



Selective Synthesis of Graphitic Carbon and Polyacetylene by Electrochemical Reduction of Halogenated Carbons in Ionic Liquid at Room Temperature



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ABSTRACT

An electrochemical deposition technique was developed to realize high yield and selective synthesis of target carbon nanomaterials. The electrochemical reduction of halogenated carbons, such as carbon tetrachloride, in an ionic liquid was found to result in the formation of a thick graphitic carbon film over a Ni substrate, whereas polyacetylene formation was confirmed in the presence of a small amount of H₂O. Such a novel high yield, selective carbon synthesis is expected to be a promising technique for the design of various carbon nanomaterials.

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1. Introduction

Carbon nanomaterials such as graphene, carbon nanotubes (CNTs), fullerenes, diamond-like carbon, graphitic carbon, and polyacetylene have been widely studied in various fields due to their unique physical, electrical, thermal, electrochemical, and mechanical properties [1–7]. For example, graphitic carbon, which consists of sp² hybridized carbon bonds, has received much attention for use in energy storage devices such as electrochemical capacitors because it possesses not only high electrical conductivity and low ion-transport resistance, but is also easier to synthesize than graphene and CNTs [8,9]. As another carbon nanomaterial, conjugated polyacetylene has also been studied as a material for electrical and optical applications due to its high electric conductivity with controlled doping [4,10]. The high potential for such materials in various industrial applications has resulted in a focus on the development of a facile method for high-yield, and selective synthesis of such carbon materials.

Conventional C–C bond formation techniques, such as arc discharge evaporation, chemical vapor deposition and RF plasma-polymerization of precursor molecules, are generally based on high temperature processes [11,12]. Although these techniques can

provide high yielding growth, the equipment such as reaction furnace, heating, gas flow and pumping systems is costly. In addition, they possess highly controllability of the C–C bond formation, however, precious control of an amount of catalyst for carbon growth is generally required. A potential alternative synthesis technique is electrochemical deposition. Recently, we have developed a room temperature synthesis method for single-wall carbon nanotubes (SWCNTs) via electrochemical reduction of acetic acid in aqueous solution over a Au surface supporting Ni nanocatalysts [3]. This room-temperature electrochemical process is a promising technique for future applications because it is a simple process compared with the conventional methods. However, the process results in a relatively low yield of SWCNTs (ca. a few tubes /μm²) due to the low efficiency of the acetic acid reduction reaction, despite the very unique characteristics that enable control of selective C–C bond formation by the size of the metal nanoparticle catalysts on the Au electrode.

Halogenated hydrocarbon molecules have high electrochemical decomposition characteristics and have been used as carbon sources for the synthesis of various carbon materials [13,14]. For example, Herrick and co-workers reported that carbonaceous fibers can be synthesized in high yield by the galvanostatic deposition of CCl₄ in acetonitrile onto a metal substrate at room temperature [15]. The reduction of other halogenated carbon molecules, such as poly(tetrafluoroethylene), hexachlorobuta-1,3-diene and diiodoacetylene, has also resulted in the production of

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graphitic carbon films [16,17]. Further analysis indicated that the carbonization process was highly sensitive to the presence of protons in the solvent. In the case of an aprotic solvent, C–C bond formation is dominated by carbon radical reactions, while in a protic solvent, carbon–hydrogen (C–H) bond formation is preferential by protonization of the carbon radicals [18,19].

In consideration of these results, electrochemical reduction of halogenated carbon molecules was employed in the present study to achieve not only high yield relative to previous our study [3] but also control of the C–C bond formation during synthesis. Ionic liquid was used as an electrolyte because it possesses not only a wide electrochemical window but can also be used to easily control the presence of proton sources such as H₂O compared to conventional organic solvents. CCl₄ was used as a carbon precursor, and the effect of H₂O addition as a proton source was investigated for selective carbon growth.

2. Experimental

An in-house-built three-electrode cell was used for the electrochemical deposition system. *N,N,N*-trimethyl-*N*-propylammonium bis-(trifluoromethane) sulfonimide (TMPA-TFSI, Kanto Chemical) was used as the electrolyte. This ionic liquid has an extremely low vapor pressure and high temperature stability; therefore, the dehydrated ionic liquid could be easily prepared by heat treatment at 120 °C for 24 h in a vacuum oven (ca. 10⁴ Pa). Carbon tetrachloride (99.5%, Wako Chemical) was used as the carbon source. The reference electrode was a Ag/Ag⁺ electrode in 0.05 M AgSO₃CF₃ (99.5% Wako Chemicals) with TMPA-TFSI. 0.1 mm thick Pt and Ni sheets were used as the counter and working electrodes, respectively. Ni sheet was ultrasonicated in ethanol for 10 min, and the Pt sheet and electrochemical cell were cleaned in piranha solution (H₂SO₄:H₂O₂ = 3:1) for 1 h and then rinsed with excess deionized H₂O. All electrodes and the cell were stored in a vacuum oven for 1 day at 120 °C to eliminate all traces of H₂O. To prevent exposure to H₂O, setup of the cell and electrochemical deposition were conducted inside a glove bag with flowing nitrogen gas at room temperature. The electrochemical system was used with a potentiostat (Hokuto Denko, HSV-110). Ar or N₂ gases were bubbled from the inlet to remove oxygen from the electrolyte, and carbon was electrochemically deposited at -2.5 V for polarization times of from 1 to 45 min. Prior to characterization, the as-deposited samples were rinsed with acetone and deionized H₂O to eliminate the ionic liquid. The influence of a proton source on carbonization was investigated by the addition of 0.1 M deionized H₂O in TMPA-TFSI. Raman spectroscopy (Thermo Scientific, DXR, 532 nm) and atomic force microscopy (AFM; Nanoscope IIIa, Veeco) in tapping mode were used to analyze the deposited carbon material.

