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

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KEYWORDS

Electrochemical deposition, Polyacetylene, Graphitic Carbon, Ionic liquid, Halogenated Carbon

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.

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 sp^2 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 / μm^2) 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 CCl_4 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 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 H_2O compared to conventional organic solvents. CCl_4 was used as a carbon precursor, and the effect of H_2O 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. 10^4 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 0.1M 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 CCl_4 in TMPA-TFSI. **Fig. 1** shows CV analysis results for TMPA-TFSI, TMPA-TFSI containing CCl_4 , and TMPA-TFSI containing CCl_4 and H_2O , respectively. In case of TMPA-TFSI, a reductive current was observed at less negative potential than -2.7 V and was -0.15 mA/cm^2 at -3.0 V. In contrast, the reduction currents for both the solutions of TMPA-TFSI containing CCl_4 in the presence and absence of H_2O were observed at less than -2.3 V, and reached -0.25 and -0.35 mA/cm^2 at -3.0 V, respectively. The increase of the current densities is attributed to the reduction of CCl_4 or CCl_4 and H_2O . Besides, hysteresis loop was appeared for TMPA-TFSI containing CCl_4 , suggesting a possibility of 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 CCl_4 in the presence and absence of H_2O , while no color change was observed in the presence of only TMPA-TFSI (**Fig. S1**). These results indicate that the electrochemical reduction of CCl_4 in TMPA-TFSI can efficiently

Fig. 1 Cyclic voltammogram for TMPA-TFSI (solid lines), TMPA-TFSI with CCl_4 (dashed lines), and TMPA-TFSI with CCl_4 and H_2O (dotted lines). All CV results were obtained at a scan rate of 50 mV/s.

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 CCl_4 in the presence and absence of H_2O 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 H_2O was different from that without H_2O ; 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 CCl_4 and H_2O is different from that of TMPA-TFSI with CCl_4 . 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

Fig. 2 Current density versus deposition time for the TMPA-TFSI (solid line), TMPA-TFSI with CCl_4 (dashed line), and TMPA-TFSI with CCl_4 and H_2O (dotted line).

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 TPMA-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 CCl_4 , a brown colored film was formed over the entire surface (**Fig. 4(a)**), and AFM analysis revealed that the film surface is covered with nanometer-sized carbon particles with an average size of 38 nm (**Fig. 4(b)**). In addition, Raman measurement showed two broad Raman peaks at ca. 1570 and 1355 cm^{-1} (**Fig. 4(c)**). It is well known that single crystal graphite, which consists of a pure sp^2 carbon structure, has a single peak at 1580 cm^{-1} arising from the tangential mode (G band), and sp^2 disordered graphite has a broad peak at around 1350 cm^{-1} (D band). The G band has E_{2g} symmetry, which is due to the in-plane vibration of sp^2 carbon atoms and the stacking order, whereas the D band has T_{2g}

Fig. 3 (a) CCD and (b) AFM images, and (c)

Raman spectrum for the as-deposited material

from TPMA-TFSI on a Ni surface.

symmetry, which is attributed to interaxial vibration on the carbon atoms. [22] It should be noted that CCl_4 was completely decomposed by electrochemical reaction in all experiments, as confirmed by Raman observation with the lack of the chlorine stretching mode from 450 to 470 cm^{-1} . Other small Raman peaks were also observed around 300 and 650 cm^{-1} , suggesting that these peaks might be associated with graphitized C-Cl vibration modes. [23] The results indicate a possibility of the formation of a small amount of Cl-modified carbon. The ratio of the D to G band intensity (I_D/I_G) enables an estimation of the degree of structural disorder in the sp^2 graphitic carbon structure. [24] Highly crystalline graphite exhibits a low I_D/I_G (typically <0.1). In contrast, polycrystalline or disordered graphitic carbon materials including disordered carbon structures have relatively large I_D/I_G (typically ~ 1). The deposited carbon material had an I_D/I_G value around 0.6, which indicate the formation of a graphitic carbon structure. The graphitic carbon particle size can be calculated according to the following equation: [25]

$$L_a(\text{nm}) = (2.4 \times 10^{-10}) \lambda_l^4 \left(\frac{I_D}{I_G} \right)^{-1}, \quad (1)$$

where L_a and λ_l are the theoretical crystallite size and the Raman laser wavelength, respectively. From this equation, the graphitic particle size was estimated to be approximately 41 nm, which is in good agreement with the size of 38 nm determined by AFM analysis (**Fig. 4(d)**). Further characterization of the carbon material deposited from the electrolyte containing both CCl_4 and H_2O was conducted, and different features from that for the

