Helical Ruthenium Compound Templated by 1-Dodecanesulfonate Assemblies and Its Conversion into Helical Ruthenium Oxide and Helical Metallic Ruthenium

Yuko Inoue,[†] Masafumi Uota,[‡] Masao Uchigasaki,[†] Shyunichi Nishi,[†] Toshio Torikai,[†] Takanori Watari,[†] and Mitsunori Yada*[,†]

Saga University, Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, 1 Honjyo, Saga 840-8502, Japan, and CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

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A helical ruthenium compound with a hexagonal mesostructure templated by 1-dodecanesulfonate assemblies was synthesized by the homogeneous precipitation method using urea. The lengths of the helical particles were between micrometers and several tens of micrometers, and the helical pitches of all the particles were constant between several tens and hundreds of nanometers. TEM observation revealed that these helical particles were either hollow (i.e., helical nanotubes) or solid. The tip of the hollow helical particles was open, and the hollow portion was also helical. A double helical structure was also observed. The helical ruthenium compound was converted into helical porous ruthenium oxide by the calcination at 500 °C or more and helical metallic ruthenium by the H_2 treatment of the 300 °C calcined helical ruthenium compound.

Introduction

Ever since Motojima et al. reported helical Si_3N_4[1] and carbon[2] synthesis by a chemical vapor deposition process, much attention has been focused on helical inorganic compounds, because of their promising applications in electromagnetic wave absorbers, micro/nanosprings for sensors and actuators, and chemical sensors with chiral recognition and chiral catalysts. For example, helical-shaped solid and hollow oxides such as SiO_2, TiO_2, and ZrO_2, those synthesized using a chemically stable and hard template consisting of carbon coil[3] or cellulose[4] with a helical morphology, and those synthesized using surfactants[5−11] and a gelator[12,13] as a template are well-known. Helical fibers of porous manganese oxide have also been prepared from colloidal solutions.[14] The formation process of these helices is considered to be related to contraction of the gel during heating with capillary pressure until solvent is removed followed by expansion of the helix,[14] which is different from the above-mentioned template synthesis.[3−13] A sophisticated helical morphology was especially observed in oxides synthesized using a small template, that is, a surfactant. However, to the best of our knowledge, only silica has been known to form a helical hexagonal structure using surfactants as a template.[5−11] In this study, we report the synthesis of a helical ruthenium compound with a hexagonal structure templated by achiral anionic surfactants or 1-dodecanesulfonate assemblies and its conversion into helical ruthenium oxide and helical metallic ruthenium. Because metallic ruthenium and ruthenium oxide are conductive materials and helical mesoporous silica is an insulator and because metals are generally known to have excellent mechanical properties compared with ceramics, the obtained products have the potential to be novel helical materials. For example, conductive ruthenium oxide and metallic ruthenium helicoids are

* To whom correspondence should be addressed. E-mail: yada@cc.saga-u.ac.jp. Phone: +81-952-28-8682. Fax: +81-952-28-8682.
[†] Saga University.
[‡] Japan Science and Technology Agency.

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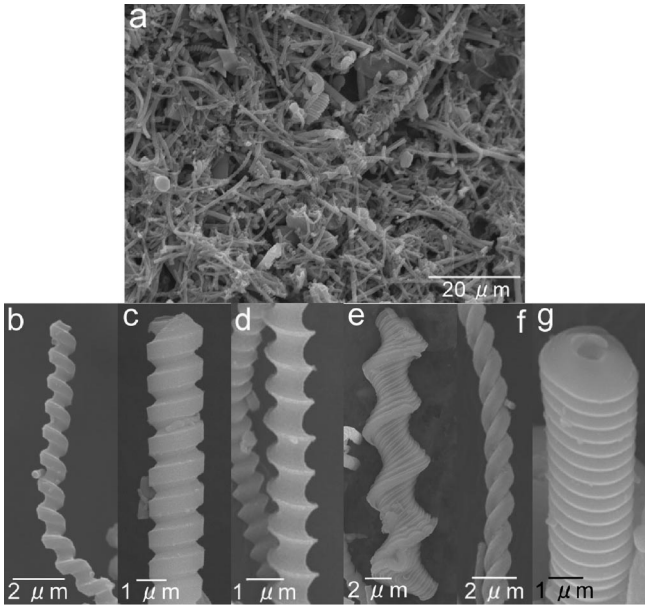

Figure 1. SEM images of the obtained ruthenium compound synthesized at 70 °C.

promising materials with electromagnetic induction properties that can be used in a nano/microdevice.

