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Olefin Separation

Surface Energy-Level Tuning of Silver Nanoparticles for Facilitated Olefin Transport**

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The energetics at organic/metal interfaces have attracted considerable research interest in recent times.[1–8] Organic charge-transfer molecules on metal surfaces have been used for tuning interfacial electronic structures, and this has led to improvements in the performance of organic optoelectronic devices such as light-emitting diodes and field-effect transistors.[6,7] Among organic charge-transfer molecules, 7,7,8,8-tetracyanoquinodimethane (TCNQ) is well known as a strong electron acceptor that enables the transfer of electrons from metals to organic molecules.[8] Recently, energy-level tuning of nanomaterial surfaces by electron acceptors has led to some novel applications.[9,10] For example, TCNQ enables graphene sheets to be stabilized and dispersed in highly polar solvents.[11]

We have previously reported that *p*-benzoquinone (*p*BQ), an electron acceptor, enables silver nanoparticles (AgNPs) to impose surface positive charges and consequently to interact reversibly with propylene;[10] in this manner, the nanoparticles act as olefin carriers for facilitated transport membranes. Such membranes comprising olefin carriers in a polymer matrix typically exhibit considerably improved separation performances resulting from a combination of carrier-mediated transport and normal Fickian transport; in such cases, the function of the olefin carrier is to interact with olefin molecules reversibly.[12–18] Therefore, the concept of facilitated transport phenomena is extremely attractive for improving the separation performances of olefin/paraffin mixtures that are currently separated by intensive-energy cryogenic distillation.[19] Typical olefin carriers are silver cations and surface-activated metallic AgNPs.[10,12–18] Although membranes containing AgNP olefin carriers are robust, they show relatively lower olefin/paraffin selectivity than membranes containing chemically labile silver ions.[10,16] Therefore, the identification of selective and robust olefin carriers for facilitated transport is an urgent requirement for the economic separation of olefin/paraffin mixtures.

Herein, we report energy-level tuning of AgNPs by TCNQ, which leads to a large positive charge on their surfaces; consequently, the AgNPs exhibit significantly enhanced chemical activity when complexing with olefins. In this manner, extremely high selectivity can be obtained, such as mixed-gas selectivity greater than 50 for the separation of propylene/propane mixtures, which to our knowledge is the highest value ever reported.

Nanocomposite membranes containing AgNPs activated by TCNQ were prepared as shown in Scheme 1. The AgNPs were prepared at a fixed poly(vinylpyrrolidone) (PVP)/$AgBF_4$ molar ratio of 1:0.5 (that is, weight ratio of 1:0.877), and they had an average particle size of 20 nm with a standard deviation of 3 nm (see Figure S1 in the Supporting Information). Although the AgNPs were successfully prepared, it is possible that Ag ions still remained in the AgNPs. Therefore, the AgNPs were continuously washed with ethanol for an additional 24 h at 80 °C by stirring the colloidal solution. Subsequently, "PVP-protected AgNPs" in ethanol, which were surface-activated by an electron acceptor, were cast on a commercial macroporous polysulfone membrane support with an average surface pore size of 0.1 μm to fabricate nanocomposite membranes.

The separation performances of PVP/AgNP nanocomposite membranes with different electron acceptors, such as TCNQ and *p*BQ on propylene/propane (50:50 v/v) mixtures, were evaluated. The mixed-gas selectivity is defined as the molar ratio of the feed composition to that of the permeate, and the gas permeance unit is GPU ($1\,\text{GPU} = 1\times10^{-6}\,\text{cm}^3\,(\text{STP})\,(\text{cm}^2\,\text{s}\,\text{cm}\,\text{Hg})^{-1}$). Figure 1 a shows that the PVP/AgNP composite membrane without TCNQ or *p*BQ exhibited practically no separation performance for propylene/propane mixtures: the mixed-gas selectivity was nearly 1. Surprisingly,

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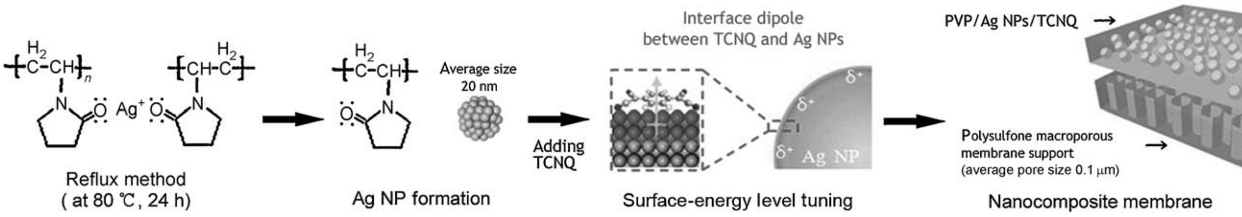

Scheme 1. Preparation of PVP/Ag metal/TCNQ nanocomposite membranes.