3. Results & discussion

3.1. Electrochemical deposition over the surface

Cyclic voltammetry (CV) was first performed to verify the electrochemical characteristics of CCl₄ in TMPA-TFSI. Fig. 1 shows CV analysis results for TMPA-TFSI, TMPA-TFSI containing CCl₄, and TMPA-TFSI containing CCl₄ and H₂O, respectively. In case of TMPA-TFSI, a reductive current was observed at less negative potential than -2.7 V and was -0.15 mA/cm² at -3.0 V. In contrast, the reduction currents for both the solutions of TMPA-TFSI containing CCl₄ in the presence and absence of H₂O were observed at less than -2.3 V, and reached -0.25 and -0.35 mA/cm² at -3.0 V, respectively. The increase of the current densities is attributed to the reduction of CCl₄ or CCl₄ and H₂O. Besides, hysteresis loop was appeared for TMPA-TFSI containing CCl₄, suggesting a possibility of

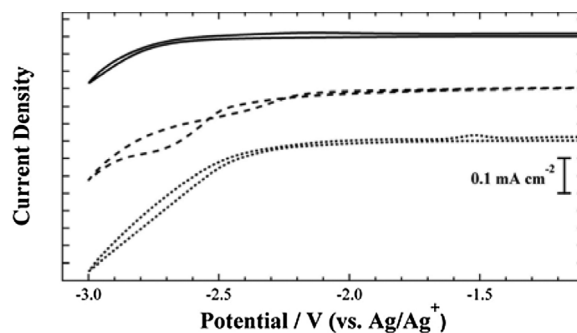


Fig. 1. Cyclic voltammogram for TMPA-TFSI (solid lines), TMPA-TFSI with CCl₄ (dashed lines), and TMPA-TFSI with CCl₄ and H₂O (dotted lines). All CV results were obtained at a scan rate of 50 mV/s.

nucleation-and-growth deposition. In addition, dark brown films were produced on the Ni substrates after reduction of both the solutions of TMPA-TFSI containing CCl₄ in the presence and absence of H₂O, while no color change was observed in the presence of only TMPA-TFSI (Fig. S1). These results indicate that the electrochemical reduction of CCl₄ in TMPA-TFSI can efficiently yield carbon materials.

The time dependence of carbon deposition was investigated at a constant potential of -2.5 V for 30 min. Fig. 2 shows the current density as a function of deposition time. For TMPA-TFSI, the current density instantaneously increased after the potential step and then quickly dropped to a state with no current flow. In contrast, the current densities for both TMPA-TFSI with CCl₄ in the presence and absence of H₂O continued to flow until the end of the deposition, which suggests that the reduction reaction proceeds on the surface during negative polarization. The current curve for the system with H₂O was different from that without H₂O; the reductive current was gradually increased until 5 min and then slowly decreased, and the current continued to flow. The observed reductive current peak strongly indicates that carbon deposition mechanism for TMPA-TFSI with CCl₄ and H₂O is different from that of TMPA-TFSI with CCl₄. According to previous studies, Radisic and co-workers reported that same tendency in current versus time curves observed for Cu electrochemical deposition on a Au surface [20], where the growth process was based on a nucleation and growth mode; carbon clusters can be grown at nucleation sites and the size of the clusters is steadily increased [21]. In the consideration of this previous study, the observed mono-current peak in Fig. 2 is attributed to the nucleation and growth mode. The deposited carbon materials were characterized using Raman spectroscopy and AFM. In the case of TMPA-TFSI, CCD and AFM analyses (Fig. 3(a) and (b)) showed only a bare Ni surface, and no Raman characteristics were observed (Fig. 3(c)). These results indicate that no carbon deposition occurred on the surface, as already shown in Fig. S1. However, in case of the electrolyte containing CCl₄, a brown

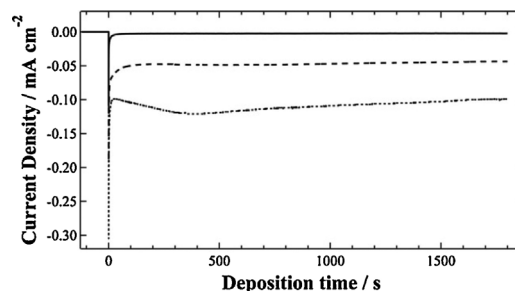


Fig. 2. Current density versus deposition time for the TMPA-TFSI (solid line), TMPA-TFSI with CCl₄ (dashed line), and TMPA-TFSI with CCl₄ and H₂O (dotted line).

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