Experimental Section

Synthesis. Nanostructured helical ruthenium compounds were synthesized by the homogeneous precipitation method using urea. $RuCl_3 \cdot nH_2O$ ($n = 1-3$) was used as a ruthenium source. Sodium 1-dodecanesulfonate was used as a template. Ruthenium chloride, sodium 1-dodecanesulfonate, urea, and water were mixed at a molar ratio of 1:2:10:500 and stirred at 40 °C for 2 h to obtain a homogeneously mixed solution. Urea was used to gradually raise the pH value of the reaction mixture because on heating at above 60 °C urea is hydrolyzed to release ammonia. The mixed solution was heated at 70−90 °C and then kept at that temperature without stirring or in the quiescent state. The pH of the reaction mixture increased due to the enhanced hydrolysis of urea, while precipitation occurred and developed. After a reaction time of 20 h, the resulting mixture was immediately cooled to room temperature to prevent further hydrolysis of urea. After centrifugation, the resulting solid was washed with ethanol and water several times and then dried in air.

Characterization. Transmission electron microscopy (TEM) was carried out using a Hitachi H-800MU instrument. Scanning electron microscopy (SEM) was performed using a Hitachi S-3000N. X-ray microanalysis (XMA) was conducted with a EDAX Genesis 2000 instrument. Powder X-ray diffraction (XRD) measurement was made on a Shimadzu XRD-6100 instrument with Cu Kα radiation. Thermogravimetric and differential thermal analysis (TG-DTA) was carried with a SEIKO TG/DTA320U. Fourier transform infrared absorption (FT-IR) spectrum was measured by a Nippon Bunko FT/IR-300 instrument.

Result and Discussion

As shown in Figure 1a, many particles with a one-dimensional morphology were observed in a product synthesized at 70 °C, and many of them had a helical morphology as shown in Figure 1b−g. A double helical morphology was also observed as shown in Figure 1f. TEM images of variously shaped and sophisticated helical particles

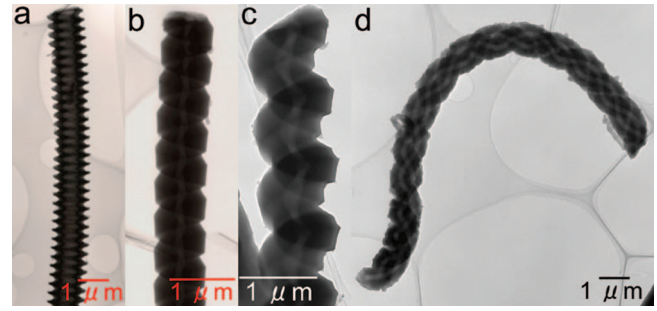

Figure 2. TEM images of the helical-shaped hollow ruthenium compounds.

