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Strong enhancement of electrical conductivity in two-dimensional micrometer-sized RuO₂ nanosheets for flexible transparent electrodes†

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The enhancement in electrical transport properties of exfoliated individual RuO₂ NSs was systematically investigated for their application in flexible electronics and optoelectronics. Decoration of Ag NPs on the surface of the RuO₂ NSs provides donor electrons and dramatically increases the electrical conductivity of the monolayer RuO₂ NSs by up to 3700%. The n-type doping behavior was confirmed via Hall measurement analysis of the doped RuO₂ NSs. The layer number- and temperature-dependence of the conductivity were also investigated. Moreover, carrier concentration and mobility were obtained from Hall measurements, indicating that the undoped RuO₂ NSs had ambipolar transport and semi-metallic characteristics. Moreover, the Ag-doped RuO₂ NS multilayer films on polycarbonate substrates were demonstrated by the Langmuir–Blodgett assembly methods, showing one-third reduction in the sheet resistance and extraordinarily high bending stability that the change in the resistance was less than 1% over 50,000 cycles.

Introduction

Since the discovery of graphene,1,2 two-dimensional (2D) inorganic materials have been of significant interest in the fields of atomic electronics,3–5 photonics,6,7 and flexible electronics⁸–¹⁰ due to their unique dimensionality, atomic-scale thickness, and flatness. Due to these intriguing physical properties and the wide range of applications of 2D materials, a number of studies have been carried out on other 2D materials such as hexagonal boron nitride (hBN)¹¹ and transition metal dichalcogenides (TMDCs: MoS₂, MoSe₂, WS₂, NbSe₂, TaSe₂, etc.),¹²–¹⁷ as well as on 2D oxide materials (such as TiO₂, MnO₂, V₂O₅, etc.).¹⁸–²¹ In particular, the 2D oxide materials have been suggested as promising transparent electrode materials due to their high flexibility, unique optical properties, and stability under ambient conditions. These merits lay the foundation for viable atomic electronics, using 2D oxide materials as transparent electrode materials. However, the poor electrical properties of 2D oxide materials, which are mostly caused by low carrier mobility (μ), as compared to those of the corresponding bulk structures constitute the main hurdle for realizing transparent electrodes using 2D oxide materials.

Rutile-type ruthenium oxide (RuO₂) is of a special technological interest due to its thermodynamic stability, semi-transparent, and distinctive metallic properties. The Fermi level of RuO₂ is positioned in the middle of a conduction band that is primarily encompassed by Ru-4d orbitals,²² typically showing metallic behavior with a single-crystalline resistivity of 35.2 μΩ cm.²³ Moreover, rutile-type RuO₂ has a layered structure, which is advantageous for the easy fabrication of nanosheets (NSs) via exfoliation. For example, the sheet resistance of single-layer RuO₂ NSs synthesized via electrostatic self-assembly was measured to be approximately 12 kΩ sq⁻¹, which was relatively high for electrodes, as observed via scanning probe microscopy.²⁴ Wang et al. obtained a sheet resistance of 4.1 and 0.9 kΩ sq⁻¹ for two- and five-layered RuO₂ NSs films at room temperature, respectively; however, most of their studies have been focused on all-NS ultrathin capacitors.²⁵ Although the electrical characteristics of RuO₂ NSs are of critical importance in predicting the feasibility of applying RuO₂ NSs to atomic-layer devices, to date, electrical properties such as
carrier concentration and mobility have not been studied in individual monolayer RuO$_2$ NSs.

Herein, we proposed an easy method for enhancing the electrical conductivity via doping RuO$_2$ NSs with Ag nanoparticles (NPs), which dramatically increased the electrical conductivity of monolayer RuO$_2$ NSs by up to 3700%. This result indicates that the electrical properties can be modulated via the decoration of metal NPs on the surface of RuO$_2$ NSs. In addition, we firstly performed a systematic study on the layer number-dependent electrical conductivities of individual pristine RuO$_2$ NSs and Ag-doped RuO$_2$ NSs via a four-probe measurement technique; it was observed that electrical transport through individual RuO$_2$ NSs was limited by the surface scattering of electrons. Moreover, transparent conductive films, which were deposited layer-by-layer on a polycarbonate substrate by the Langmuir–Blodgett (LB) assembly method, were fabricated using the Ag-doped RuO$_2$ NSs with the lateral sizes ranging from a few to $\sim 10 \mu$m. This result demonstrates the feasibility of using 2D oxide materials as transparent electrodes in flexible electronics and optoelectronics.

