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Fabrication of Transition Metal Oxide Nanoparticles Highly Dispersed in Ionic Liquids by Sputter Deposition

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Sputter deposition of transition metals W, Mo, Nb, and Ti into ionic liquids (ILs) produced corresponding metal oxide nanoparticles (NPs) smaller than 6 nm. The NPs were obtained in a highly dispersed manner without any additional stabilizing agent in ILs.

Nanoparticles (NPs) are well known to show enhanced and/or to altered properties compared to the original bulk material.[1–5] Transition metal oxide NPs are of particular importance in various fields of science and technology, such as in heterogeneous catalysis,[6] where they are used as catalyst supports for a wide variety of metals or as selective oxidation catalysts by themselves. Applications to electric devices and sensors are also important because metal oxides can be used as insulators, semiconductors, conductors, and even superconductors. These characteristics result from the electronic states in the bulk or localized surface states. Hence, there is much interest in how the properties change with change in the size of metal oxide NPs.

There are several methods for fabricating metal oxide NPs, and they can be classified into physical and chemical techniques: physical methods include sputtering (dc, RF, and reactive), evaporation (thermal and electron beam),[7] and pulse laser deposition,[8] and chemical methods include sol–gel, coprecipitation, impregnation, chemical vapor synthesis, and hydrothermal treatment.[9–12] Ionic liquids (ILs) are suitable media for the synthesis of metal oxide NPs by decomposition of metal carbonyl or alkoxide,[13,14] because ILs are utilized as nonflammable and nonvolatile solvents. We have recently reported that sputter deposition of noble metals such as Au and Ag into ILs results in the production of highly dispersed metal NPs. This method has the potential to synthesize other kinds of transition metal or metal oxide NPs if the source materials can be properly sputtered and deposited in ILs. However, such an attempt has not been made yet. In this study, we applied the method to the synthesis of metal oxide NPs in ILs by sputter deposition of transition metals of W, Mo, Nb, and Ti into ILs, and corresponding metal oxide NPs smaller than 6 nm were produced.

We used a DC sputtering apparatus (Sanyu Electron Co., Ltd., SC-701HMCII) with four metal targets of W, Mo, Nb, and Ti. An IL of 1-ethyl-3-methylimidazolium tetrafluoroborate ($\mathrm{EMI\text{-}BF_4}$), purchased from Kanto Chemical Co., Inc., was dried for 3 h at 393 K under vacuum. A 0.60 $\mathrm{cm^3}$ portion of the dried IL solution was spread on a glass plate (10 $\mathrm{cm^2}$) which was horizontally set in the DC sputtering apparatus. The glass plate was 2.0 cm away from the metal target. After presputtering for 10 min to clean the metal target, metal sputter deposition into $\mathrm{EMI\text{-}BF_4}$ was carried out for 20 min under 2.0 Pa of Ar gas ($>99.9999\%$) with 40 mA of ion current. The size distribution and shape of NPs formed in $\mathrm{EMI\text{-}BF_4}$ were determined by TEM (HITACHI H-7650) operated at an acceleration voltage of 100 kV. TEM samples were prepared by dipping a copper TEM grid with amorphous carbon overlayers (Oken shoji, #10-1012) into the thus-obtained $\mathrm{EMI\text{-}BF_4}$. The excess IL was rinsed off with acetonitrile, followed by drying under vacuum. Additionally, elemental compositions and crystallographic structures of NPs were analyzed by XPS (JEOL JPS-9000MC) and XRD (RIGAKU 2100HL), respectively. For the preparation of XPS and XRD samples, the NPs in the thus-obtained IL were precipitated by a 5 $\mathrm{mmol\,dm^{-3}}$ octadecane-1-thiol/ethanol solution, followed by centrifugation. The concentrated NPs were settled on a small Si substrate.

Figure 1 shows typical TEM images of NPs synthesized by sputter deposition of W, Mo, Nb, and Ti targets in $\mathrm{EMI\text{-}BF_4}$. Strong and vague contrasts were observed; the former was assigned to NPs obtained by sputter deposition, and the latter could be attributed to the residue of $\mathrm{EMI\text{-}BF_4}$ after washing with acetonitrile. The NPs were well dispersed, and no secondary particle formation was observed. Figure 2 shows the size distribution of NPs obtained by measurements of the diameter of 100 NPs in TEM images. Most of the NPs were spherical or polyhedral in shape, and no anisotropic particles were found. The ranges of particle size were 3.2–4.8 nm for W target, 2.7–3.7 nm for Mo target, 1.9–2.9 nm for Nb target, and 3.4–4.6 nm for Ti target. Average diameters (D_{ave}) of NPs obtained for Mo and Nb sputtering were 3.2 and 2.4 nm, respectively, being relatively smaller than those for W and Ti targets ($D_{\mathrm{ave}} = 4.0$ in both cases). The size distributions of NPs prepared from the Mo or Nb targets were quite narrow, in which the standard deviations (σ) were 0.5 nm.