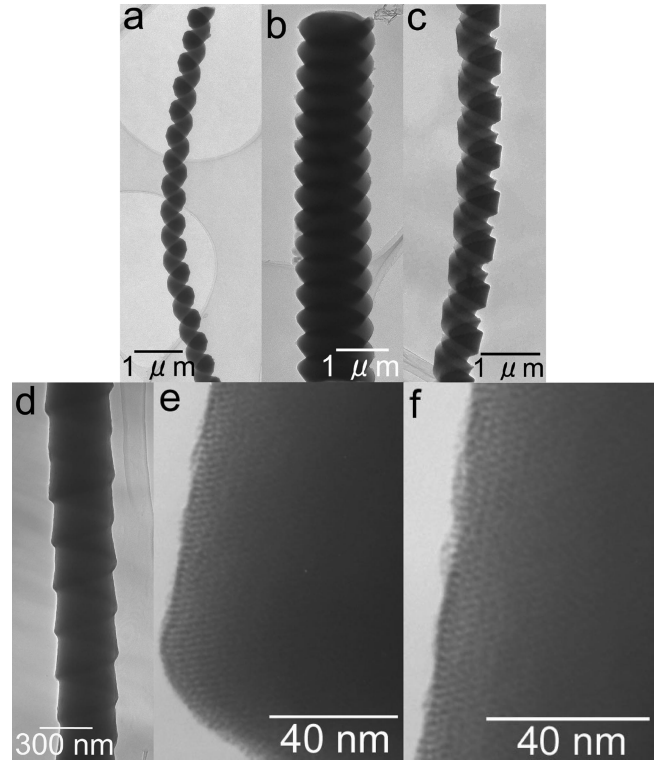

Figure 3. TEM images of (a−d) the helical-shaped solid ruthenium compounds and (e, f) enlarged images of (d).

are shown in Figures 2 and 3. The lengths of these helical particles ranged from micrometers to several tens of micrometers, and the helical pitches of all the particles were constant between several tens and hundreds of nanometers. TEM observation revealed that these helical particles were either hollow (i.e., helical nanotubes; Figure 2) or solid (Figure 3). As shown in Figures 1g and 2a−c, the tip of the hollow helical particles was open and the hollow portion was also helical. A double helical tubular structure was also observed, as shown in Figure 2d. These nanotubular morphologies are completely different from those of previously reported straight RuO_2 nanotubes[15,16] templated by anodic porous alumina. As a typical case of magnified images of the helical products, enlarged TEM images of Figure 3d are shown in Figure 3e,f. A stripe image at approximately 2.0-nm intervals along the helical direction (Figure 3e) and a

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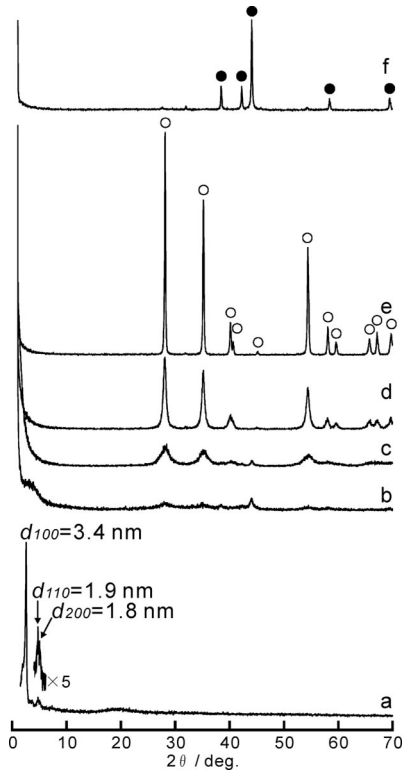

Figure 4. XRD patterns of (a) the as-grown product synthesized at 70 °C, (b−e) the calcined ruthenium compounds, and (f) the H_2-treated 300 °C calcined ruthenium compound; (b) 300 °C, (c) 500 °C, (d) 700 °C, and (e) 900 °C calcined products. Peak assignment: ○ ruthenium oxide (RuO_2), ● metallic ruthenium.

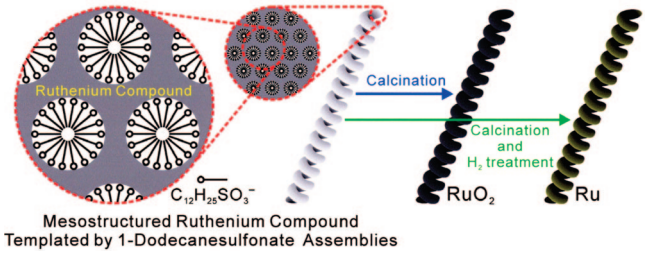

Figure 5. Schematic representation of a helical ruthenium compound with a hexagonal structure templated by 1-dodecanesulfonate assemblies.