Fig. 4 (a) CCD and (b) AFM images, and (c) Raman spectrum for the as-deposited material from TPMA-TFSI with CCl_4 on a Ni surface. (d) Count histogram for graphitic carbon particle size (total count 50). **Deposition time is 30 min.**

material deposited from the electrolyte containing CCl_4 were determined. Unlike the graphitic film formation in the electrolyte containing CCl_4 , CCD images revealed black particle structures over the entire surface (**Fig. 5(a)**). Several sharp Raman peaks were observed, which correspond to C-C (1115 cm^{-1}), C=C (1500 cm^{-1} and 2610 cm^{-1}), and C-H (2230 cm^{-1} and 3000 cm^{-1}) stretching modes of trans-polyacetylene (Fig. 5(b)). [26] Although polyacetylene is well-known to have either cis or trans configuration, Raman bands originating from cis-polyacetylene (ca. 920 , 1260 and 1550 cm^{-1}) were never observed in this study, indicating the formation of only trans-polyacetylene. Furthermore, several small Raman peaks around 390 , 580 and 870 cm^{-1} were also observed, suggesting the formation of a small amount of Cl-modified polyacetylene. [23] These results demonstrate that the addition of H_2O effectively inhibits the formation of graphitic carbon and promotes the selective production of polyacetylene. Polyacetylene with high molecular weight was for the first time reported by Natta and coworkers using acetylene gas and catalysts that consist of organoaluminum and metallocene complex. [27–29] Dů and co-workers proposed new synthesis technique using RF plasma-polymerization of acetylene. [30] The polyacetylene formation by electrochemical reduction of CCl_4 and H_2O has been never reported before, suggesting high potential for new synthesis technique of polyacetylene derives.

In addition, deposited carbon densities could be estimated. In our previous work, [3] synthesized carbon nanotubes were covered about a few tubes per $1\text{ }\mu\text{m}^2$, which corresponds with the density of 10^{-18} g/cm^2 . On the other hand, densities of synthesized graphitic carbon and polyacetylene in this study were gained about 10^{-6} and 10^{-5} g/cm^2 , by calculating total electric charges in Fig. 2. These comparisons clearly indicate that the yield in our system is enormously higher than that in the previous our work. [3] Furthermore, the current efficiencies for both carbon depositions were also roughly estimated to be $\sim 10^5\%$, indicating

Fig. 5 (a) CCD and (b) Raman spectrum for the as-deposited material from TPMA-TFSI containing both CCl_4 and H_2O .

that our deposition system possesses highly conversion efficiency to the carbon materials.
(see supporting information)

3.2 Reaction mechanism

We consider the selective carbon growth mechanism. According to previous studies, [31] the dehalogenation process of a carbon-halogen bond on a cathode occurs as follows:

Electron transfer from the cathode to the halogenated carbon molecule R-X (X = halogen

atom) initially dissociates the carbon-halogen bond through intermediate molecular anion formation, and then slowly generates carbon radicals $R^\cdot$ (Eq. (2)). These carbon radicals induce various radical reactions and form electrochemical carbonization products (Eq. (4)). In the presence of a proton source, C-H bond formation also occurs by protonization of the carbon radicals (Eqs. (3a) and (3b)).

Considering these reactions, the electrochemical reduction reaction with CCl_4 is contributes to the production of carbon radicals (Eq. (2)). **These carbon radicals such as $:\text{CCl}_2$ and $^\cdot\text{CCl}_3$ react with each other (Eq. (4)) followed by a propagation step of the radicals with the products. Finally, further dehalogenation of these products occurs on the surface, which results in graphitic carbon film formation.** For the electrochemical reduction reaction of CCl_4 in the presence of H_2O , it is suggested that protonation (Eq. (3a) or Eq. (3b)) proceeds after the dehalogenation process in Eq. (2).

To confirm the origin of the carbon source, polyacetylene deposition was conducted in TPA-TFSI containing CHCl_3 , CDCl_3 or $^{13}\text{CHCl}_3$ as a carbon source. These carbon sources contain a hydrogen atom, so that polyacetylene can be produced even without the addition H_2O . Raman measurements showed that the peak positions of the C-C and C=C stretching mode of polyacetylene produced from $^{13}\text{CHCl}_3$ were clearly shifted to lower frequency than that produced from CHCl_3 and CDCl_3 . These results demonstrate that the deposition of polyacetylene is due to the carbon source not to the breakdown of the TPA-TFSI ionic liquid (**Fig. S2** and **Table S1**).