Figure 3 shows XPS spectra of the obtained NPs. The solid lines indicate observed data after subtracting background variation of photoelectron spectra. The dotted lines and the dashed line indicate peak separation results and a summation of the results, respectively. In all cases, we observed not only a metal phase but also oxide phases. From the XPS peak analysis, at least two oxide phases could be recognized, and the total amount of oxide phases was more than 80% in all cases. However, the XRD measurements showed no peak corresponding to crystal phases of these oxides. The amorphous oxide phases were formed by oxidation of metal NPs in the IL. Further

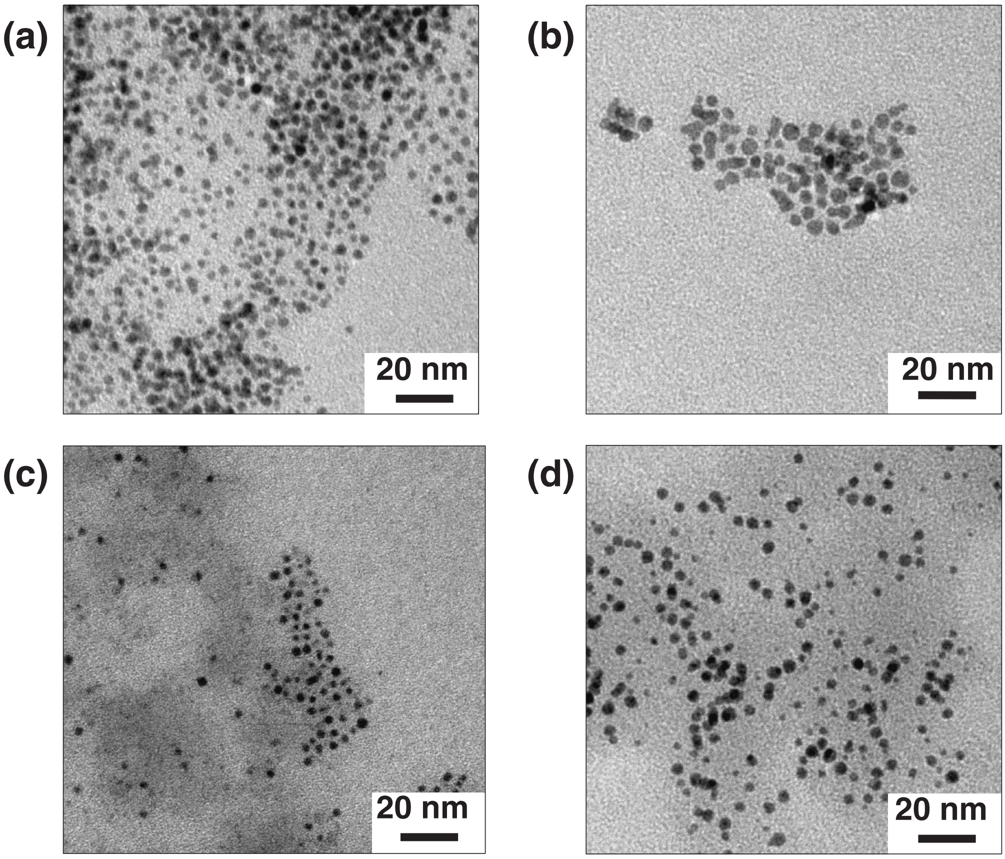

Figure 1. Typical TEM images of nanoparticles obtained by sputter deposition of transition metal targets: (a) W, (b) Mo, (c) Nb, and (d) Ti into ionic liquids of EMI-BF_4.

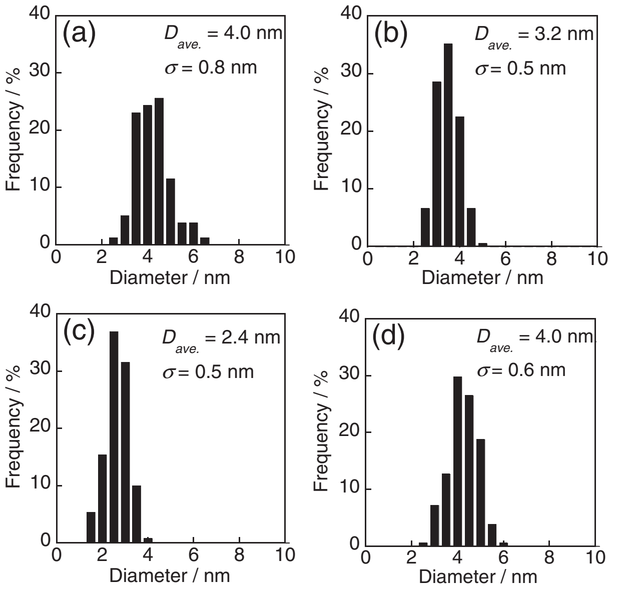

Figure 2. Size distribution of nanoparticles obtained by sputter deposition of (a) W, (b) Mo, (c) Nb, and (d) Ti targets into ionic liquids of EMI-BF_4, derived from Figure 1.