part of a honeycomb image (Figure 3f) were observed. In the X-ray diffraction pattern of the product with a hexagonal structure and lattice constant $a = 3.9$ nm (Figure 4a), the diffraction peaks observed at $d = 3.4$, 1.9, and 1.8 nm could be nearly attributed to diffraction lines of 100, 110, and 200, respectively. The intervals of 2.0 nm are in good agreement with the 1.9-nm spacing of $a/2$ when the samples are viewed along the [210] zone axis of the hexagonal cell. Therefore, because the hexagonal structure grew helically with high regularity, a helical morphology of nanometer size was formed, as schematically shown in Figure 5. EDX analysis of this sample detected Ru, S, O, C, and N in the ratio of Ru:S:O:C:N = 4.20:3.41:18.11:60.93:13.34. S originated from a surfactant or 1-dodecanesulfonate. Moreover, because NH_3 is coordinated with Ru in compounds such as $[(NH_3)_5Ru{-}O{-}Ru(NH_3)_4{-}O{-}Ru(NH_3)_5]Cl_6 \cdot 4H_2O$, and $[Ru(NH_3)_6]Cl_3$, N is considered to originate from NH_3, which was generated by the hydrolysis of urea and then coordinated to Ru. Furthermore, because the amount of C measured in this experiment was greater than that expected from 1-dodecanesulfonate, CO_3^{2-} generated by the hydrolysis of urea was also present in the product. In the FT-IR spectrum shown in the Supporting Information (1), peaks observed at 1500−1700 cm^{-1} indicate the existence of CO_3^{2-}.[17] On the other hand, particles with turbinate and irregular shapes were also slightly observed during the SEM observations, as shown in the Supporting Information (2). These particles were confirmed to have a nanostructure or a hexagonal structure similar to that of the helical particles. Similarly shaped particles have been observed for hexagonal mesostructured silica.[18] The existence of the irregularly shaped particles also agreed with the results of helical mesoporous silica reported by Yang et al.[5] To raise the proportion of helicoids and nanotubes formed, synthetic conditions are currently being investigated. Furthermore, as shown in the Supporting Information (3a), when the synthesis was carried out under the same conditions except for stirring, irregularly shaped particles were visible, although helical particles were not observed. In addition, a layered structure with an interlayer spacing of 3.4 nm and a nanostructure with regularity of 2.3 nm were confirmed as shown in the Supporting Information (3b). Therefore, it is evident that stirring inhibited helical self-assembly of Ru species and 1-dodecanesulfonates at the micrometer level. Helical particles were also observed in a product synthesized at 80 °C, although the proportion of one-dimensional particles in the product synthesized at 80 °C was smaller than that in the sample synthesized at 70 °C, and no helical particles were formed at 90 °C. This could be because the most stable phase of the surfactant assembly changed with increasing temperature, irregularly shaped particles formed easily due to the faster formation rate of inorganic compounds and the faster hydrolysis rate of urea, and the effect of stirring the solution was observed due to an increase in the amount of CO_2 gas generated by the hydrolysis of urea. Therefore, the helical hexagonal structure was slowly formed by cooperative self-assembly between the negatively charged surfactants and the positively charged Ru compound species, which consisted of Ru oxyhydroxide, CO_3^{2-}, and NH_3. When the formation of this structure was not affected by external forces such as stirring, the formed hexagonal structure grew to a helical morphology of micrometer size, which is the most stable phase under this condition.

In general, formations of various sophisticated morphologies of nanostructured inorganic compounds templated by surfactants are considered to be due to cooperative assembly between surfactants and inorganic species. In fact, when $AlCl_3$, $YbCl_3$, and $SnCl_4$ were used as metal sources instead of $RuCl_3$, no helical morphologies were observed. However, many similarities existed between the results obtained in this study and the report of helical mesoporous silica by Yang et al.,[5] in which cetyltrimethylammonium chloride was used as a template. In the study on helical mesoporous silica, the helical morphology was formed in a quiescent state and at a