**Experimental**

**Synthesis and exfoliation of RuO$_2$ NSs**

Exfoliation of layered alkali metal ruthenates was employed to synthesize RuO$_2$ NSs, as shown in Fig. 1a.$^{24,25}$ Potassium ruthenates were produced by annealing a mixture of potassium carbonate (K$_2$CO$_3$, >99.0%, Aldrich) and ruthenium dioxide (RuO$_2$, 99.9%, Aldrich). K$_2$CO$_3$ and RuO$_2$ were calcined at 500 °C for 6 hours. After calcination, K$_2$CO$_3$ and RuO$_2$ were mixed in a 5 : 8 molar ratio and annealed at 900 °C under N$_2$ with a flow rate of 2 L min$^{-1}$ for 24 hours using a furnace. Then, the annealed compounds were ground to fine powder using an agate mortar and washed with 1 L deionized water (obtained by an 18 MΩ system) under magnetic stirring at room temperature for 24 hours to acquire the potassium ruthenates with the composition of K$_x$RuO$_{2.1}$·nH$_2$O ($0 < x \leq 0.3$). After washing, potassium ruthenates with the lateral sizes over 1 mm were obtained. Potassium ions were exchanged with protons by immersing the potassium ruthenates in 1 M hydrochloric acid (HCl, 35%, Samchun Chemicals) for 3 days at 60 °C. As shown in the field emission scanning electron microscopy (FE-SEM, FEI Nova 450) images in Fig. 1b, the layers were clearly separated in the protonic-layered ruthenates after the proton exchange reaction. The acid-treated protonic-layered ruthenates were exfoliated via the intercalation of tetrabutylammonium hydroxide (TBAOH, 99.0%, Aldrich) solution (40 wt% in H$_2$O). The TBAOH solution containing the protonic-layered ruthenates was gently stirred for 2 weeks at room temperature. After finishing the exfoliation, RuO$_2$ NSs were obtained via centrifuging (2000 rpm, 60 min) and stably suspended in deionized water, as shown in Fig. 1c.

Exfoliation of the layered structure into individual nanosheets was confirmed via high-resolution transmission electron microscopy (HR-TEM, FEI Titan Cubed) and atomic force microscopy (AFM, JPK Instruments Nanowizard 1). The TEM image, as depicted in Fig. 1d, clearly shows that the exfoliated RuO$_2$ NSs have a smooth surface without the wrinkled surface texture and are well separated from other RuO$_2$ NSs without aggregation. The monolayer RuO$_2$ NSs were measured using AFM and found to be approximately 1 nm thick with a lateral size of more than 8 $\mu$m, as shown in Fig. 1e. The measured thickness was close to the theoretical thickness of the nanosheets.$^{23}$ The optical transmittance of an individual RuO$_2$ NS was measured to be approximately 98.4% and 96.2%
for monolayer and two-layered nanosheets, respectively, in the visible region at the wavelength ($\lambda$) of 400–700 nm via a UV-Vis absorption spectrometer capable of microscopic characterization (QDI 2010, Craic Technologies Inc.) (Fig. S1†). Note that this value is higher than that of single-layer chemical vapor-deposited (CVD) graphene.26

Characterization of the Ag-doped RuO$_2$ NSs

For the enhancement of the electrical conductivity, metal doping on the RuO$_2$ NSs was carried out by decorating Ag NPs on the surfaces of the RuO$_2$ NSs. The decoration of Ag NPs was conducted by immersing the RuO$_2$ NSs in a 0.05 M Ag-acetate (CH$_3$COOAg, >99%, Aldrich) solution for 2 days at room temperature. After immersion, the extra Ag NPs on the surfaces of the RuO$_2$ NSs were removed by dipping the samples in de-ionized water. To reduce the number of silver oxide (AgO$_x$) NPs on the surfaces of the RuO$_2$ NSs, which were formed as a by-product of the Ag-acetate solution treatment, the samples were placed in a 0.05 M sodium borohydride (NaBH$_4$, >99.99%, Aldrich) solution for 2 min. The TEM images (Fig. 2a–c) show the surface of a Ag-doped RuO$_2$ NS on the TEM grid with different resolutions; the images prove that the Ag NPs were well dispersed on the surface. HR-TEM image in Fig. 2c shows that the average diameters of the Ag NPs were 2–3 nm. TEM energy dispersive X-ray spectroscopy (TEM-EDX, Super-XTM XEDS detector) pattern, as shown in Fig. 2d, clearly shows Ag NPs absorbed on the surface of the RuO$_2$ NS. Fig. 2e shows the topographic AFM image of a Ag-doped RuO$_2$ NS dispersed on a Si/SiO$_2$ substrate, revealing that the Ag NPs are only decorated on the RuO$_2$ NSs. It was expected that the Ag NPs were located at the defect sites on the surface, bonding with the oxygen atoms of RuO$_2$ NSs and providing donor electrons to RuO$_2$ NSs.