XPS analysis showed that fluorine and sulfur were involved in each case. Typical representatives are shown in Figures 3a and 3b, respectively. The former was attributed to the residue of the IL of EMI-BF_4, and the latter originated from the octadecane-1-thiol used in the preparation of XPS samples. These species were difficult to remove completely by repeating the washing procedures, indicating that these species were strongly adsorbed on the nanoparticle surfaces.

In our previous studies of Au and Ag NPs, we concluded that the ILs could stabilize metal NPs without aggregation of NPs.[15–17] The local structure of the IL surrounding the nanoparticle might have a role to protect the NPs from uncertain transformation. Actually, we did not find any oxidized NPs in these experiments. In the present study, however, we observed that the metals W, Mo, Nb, and Ti sputter-deposited in ILs were oxidized to form metal oxide NPs. This means that the IL layer of EMI-BF_4 on the particle surface did not have sufficient ability to prevent the oxidation of NPs of transition metal with negative oxidation potentials from oxidants contained in the IL as impurities. Nevertheless, the metal phases still remained in each XPS spectrum, suggesting that oxidation of metal NPs was limited by initial concentrations of oxidants or did not rapidly proceed in the IL. We propose oxygen and/or water molecules as possible candidates as oxidants. Before the sputter deposition, we actually dried the IL for 3 h at 393 K under vacuum in the order of 10^{-1} Pa, but the degree of vacuum might not have been sufficient to completely remove the dissolved water introduced

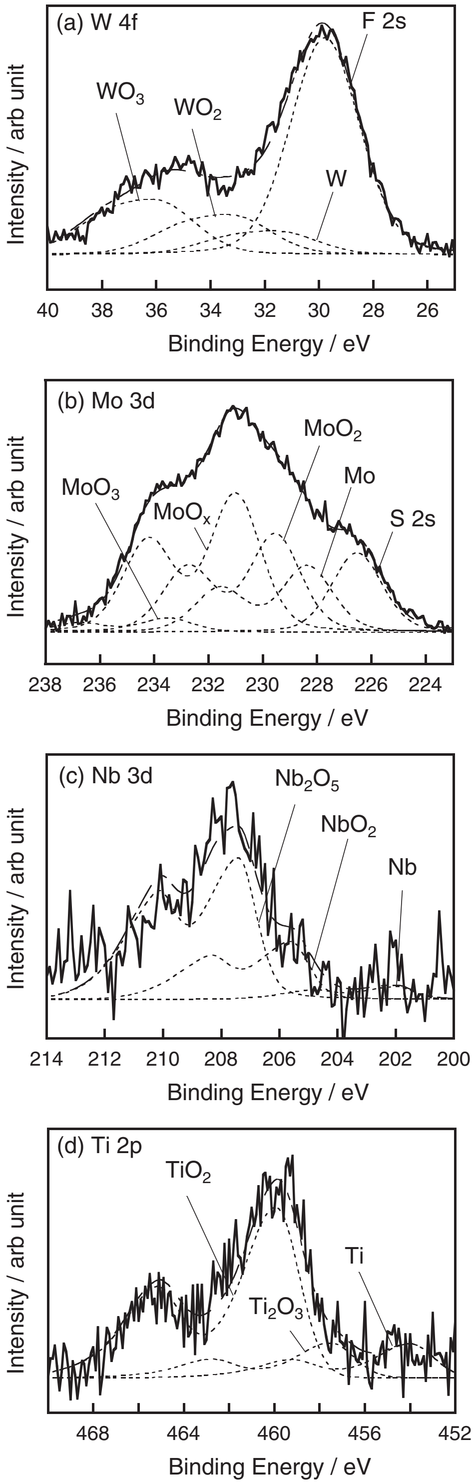

Figure 3. XPS spectra for nanoparticles obtained by sputter deposition of (a) W, (b) Mo, (c) Nb, and (d) Ti targets into ionic liquids of EMI-BF_4.

from the atmosphere in advance. Alternatively, the metal NPs might have been oxidized by oxygen molecules that were contained as an impurity in Ar gas and/or dissolved into the IL from air during sample preparation for TEM, XPS, and XRD. Such dissolved oxidants may affect the stability of metal NPs in ILs and oxidize metal NPs to form amorphous oxide phases. Although it is difficult to synthesize metal oxide NPs of various diameters with a single oxidation state at the present, we expect further precise control of the concentration of oxidants and/or temperature of IL during the sputter deposition provides both the uniform composition of NPs and the tunability of particle size.

In summary, we have synthesized transition metal oxide NPs of WO_x, MoO_x, NbO_x, and TiO_x by sputter deposition in the IL of EMI-BF_4. These metal oxide NPs were obtained in a dispersed manner with the size of 3.2–4.8 nm for W, 2.7–3.7 nm for Mo, 1.9–2.9 nm for Nb, and 3.4–4.6 nm for Ti. Our results indicate that sputter deposition in ILs has the potential to provide various types of highly dispersed transition metal oxide NPs without any additional stabilizing agent to prevent aggregation of NPs.

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