Electrochemical Formation of Selenium Nanoparticle in an Amide-type Ionic Liquid

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ABSTRACT

Electrochemical formation of selenium (Se) nanoparticles in an amide-type ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMPTFSA) containing selenium tetrachloride (SeCl_4) was investigated in the presence of excess chloride anion on a glassy carbon electrode. Electrochemical reduction of $[\text{SeCl}_6]^{2-}$ resulted in deposition of Se on the electrode surface. The deposited Se was further reduced electrochemically at the more negative potential region to form $[\text{Se}_2]^{2-}$, which was suggested to exist by ultraviolet-visible spectroscopy. Se nanoparticles dispersed in the ionic liquid were formed by the proportionation reaction between $[\text{SeCl}_6]^{2-}$ and $[\text{Se}_2]^{2-}$ in the ionic liquid. The Se nanoparticles were characterized by energy dispersive X-ray spectroscopy and transmission electron microscopy.

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1. Introduction

Selenium (Se) is an optically important metal because of its photoconductivity and photovoltaic properties, and is widely used for X-ray detectors,¹ toners and so on. In particular, such Se compounds as CdSe , ZnSe , CuInSe_2 (CIS), and $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS)^{2–5} are well known as promising compound semiconductors for solar cells. Although there have been number of reports on electrodeposition of Se in aqueous system,^{6–8} the electrochemical behavior of selenium species has not been clarified completely due to the complexities, such as generation of H_2Se , alloy formation with substrates and under potential deposition (UPD). Aprotic room-temperature ionic liquids (RTILs) have been investigated as the electrolytes for electrolysis of Se^{9–11} due to their advantageous properties, such as acceptable intrinsic ionic conductivity, high chemical and thermal stability, negligible vapor pressure, and wide electrochemical potential window.¹² It has been reported that SeCl_4 dissolves as $[\text{SeCl}_6]^{2-}$ in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMPTFSA) in the presence of excess chloride anion, and that the reduction of $[\text{SeCl}_6]^{2-}$ to Se and that of Se to $\text{Se}(-\text{II})$ occurs successively.¹³ In addition, Se deposits were suggested to be obtained by the proportionation reaction between $[\text{SeCl}_6]^{2-}$ and $\text{Se}(-\text{II})$.

Recently, nanoparticles or quantum dots of the compound semiconductors containing Se have been attracting attention as fluorescent materials.¹⁴ RTILs have also been studied for preparation and stabilization of metal nanoparticles because of their excellent ability to disperse the nanoparticles without any stabilizing agent.^{15,16} We have reported on electrochemical preparation of various metal nanoparticles in some aprotic ILs.^{17–19} Electrochemical preparation of nanoparticles can be performed easily and inexpensively compared to other methods, including electron beam irradiation, chemical reduction, and sputtering.^{20–22} However, electrochemical preparation of the nanoparticles of intermetallic compounds has not been attempted although it may be achieved by codeposition of different metals in RTILs. The nanoparticles of

the compound semiconductors containing Se are also expected to be formed by electrochemical reduction of selenium species in RTILs while formation of $\text{Se}(-\text{II})$ may prevent codeposition of the compound semiconductors. In the present study, electrochemical formation of Se nanoparticles was studied in BMPTFSA containing SeCl_4 in the presence of excess chloride anion.

2. Experimental

BMPTFSA (Kanto Chemical, 99.5%) and SeCl_4 (Alfa Aesar, 99%) were used as supplied. The water content in BMPTFSA was found to be below 30 ppm by Karl Fischer titration (Metrohm, 831KF). BMPCl was prepared by interacting butyl chloride (Wako Pure Chemical Industries, >98%) and 1-methylpyrrolidine (Tokyo Chemical Industries, >98%), purified by distillation under reduced pressure, in acetonitrile (Kanto Chemical, >99.5%) at 70°C for 24 hours, followed by recrystallization and vacuum drying at 100°C for 24 hours.