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low pH (pH 1.9), similar to the synthetic conditions adopted in this study. In this study, the pH of the reaction mixture increased from 1.5 at its initial level to 6.8 after 20 h due to the enhanced hydrolysis of urea, while precipitation occurred and developed. Moreover, when the synthesis was carried out under the same conditions without using a surfactant, irregular shaped ruthenium compound particles with an amorphous structure were formed, as shown in the Supporting Information (4). Because the phase of the ruthenium compound in the product had an amorphous structure similar to silica, the degrees of freedom of both the structure and the morphology of the ruthenium compound were considered to be as high as those for silica. Therefore, various morphologies strongly reflecting the various shapes of organic molecular assemblies could be formed, similar to silica. For example, it is considered that the molecular assembly formed by surfactants easily attained a helical morphology of micrometer size in a quiescent state at low pH or below approximately pH 2 and that the product reflecting this morphology is formed. Because only silica has been known to form a helical hexagonal structure using surfactants as templates, the product obtained in this study is the only example of an inorganic compound with a helical hexagonal structure besides silica. Therefore, results suggest that a fine or sophisticated helical morphology can be obtained in various oxides using a surfactant if the synthetic conditions and crystal structural design of the inorganic phase are appropriately controlled.

Next, the as-grown product was calcined. As shown in the Supporting Information (5), a TG-DTA curve for the as-grown product indicates a large exothermic weight loss at approximately 200−300 °C and an insignificant weight loss above 400 °C. The weight loss is considered to be mainly due to the partial desorption of the degradable 1-dodecanesulfonate moiety through combustion and desorption of water formed by condensation of hydroxyl groups in the ruthenium compound phase, NH_3, and carbonate species. XRD patterns of the calcined products are shown in Figure 4b−e. The single peak at $d = 3.4$ nm observed for the as-grown product decreased in intensity and narrowed by calcination at 300 °C. These results indicate that the hexagonal mesostructure for the as-grown product slightly collapsed into a less ordered mesostructure in the 300 °C calcination. Moreover, weak peaks attributable to RuO_2 appeared at 300 °C and increased in intensity with an increase in the calcination temperature, indicating that crystallinity of RuO_2 increased with the increase of the calcination temperature. The RuO_2 content in the as-grown product was therefore determined to be 28.2 wt %, which corresponds to the weight loss at 600 °C. In the TEM images of the 300 °C product, although helical morphologies similar to those of the as-grown product were observed, the ordered hexagonal mesostructure was not observed. The TEM images of the 500, 700, and 900 °C products indicated that the helical morphologies were maintained up to 900 °C and that the helicoids were composed of aggregates of nanoparticles and were porous solids. As a typical case, the TEM images of the 700 °C calcined product are shown in Figure 6. The average diameter of the nanoparticles increased from 4 nm

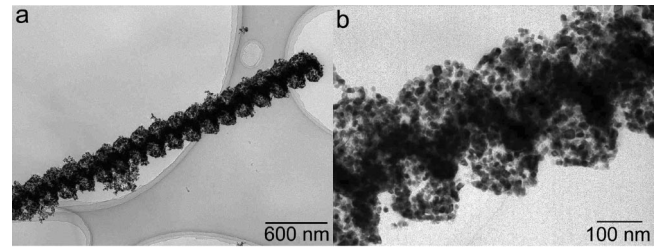

Figure 6. TEM images of (a) the 700 °C calcined helical ruthenium compound and (b) enlarged image of (a).

for the 500 °C calcined product to 111 nm for the 900 °C calcined product, via 11 nm for the 700 °C calcined product, as shown in Figure 6b. EDX analysis showed molar ratios of S/Ru = 0.540 and N/Ru = 0 in the 300 °C calcined product. This indicates that the amount of 1-dodecanesulfonate moiety decreased remarkably in comparison with 1-dodecanesulfonate/Ru = 0.812 for the as-grown product and that NH_3 was completely removed by the 300 °C calcination. Moreover, in the product calcined at 500 °C, a ratio of O/Ru = 2.10 was obtained, and S and N were not detected. Even in the product calcined at 700 °C, a ratio of O/Ru = 2.09 was obtained, and S and N were not detected. Therefore, EDX analyses also indicated that almost all the components of 1-dodecanesulfonate and NH_3 were apparently removed from the as-grown product, and RuO_2 was formed at 500 °C or higher. Considering these TEM images, XRD patterns, EDX analyses, and the TG-DTA curve, the helical ruthenium compound template for 1-dodecanesulfonate assemblies was transformed into a helicoid composed of aggregates of RuO_2 nanoparticles by the calcination.