3.3 Growth mechanisms

To obtain further insight, the dependence of film formation on the deposition time was investigated. **Figures 6(a)-(c)** show CCD images of the deposition surface with the electrolyte containing CCl_4 before deposition and at 1 and 30 min after deposition. The color of the film became uniformly darker with the deposition time. The I_D/I_G values from the Raman bands intensities (D- and G-bands) shown in **Fig. 6(d)** gradually increased with the deposition time. These trends indicate that after nucleation of the graphitic nanoparticles formed by the reaction in Eq. (2), the particles homogeneously grow in size and thicken as the reduction reaction progresses to the edge and defect sites of the particles, which results in the formation of a uniform graphitic carbon film. **In addition, the I_D/I_G value also increased with the deposition time, suggesting an increase of the degree of order.**

Fig. 6 CCD images for the surface (a) before, and after deposit from CCl_4 in TMPA-TFSI at (b) 1 and (c) 30 min of deposition. (d) Raman spectra of deposits after 1 min (solid line) and 30 min (dashed line).

For polyacetylene growth in the electrolyte containing CCl_4 in the presence of H_2O , CCD images revealed that small black particles nucleate over the surface during the initial growth stage, and the number of nucleation sites and the particle size increase with the deposition time (**Figs. 7(a)-(d)**). The observed features of these deposits are different from those of the graphitic carbon formation. Although the Raman spectral intensities also increased during the formation of the deposits, no changes in the features of Raman spectra were observed. These results indicate that polyacetylene tends to nucleate and grow in size on the substrate. As shown **Fig. 2** (dotted line), it was suggested that the observed mono-current peak is due to the nucleation and growth mode, which is in good agreement with the results shown in **Figs. 7(a)-(d)**. Therefore, it is considered that at the initial stage, the reduction reactions of Eq. (2) and (3) produce polyacetylene “particles” on the surface. The ionic liquid is considered to be a poor solvent for polyacetylene; therefore, aggregated particles are expected to form on the surface. These polyacetylene particles must have electric conductivity, and thus the reduction reaction preferentially occurs on the polyacetylene particles rather than on the bare surface, which results in further nucleation and growth.

It was also observed that the particles tend to nucleate at imperceptible scratches on the substrate, as shown **Figs. 7(a)-(c)**. Further investigation is necessary to confirm this; however, it is suggested that the scratch edges behave as active sites for nucleation due to of the local electric field or dangling bonds on the surface.

Fig. 7 CCD images for deposits formed from TMPA-TFSI with CCl_4 and H_2O at (a) 5 (b) 15, (c) 30, and (d) 45 min. (e) Raman spectra for deposits formed at 5 min (solid lines), 15 min (dotted lines), 30 min (solid bold lines) and 45 min (dashed line).

4. Conclusions

Carbon nanomaterial synthesis by the electrochemical reduction of a halogenated carbon source in an ionic liquid at room temperature was investigated to achieve relatively simple and high yield selective synthesis of C-C bonds. **It was demonstrated that carbon nanomaterials could be deposited on the cathode at higher yields than previously reported**

carbon synthesis by electrochemical reduction of acetic acid in aqueous solution. [3]

Application of an ionic liquid as the electrolyte resulted in the successful control of C-C bond formation of nanosize graphitic carbon particles on the electrodes. In the presence of small amount of H₂O, the present method leads to the formation of trans-polyacetylene. Over the deposition time, graphitic nanocarbon particles grow homogeneously in size and thicken to form a graphitic carbon film. In contrast, polyacetylene tends to aggregate on the surface as a particle structure, an inhomogeneous film of many particles was produced. The present findings provide information on a promising technique for the preparation of selective carbon materials synthesis, which may lead to the synthesis of low-cost and low-energy consumption carbon materials for future industrial applications.

5. Acknowledgments

This work was partially supported by the Canon Foundation, Japan Science and Technology Agency, PRESTO and Grants-in-Aid for Scientific Research (Nos. 22710127, 25109701, 25620003, and 24655162), from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. The authors thank Prof. T. Torimoto of Nagoya University for useful discussions regarding the electrochemical reactions in the ionic liquid.

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