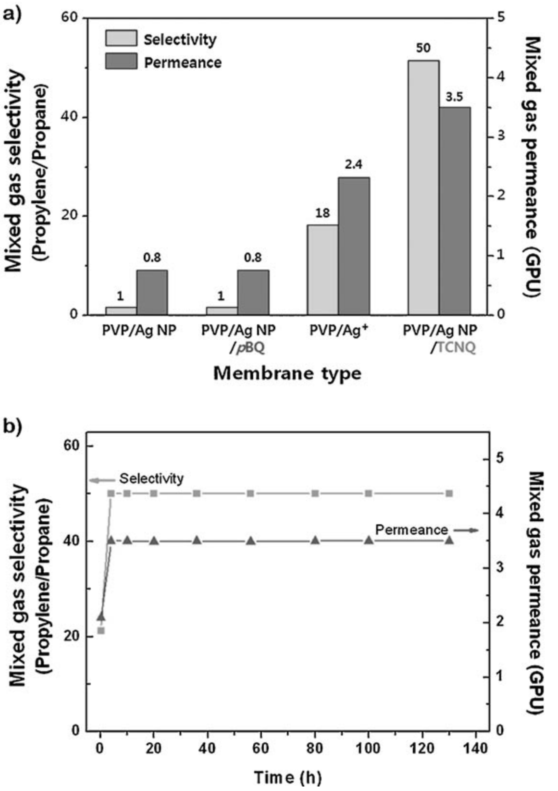

Figure 1. a) Separation performances of various membrane types for 50:50 (v/v) propylene/propane mixture. b) Mixed-gas selectivity and permeance of the PVP/AgNPs/TCNQ (1:05:0.01) membrane A as a function of time.

the introduction of 0.01 weight ratio of TCNQ into the PVP/AgNP composite membrane (PVP/AgNPs/TCNQ = 1:0.5:0.01; membrane A) dramatically increased the selectivity from 1 to 50, while the gas permeance increased by nearly 500 % up to 3.5 GPU. Such an increase in the selectivity after TCNQ addition can be attributed to facilitated propylene transport from the increased polarity or positively induced charge density on the AgNP surfaces. Moreover, both the selectivity and permeance of membrane A remained nearly constant for up to 130 h, which confirms the robustness of the carrier activity, as shown in Figure 1 b.

Interestingly, the separation performance of membrane A was observed to be better than that of the PVP/Ag^+ membrane for the same weight ratio of Ag atoms. Moreover, note that the PVP/Ag^+ membrane had a mixed-gas selectivity of approximately 18.[17] This is the first result demonstrating that the separation performance for propylene/propane mixtures using a membrane comprising surface-activated AgNPs is considerably better than that using polymer/Ag salt complex membranes.

In contrast, negligible improvements in the selectivity and permeance were observed when identical amounts of *p*BQ were introduced (PVP/AgNPs/*p*BQ = 1:0.5:0.01; membrane B), as shown in Figure 1 a. These results suggest that TCNQ is a considerably more efficient polarizer than *p*BQ for activating the surface of AgNPs.

To verify the formation of positive charges on the surface of AgNPs of membrane A, their electronic properties were investigated. First, the binding energies of Ag atoms in PVP/AgNP membranes with different TCNQ or *p*BQ loadings were measured by X-ray photoelectron spectroscopy (XPS). As shown in Figure 2, the binding energy shift for the $d_{5/2}$ orbital of the Ag atoms upon TCNQ addition was larger than that upon adding *p*BQ. Note that the binding energy of PVP/AgNPs/TCNQ is higher than the value (369.2 eV) of pure $AgBF_4$.[18] This suggests that an extremely high positive charge density is induced by TCNQ on the nanoparticle surface.

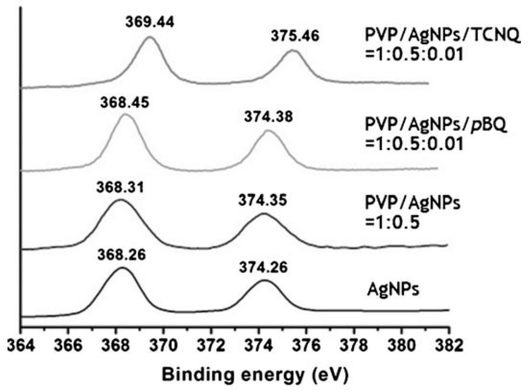

Figure 2. Binding energies for silver atoms in PVP/AgNP membranes with TCNQ or *p*BQ.

Second, the work functions of the AgNPs in these membranes were measured by using a Kelvin probe system.[20,21] As shown in Table 1, the work function of the AgNPs in membrane A increased from 4.70 to 4.99 eV when TCNQ was added, whereas negligible increases were observed when *p*BQ was added. Note that the PVP-protected AgNPs have a work function of 4.70 eV. This result can be

Table 1: Electron affinities[22] and Ag work functions [eV] of the PVP/AgNP membranes containing different electron acceptors.