Next, the resistivity of the products calcined at various temperatures was measured. The measurement of the resistivity of the products was performed as follows. A pellet (diameter, 1.3 cm, and thickness, ca. 1 mm) was produced from the powder of the product by uniaxial molding with 500 kg/cm^2, and its resistivity was measured by a four-point probe method. Since the resistivity of the as-grown product was as large as 4.1×10^7 Ω·cm, the as-grown product was determined to be an insulator. However, the resistivity of the product calcined at 300 °C remarkably decreased to 9.7×10^{-2} Ω·cm. Therefore, an insulator for the as-grown product transformed into an electrical conductor after calcination. Moreover, the resistivity of the product calcined at 500 °C decreased only slightly to 1.9×10^{-2} Ω·cm, which is close to a measured value obtained from commercially available RuO_2. These results suggest that because the components of the 1-dodecanesulfonate, carbonate ion, and NH_3 were apparently removed from the as-grown product by calcination, the composition of the calcined product was almost the same as RuO_2, which is known as an electrical conductor. Because nanotubes and helicoids of various oxide ceramics have been reported as either semiconductors or insulators, the conductive helicoids of the ruthenium oxide obtained in this study can be considered as peculiar inorganic helicoids in terms of conductivity.

Furthermore, the 300 °C calcined product was treated with H_2 gas at 4.8 MPa and at room temperature, because the 300 °C calcined product is considered to have many

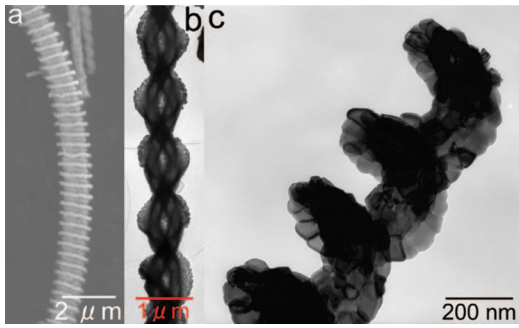

Figure 7. SEM (a) and TEM (b, c) images of the H_2-treated 300 °C calcined helical ruthenium compound.

mesopores into which H_2 gas can diffuse and a thin ruthenium compound phase, which could be easily reduced. The XRD pattern of the H_2-treated product (Figure 4f) indicates that the less ordered mesostructure of the 300 °C calcined product (Figure 4b) transformed into metallic ruthenium. SEM and TEM observations revealed that a helical morphology was maintained even after the H_2 treatment, as shown in Figure 7a,b, and the less ordered mesostructure of the 300 °C calcined product was transformed into an aggregate of nanoparticles with an average diameter of 58 nm by the H_2 treatment, as shown in Figure 7c. The nanotubular morphology was also maintained after the H_2 treatment as shown in Figure 7b. These results indicate that the helical ruthenium compound with the less ordered mesostructure of the 300 °C calcined product was reduced to helical metallic ruthenium by H_2 gas. On the other hand, the as-grown helical ruthenium compound templated by 1-dodecanesulfonate assemblies and the 700 °C calcined product or helical RuO_2 could not be converted into helical metallic ruthenium by a similar H_2 treatment. Therefore, the formation of the mesoporous ruthenium compound with a larger specific surface area than that of the bulk ruthenium compound by the removal of surfactants is essential for the reduction of the as-grown ruthenium compound into metallic ruthenium.

Conclusion

In this study, we successfully synthesized a helical ruthenium compound templated by surfactants, helical ruthenium oxide, and helical metallic ruthenium. Ruthenium compounds such as ruthenium oxide (RuO_2) and ruthenium oxide hydrate ($RuO_2 \cdot nH_2O$) have been investigated for their application as an electrocatalyst,[19] an electrochemical supercapacitor,[20] a catalyst for hydrogen production,[21] or a catalyst for CO oxidizing,[22] and metallic ruthenium is also employed as a catalyst in a fuel cell. Therefore, the obtained helical ruthenium compounds are promising as a novel functional catalyst as well as materials for applications in micro/nanosprings for sensors and actuators and as a material with electromagnetic induction function for a nano/microdevice.

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Supporting Information Available: FT-IR spectrum, TEM image, SEM images, XRD patterns, and TG-DTA curve (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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