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Modification of carbon nanotube surfaces with precious metal and transition metal oxide nanoparticles using thin silica layers

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ABSTRACT

The surfaces of carbon nanotubes (CNTs) were covered with thin silica layers through the application of 3-aminopropyltriethoxysilane (APTES) in order to enhance the deposition of precious metal and transition metal oxide nanoparticles. Pt metal particles smaller than 2 nm in diameter could be deposited, using a conventional impregnation method, on CNTs coated with silica layers, whereas Pt particles supported on bare CNT surfaces were approximately 3 nm in diameter. Thus, coating CNTs with thin silica layers enhanced the catalytic activity of the Pt catalysts. In addition, CNTs with thin silica layers could be uniformly covered with transition metal oxide layers (ZrO_2, Nb_2O_5 and Ta_2O_5) by hydrolysis of the corresponding metal alkoxides. In contrast, metal oxides were very difficult to deposit on bare CNTs. The thin silica layers produced on the CNTs via the use of APTES evidently function as adsorption sites for precursor metals and metal oxides, as well as nucleation sites for metals and metal oxides, allowing the formation of precious metal-CNT and transition metal oxide-CNT composites.

1. Introduction

Carbon nanotubes (CNTs) have a number of unique physical and chemical properties, including high surface areas, high electrical and thermal conductivities, and good chemical stability. CNTs have been studied as catalyst supports [1–4], and precious metal particles such as Pt, Rh and Ru supported on CNT surfaces exhibit excellent selectivity for unsaturated alcohols in the hydrogenation of α, β-unsaturated aldehydes, even though saturated alcohols are preferentially formed over these precious metal particles when supported on conventional carriers such as alumina and silica [5–9]. CNT-supported Pt metal catalysts also show high durability as cathode catalysts in polymer electrolyte fuel cells (PEFCs) compared to the carbon black-supported Pt catalysts that have been used as cathode catalysts in state-of-the-art PEFCs, since CNTs are exceptionally resistant to oxidative corrosion due to their high degree of graphitization [10,11]. In addition, composites of CNTs and TiO_2 have been applied as highly active photocatalysts [12,13]. In this system, photo-generated electrons in the TiO_2 are transferred to the CNTs during photoirradiation of the composite, preventing the recombination of electron–hole pairs in the TiO_2. However, the deposition of precious metal particles and metal oxide particles on CNT surfaces is a challenging task because these CNT surfaces are chemically inert. Thus far, the precious metal particles that have been supported on CNT surfaces have been relatively large [14–17] and reducing their size is necessary both to decrease the precious metal loading in the catalysts and to enhance their chemical interactions without compromising their catalytic performance [18,19]. Additionally, it is difficult to deposit metal oxide particles over the entire surface structures of CNTs. This is detrimental since dense coverage of metal oxides on CNTs leads to excellent functionality in the resulting CNT-metal oxide material [20–22]. The use of surfactants in conjunction with CNTs and particles of metals or metal oxides often allows the deposition of smaller metal particles on the CNTs. As an example, triphenylphosphine (PPh_3) has been shown to stabilize Pt metal nanoparticles as well as to act as a linker molecule between Pt metal nanoparticles and CNT surfaces [23], allowing Pt metal particles smaller than 2 nm in diameter to be deposited. However, high temperature treatment of the resulting composites to remove the PPh_3 prior to catalytic reactions results in an increase

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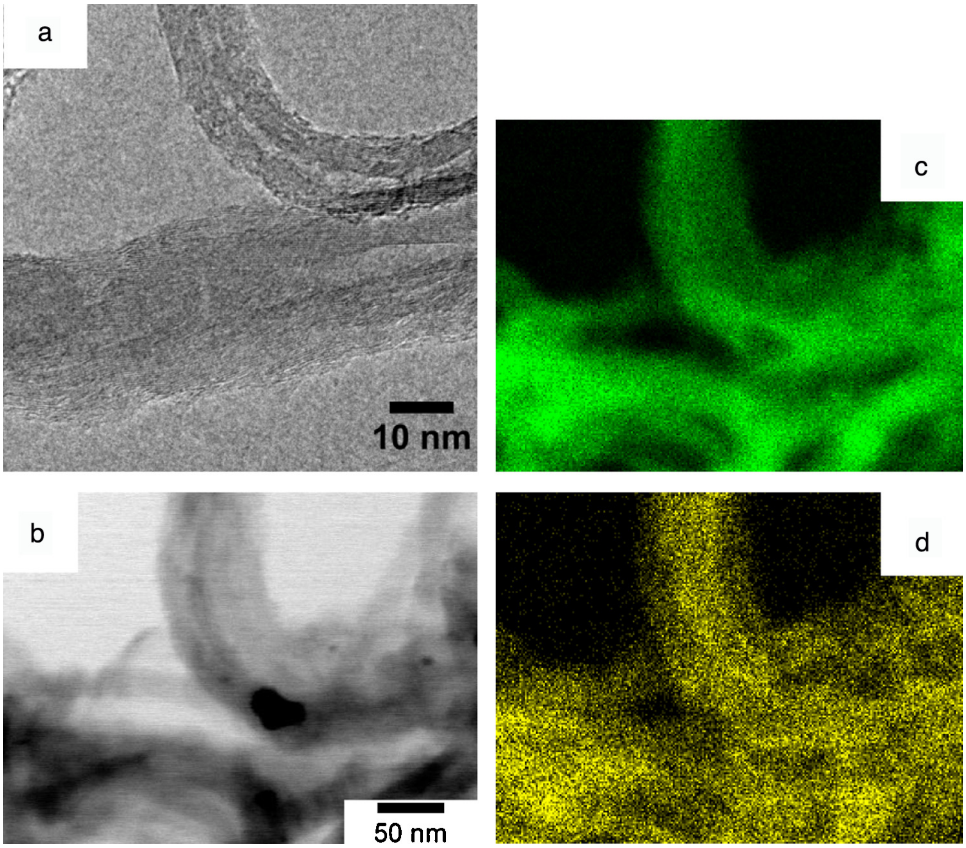

