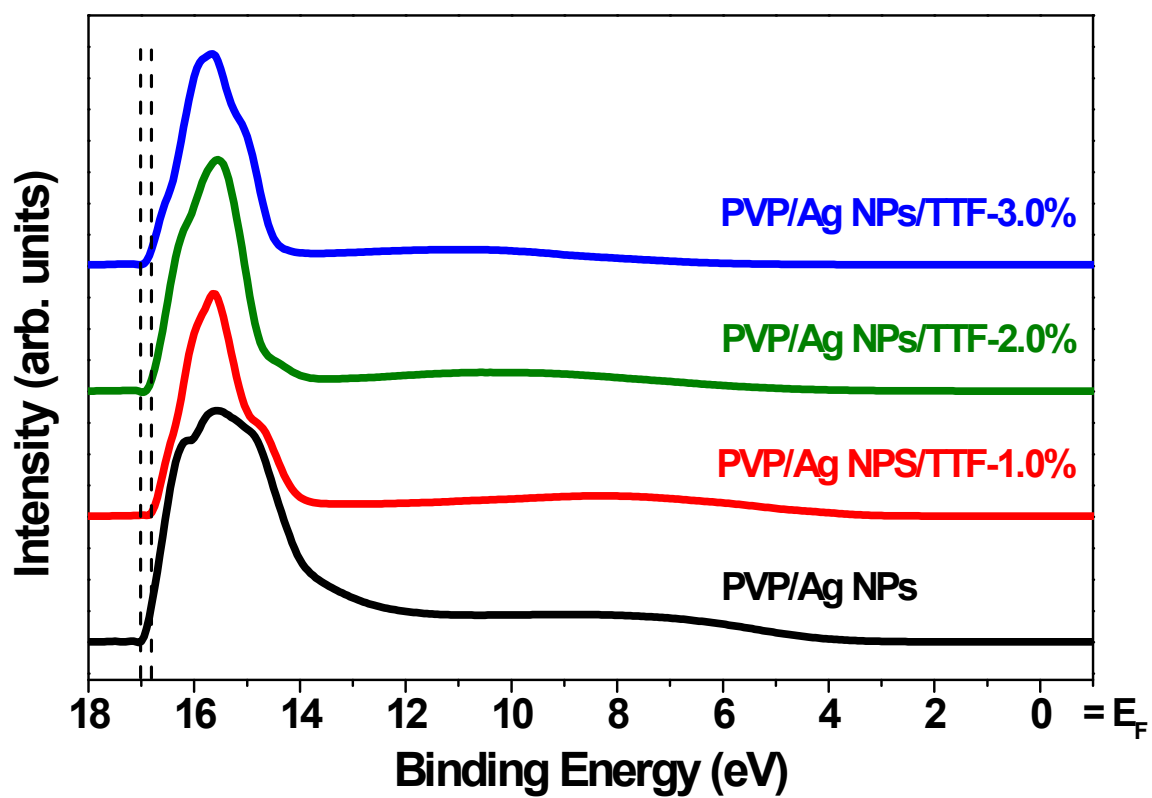


Fig. S3 UPS spectra of Ag NPs in PVP/Ag NPs/TTF-X as a function of the TTF concentration.

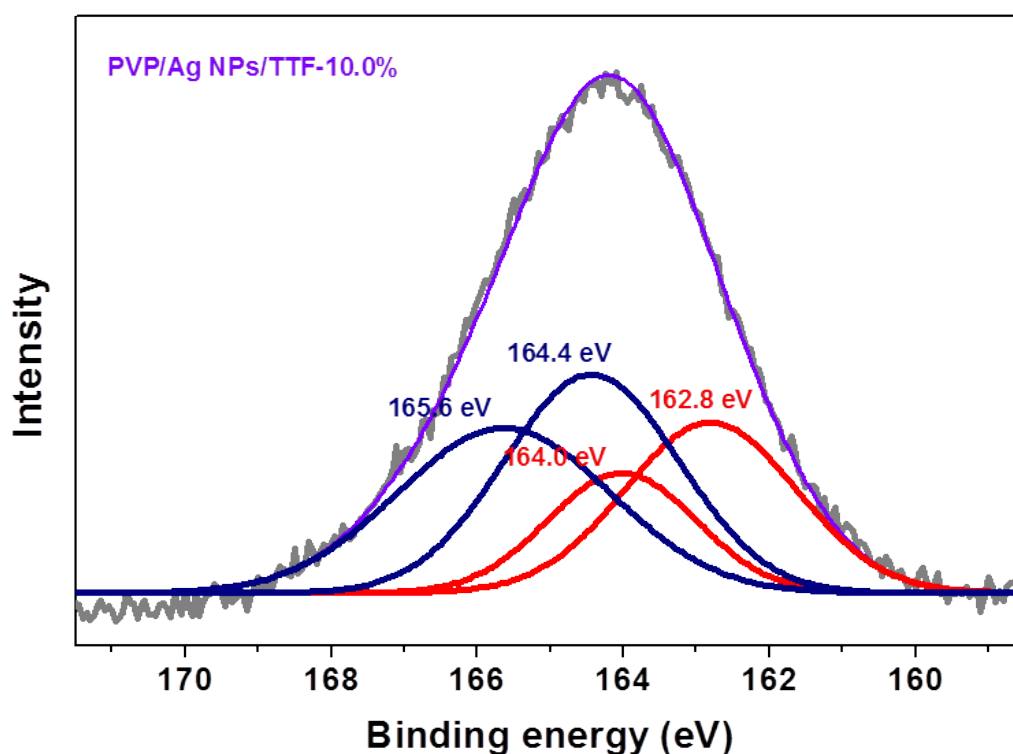


Fig. S4 XPS spectra for the binding energies of S 2p electrons for PVP/Ag NPs/TTF-10.0%.

Fig. S4 shows the S 2p spectra of the excess amount of TTF (10 mol%) in PVP/Ag NPs examined via XPS measurement. The binding energies of S 2p_{3/2} in PVP/Ag NPs/TTF-10.0% are observed with two peaks: 162.8 and 164.4 eV. The former peak at 162.8 eV (red line) is attributed to the negatively charged TTF, which is the same as the S 2p_{3/2} peaks at the lower TTF concentrations (1.0, 2.0, and 3.0 mol%), whereas the latter peak at around 164.4 eV (blue line) originates from the neutral state of TTF, which is similar to the previous report with the neutral TTF. Therefore, with the excess amount of TTF, the surfaces of Ag NPs were saturated with the adsorbed TTF molecules so that the residual TTF molecules existed as the neutral state. That is the reason why two differently charged states of TTF were shown in the PVP/Ag NPs/TTF-10.0%.