A two-compartment three-electrode cell was used for electrochemical measurements with a potentiostat/galvanostat (Hokuto Denko, HABF501A) or automatic polarization system (Hokuto Denko, HSV-110). A Pt wire was used for a counter electrode. A disk (3 mm ϕ , 7.07 $\times$ 10^{–2} cm²) and plate (14 mm ϕ , 1.54 cm²) of glassy carbon (GC, Tokai Carbon, GC-20SS) were used as the working electrode for cyclic voltammetry and potentiostatic electrolysis, respectively. The surfaces of the GC electrodes were mirror polished, rinsed with distilled water and dried before use. A reference electrode was composed of a silver wire dipped in BMPTFSA containing 0.1 M AgCF_3SO_3 (Aldrich, >99%) and isolated from the electrolyte by porous glass (Vycor). The redox potential of ferrocenium (Fc^+)/ferrocene (Fc) was observed at –0.43 V against this reference electrode.²³ The counter electrode was placed in the compartment isolated by a polytetrafluoroethylene membrane filter (Merck Millipore, Durapore[®] Membrane Filters) with the average pore size of 1 μm . Potentiostatic electrolysis was carried out at 60°C to increase the electronic conductivity of Se. The obtained electrodeposits were washed with acetonitrile and characterized by an energy dispersive X-ray analyzer (EDX, Oxford

Figure 1. Cyclic voltammogram of a GC electrode in 0.5 M BMPCl/BMPTFSA containing 30 mM SeCl₄ at 25°C. Scan rate: 50 mV s⁻¹.

Instruments, INCA-E250×3K) and a scanning electron microscope (SEM, Keyence, VE-9800). The nanoparticles were characterized using a transmission electron microscope (TEM, FEI, TECNAI F20) equipped with an EDX (Oxford Instruments, X-Mat 80T). The TEM sample was prepared by dropping the IL on a TEM grid (Okenshoji, HRC-C10) and washing the grid with acetonitrile to remove the excess IL.

Handling of hygroscopic reagents and electrochemical measurements were conducted in an argon-filled glovebox with a continuous gas purification apparatus (Miwa MFG, DBO-1KP-K03).

A Se electrode was prepared by potentiostatic cathodic reduction on a GC electrode in 50 mM SeO₂ aqueous solution containing 1 M NaNO₃ as a supporting electrolyte at -0.7 V vs. Ag|AgCl. The needle-like deposits obtained on the electrode were confirmed to be hexagonal Se by XRD. BMPTFSA containing reduced Se was prepared by potentiostatic cathodic reduction of the Se electrode in BMPTFSA at -1.7 V (electric charge: 10 C) and characterized by ultraviolet-visible (UV-vis) spectroscopy (JASCO, V-770).

3. Results and Discussion

Figure 1 shows the cyclic voltammogram of a GC electrode in 0.5 M BMPCl/BMPTFSA containing 30 mM SeCl₄ at 25°C. Two cathodic current peaks (C1 and C2) were observed at -1.4 and -1.7 V. The cathodic current peak at -1.4 V (C1) was attributable to the following four electron transfer reaction according to the previous report.¹³

The cathodic current peak at -1.7 V is reported to correspond to reduction of Se(0) to Se(-II). However, there have been known several polyselenide species like [Se_n]⁻ (*n* = 2, 3) and [Se_n]²⁻ (*n* = 1–4).²⁴ In order to identify the reduced product of Se(0), BMPTFSA containing the reduced product was prepared by potentiostatic cathodic reduction of a Se electrode. Figure 2 shows the UV-vis spectrum of BMPTFSA after the potentiostatic electrolysis at -1.7 V (electric charge: 10 C). Two absorption bands observed at 310 and 420 nm were in good agreement with those assigned to [Se₂]²⁻ in an aqueous solution.²⁵ Therefore, the reduced product of Se in BMPTFSA at -1.7 V was found to be [Se₂]²⁻. Thus, the cathodic current peak at -1.7 V (C2) was represented by the following reduction reaction.

Figure 2. UV-vis spectrum of BMPTFSA after potentiostatic cathodic reduction of Se at -1.7 V. Electric charge: 10 C.

Figure 3. Current density during potentiostatic electrolysis at -1.4 and -1.7 V on a GC electrode in 0.5 M BMPCl/BMPTFSA containing 30 mM SeCl₄ at 60°C.

Figure 3 shows the current density observed during potentiostatic cathodic reduction at -1.4 and -1.7 V on a GC electrode in 0.5 M BMPCl/BMPTFSA containing 30 mM SeCl₄ at 60°C. The current density at -1.4 V decreased with the elapse of time probably due to the coverage of the electrode surface with low conductive Se. On the other hand, the continuous current was observed at -1.7 V, indicating the coverage of the electrode surface with Se was suppressed by reduction of deposited Se to [Se₂]²⁻, which was soluble in the IL. Electrodeposits of Se were obtained on the electrode after potentiostatic cathodic reduction at -1.4 V. On the other hand, potentiostatic cathodic reduction at -1.7 V resulted in not only deposition of Se on the electrode surface but also formation of the black precipitate in the IL. The XRD pattern of the precipitate gave the diffraction peaks corresponding to metallic Se, indicating Se was formed during reduction of Se in the presence of [SeCl₆]²⁻ by the proportionation reaction between [SeCl₆]²⁻ and [Se₂]²⁻.