Electron acceptor	Electron affinity	Ag work function
p-benzoquinone (*p*BQ)	+1.86	4.71
tetracyanoquinodimethane (TCNQ)	+2.8	4.99

explained in terms of the interfacial electronic structure and interface dipole.[1–7] Figure 3 demonstrates the electronic structure of the AgNPs before and after contact with TCNQ. Here, the work function of the Ag atom is given by the energy difference between the vacuum energy level (E_{vac}) and Fermi energy level (E_F). When TCNQ is in contact with an AgNP, the interface dipole is induced, and hence the local vacuum energy level is shifted. In particular, when the interface dipole is formed such that a positive charge is induced on the metallic surface, a positive shift in the local vacuum energy level can be expected, as shown in Figure 3. Consequently, the work function will increase, which is consistent with our experimental data.

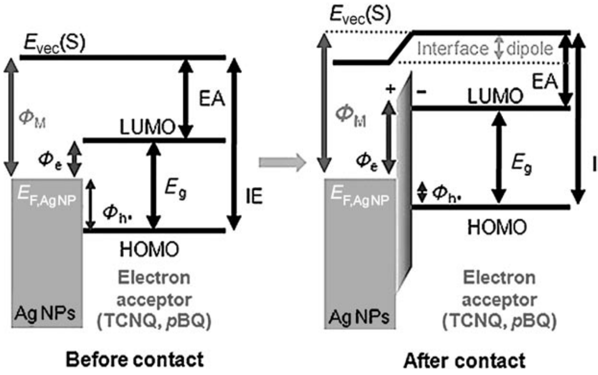

Figure 3. Energy diagrams at interfaces between metal and electron acceptor with the metal work function, Φ_M, located within the HOMO–LUMO gap (E_g) of electron acceptor, electron injection barrier (Φ_e), and hole injection barrier (Φ_h), Fermi energy of AgNP ($E_{F,AgNP}$), local vacuum energy level (E_{vac}(S)), electron affinity (EA), and ionization energy (IE). After contact, TCNQ imposes an interface dipole that increases Φ_e and decreases Φ_h. + and − show the direction of the interface dipole. (Modified from de Boer et al.[6])

Therefore, it can be concluded that the electronic structure of AgNP surfaces was tuned by a strong electron acceptor (TCNQ) to induce high positive charges, which resulted in significant improvements in the separation performance for olefin/paraffin mixtures (mixed-gas selectivity of up to 50). However, practical applications for the membrane should be carefully considered after investigating potential side reactions of AgNPs with reactive compounds such as H_2, H_2S, and C_2H_2.

Experimental Section

Silver tetrafluoroborate ($AgBF_4$, 98%) was used as the precursor of AgNPs. PVP (28–32 K value) was used as a colloidal stabilizer. Anhydrous ethanol was used as a solvent. TCNQ and *p*BQ were used as electron acceptors to induce positive charge on the surface of AgNPs. All the chemicals were used as received from Aldrich Chemical Co.

The PVP/AgNPs/TCNQ and *p*BQ composite membranes were prepared by dispersing TCNQ and *p*BQ into PVP-protected silver colloidal solution in EtOH (20 wt%, that is, weight ratio "PVP/AgNPs (1/0.5)"/EtOH = 0.2:0.8). For the fabrication of the separation membranes, the mixed solution was coated onto polysulfone macroporous membrane supports (Woongjin Chemical Industries Inc., Seoul, Korea) using an RK Control Coater (Model 101, Control Coater RK Print-Coat Instruments Ltd., UK); the average thickness of the selective layer was approximately 20 μm. The average pore size of the surface of the macroporous membrane support was 0.1 μm, while the thickness was approximately 40 μm for the asymmetric structure. After the solvent was evaporated in a convection oven at room temperature (RT) under N_2, the PVP/AgNPs/TCNQ and *p*BQ composite membranes were dried completely in a vacuum oven for two days at RT.

The XPS data were acquired using a Perkin–Elmer Physical Electronics PHI 5400 X-ray photoelectron spectrometer. This system was equipped with an Mg X-ray source operating at 300 W (15 kV, 20 mA). The carbon (C1s) line at 285.0 eV was used as the reference for determining the binding energies of the Ag atom. The work function data were acquired using the McAllister Technical Services KP-6500 Kelvin probe system. The 50:50 propylene/propane mixed-gas separation properties of the PVP/AgNPs/TCNQ and *p*BQ composite membranes with a membrane area of 2.25 cm^2 were evaluated by using a gas chromatograph (Hewlett–Packard G1530A, MA) equipped with a TCD detector and a unibead 2S 60/80 packed column. Gas flow rates and gas permeances were measured with a mass flow meter (MFM; see Figure S2 in the Supporting Information).

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