Fig. 1. (a and b) TEM images and elemental mappings for (c) C and (d) Si atoms for AP10/CNT.

in the Pt metal particle size. Surfactant molecules such as sodium dodecylsulfate or polyethyleneimine have also been used for deposition of TiO_2 on CNT surfaces [24–26] and, while these surfactants generate strong interactions between the CNTs and TiO_2 particles, they frequently poison the catalytic activity of the metal oxide.

We have previously covered CNT-supported precious metal particles such as Pt, Pd, Ru, Rh and Au with silica layers [27–30], and these silica-coated precious metal catalysts showed high resistance to sintering of the metal particles at high temperatures. We have also utilized these silica-coated Pt/CNT catalysts as cathodes in PEFCs [31–33]. Carbon black-supported Pt catalysts are typically employed as cathode catalysts in PEFCs, but these catalysts are severely deactivated under PEFC cathode conditions through the aggregation of Pt metal particles and the dissolution and redeposition of the Pt metal (also known as Ostwald ripening) [34–37]. The application of silica layers around the Pt metal particles was found to prevent the migration of Pt over the CNTs and to retard the diffusion of dissolved Pt cations through the silica. Thus, silica-coated Pt/CNT cathode catalysts showed excellent durability. These silica-coated Pt/CNT catalysts have been prepared by the successive hydrolysis of 3-aminopropyltriethoxysilane (APTES) and tetraethoxysilane (TEOS) [28]. In this process, APTES is adsorbed on the surfaces of both the Pt particles and the CNTs through interactions with the amino groups in APTES, forming thin silica layers. These layers subsequently work as nucleation sites for silica formed during the subsequent hydrolysis and polycondensation of TEOS. The thin silica layers generated by the APTES are vital in terms of ensuring uniform coverage of the Pt/CNT surfaces with silica layers a few nanometers thick. It is believed that the silica layers formed in this manner function as nucleation sites for precious metals or metal oxides, stabilizing nanoparticles of these substances on the CNT surfaces. In the present study, thin silica layers resulting from the application of APTES were used to modify CNT surfaces by the addition of precious metal and transition metal oxide nanoparticles, and it was determined that smaller particle sizes of these substances could be densely deposited on the CNT surfaces when these surfaces were covered with thin silica layers.

2. Experimental

2.1. Preparation of catalysts

CNT surfaces were covered with thin silica layers by the application of APTES. In this process, CNTs (0.1 g) were dispersed in water (22 mL) and the pH of the dispersion was adjusted to approximately 10 by the addition of aqueous NH_3. APTES was then added at a concentration of 4, 10, 15 or 40 mM and the dispersion was stirred at 333 K for 2 h. The silica-coated CNTs prepared at APTES concentrations of 4, 10, 15 and 40 mM were denoted as AP4/CNT, AP10/CNT, AP15/CNT and AP40/CNT, respectively. The resulting AP/CNT samples were again dispersed in water to prepare supported Pt catalysts (Pt/AP/CNT) through the addition of an aqueous solution of $Pt(NO_2)_2(NH_3)_2$. The resulting dispersions were dried at 333 K and the supported catalyst samples were reduced under hydrogen at 623 K. The nominal loading of Pt in each sample was adjusted to 15 wt%. The loading of Pt and Si in the catalysts was evaluated with inductively coupled plasma atomic emission spectroscopy (ICP-AES).

CNT-supported Pt (Pt/CNT) catalysts were also covered with transition metal oxides (ZrO_2, Nb_2O_5 and Ta_2O_5) in order to modify their catalytic performance. The initial Pt/CNT materials were prepared using a conventional impregnation method, in which CNTs were dispersed in an aqueous $Pt(NO_3)_2(NH_3)_2$ solution that was subsequently evaporated to dryness. The samples thus obtained