Figure 4. (a) TEM image and (b) EDX spectrum of the nanoparticle obtained by potentiostatic cathodic reduction at -1.7 V on a GC electrode in 0.5 M BMPCl/BMPTFSA containing 30 mM SeCl_4 at 60°C . Electric charge: 28.9 C. The inset in (a) shows the electron diffraction image of a nanoparticle.

Although it was difficult to deposit Se on the electrode due to the low electronic conductivity of Se, continuous preparation of metallic Se was found to be possible by potentiostatic cathodic reduction at -1.7 V. In addition, the TEM image of the IL after the potentiostatic cathodic reduction indicated formation of the nanoparticles dispersed in the IL, as shown in Fig. 4(a). The inset of Fig. 4(a) shows the electron diffraction image of the nanoparticle. The interplanar spacing calculated from the spots was 0.358 nm, which was close to that of Se (100), 0.351 nm (ICDD #01-072-4526). The nanoparticles were found to contain Se by the EDX spectrum, as shown in Fig. 4(b). The peaks attributed to carbon (C) and copper (Cu) were derived from the TEM grid. Thus, it was found that Se nanoparticles were also obtained by electrochemical reduction of $[\text{SeCl}_6]^{2-}$ at -1.7 V in addition to the precipitation of Se.

Se is considered to form by the proportionation reaction between $[\text{SeCl}_6]^{2-}$ and $[\text{Se}_2]^{2-}$ as represented by the following reaction.²⁶

In order to confirm this reaction occurs in the IL, BMPTFSA containing $[\text{Se}_2]^{2-}$ was mixed with 0.5 M BMPCl/BMPTFSA containing 30 mM SeCl_4 . When BMPTFSA containing $[\text{Se}_2]^{2-}$ (green) and 0.5 M BMPCl/BMPTFSA containing 30 mM SeCl_4 (yellow) were mixed at 25°C , the mixture once became red and immediately turned yellow. Although no precipitate formed in the mixture, the TEM image of the mixture showed formation of nanoparticles, as shown in Fig. 5(a). The nanoparticle was confirmed to be Se from the electron diffraction image, as shown in the inset of Fig. 5(a). The nanoparticles were confirmed to be Se from the EDX spectrum, as shown Fig. 5(b), verifying Se nanoparticles formed by the proportionation reaction between $[\text{SeCl}_6]^{2-}$ and $[\text{Se}_2]^{2-}$. On the other hand, no precipitate of Se was obtained in the case of mixing the ILs containing $[\text{SeCl}_6]^{2-}$ and

Figure 5. (a) TEM image and (b) EDX spectrum of the nanoparticle obtained by mixing BMPTFSA containing $[\text{Se}_2]^{2-}$ and 0.5 M BMPCl/BMPTFSA containing 30 mM SeCl_4 at 25°C . The inset in (a) shows the electron diffraction image of a nanoparticle.

$[\text{Se}_2]^{2-}$, probably because formation of Se nanoparticles occurs homogeneously in the IL. In the case of electrolysis, Se nanoparticles are considered to form near the electrode, where $[\text{Se}_2]^{2-}$ is produced electrochemically at higher concentration. Thus, aggregated Se particles may form in addition to Se nanoparticles.

4. Conclusion

Electrochemical preparation of Se nanoparticles dispersed in the IL was found to be possible by reduction of $[\text{SeCl}_6]^{2-}$ and proportionation reaction of $[\text{SeCl}_6]^{2-}$ and $[\text{Se}_2]^{2-}$. The compound semiconductors containing Se are expected to be prepared by the reaction of $[\text{Se}_2]^{2-}$ with other metal species. However, $[\text{SeCl}_6]^{2-}$ is not suitable for the Se source because the proportionation reaction between $[\text{SeCl}_6]^{2-}$ and $[\text{Se}_2]^{2-}$ leads to formation of Se nanoparticles instead of the compound semiconductors.

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