Device fabrication and transport characterization

The electron-beam lithography (EBL, JSM-7001F JEOL and ELPHY Quantum Raith) method was employed for the fabrication of individual RuO$_2$ NS devices. Prior to dispersing the RuO$_2$ NSs by drop-casting on thermally oxidized Si (100) substrates, where the alignment markers were patterned for EBL, the surface of the substrates were exposed for 30 minutes via ultra violet(UV)-ozone treatment to obtain hydrophilic surface. The electrodes of Cr (5 nm)/Au (50 nm) were deposited using an ultra-high vacuum sputtering system (custom-made). The resistances ($R$) of individual RuO$_2$ NS devices were measured using the combination of National Instruments Labview software and I–V measurement system (Keithley Model nanovoltmeter 2182A and 236). The conductivities were calculated from $R$ by the relation, $\sigma = 1/\rho = L/(Rtw)$, where $L$, $t$, and $w$ are the length, thickness, and width, respectively. The temperature-dependent resistances were obtained in the temperature range of 10–300 K using a closed cycle cryostat. All measurements were carried out in a high vacuum of less than $5 \times 10^{-6}$ Torr to eliminate convectional thermal fluctuation. The thickness of

Fig. 2  (a), (b), and (c) TEM images of the Ag NPs decorated on the surface of RuO$_2$ NS, which produced the electrical doping effect of the pristine RuO$_2$ NS. (d) EDX pattern of the samples obtained from the TEM image. The two points on the Ag-doped RuO$_2$ NS (yellow cross and circle in (c) were examined. (e) Topographic AFM image of a Ag-doped RuO$_2$ NS dispersed on a Si/SiO$_2$ substrate.
all the individual RuO$_2$ NS devices was measured by AFM, and the length and width of the channel were defined by FE-SEM after the electrical measurements.

**LB-deposition and mechanical bending test**

To utilize the monolayer RuO$_2$ NSs in LB-deposition, the RuO$_2$ NS colloidal suspension was centrifuged under the condition of 11,000 rpm for 30 minutes. Deionized water (210 ml) was carefully poured into the LB trough (KSV Instruments Ltd, MiniMicro LB System) and a diluted RuO$_2$ NSs colloidal suspension was gently placed on the surface of DI water using a syringe. After stabilizing for 10 min, the monolayer of RuO$_2$ NSs was compressed by the barriers at the speed of 10 mm min$^{-1}$. During the deposition, the surface pressure, which was provided by an observed microelectronic feedback system connected to Wilhelmy platinum plate, was controlled to be 12 mN m$^{-1}$. The deposition speed of the RuO$_2$ NSs on the PC substrates was 5 mm min$^{-1}$. The sheet resistance and optical transmittance of the RuO$_2$ NSs multilayer films on a PC substrate were characterized via an optical turbidity meter (NDH 7000SP, Nippon Denshoku, JP) and a non-contact resistance meter (EC-80P, Napson, JP), respectively. The cyclic bending test was carried out using an automatic bending tester (CFT-200R, Covotech Co., Ltd, KR).

**Results and discussion**

**Enhancement of electrical conductivity in Ag-doped RuO$_2$ NSs**

To examine this doping mechanism, individual RuO$_2$ NS devices were fabricated using electron beam lithography, and their electrical conductivity, carrier concentration, and mobility before and after Ag doping were measured. Fig. 3 shows a four-terminal device based on an individual RuO$_2$ NS and the electrical transport properties of the NSs. To determine the absolute resistance of the NS, transport properties were obtained using the four-probe technique without contact resistance between the NSs and the electrodes (Fig. 3a). The contact resistance was found to be two orders of magnitude less than that of the NSs, indicating ohmic contact. Fig. 3b shows the measured electrical conductivities ($\sigma$) of the pristine RuO$_2$ NS, the Ag-acetate-treated RuO$_2$ NS, and the Ag-doped RuO$_2$ NS at room temperature. Herein, two features were apparent: (i) the layer number-dependency of the conductivity and (ii) the effect of doping metal NPs on the conductivity.

As shown in Fig. 3c, the conductivities of the pristine NSs linearly increased with the increasing number of layers, indicating that the surface scattering of the carriers dominated the transport mechanism. If $\ell_b$ and $\ell_s$ were the mean free path of the bulk crystal and the surface scattering, respectively, the overall mean free path ($\ell$) of the NSs was determined according to Matthiessen’s rule: $1/\ell = 1/\ell_b + 1/\ell_s = 1/\ell_b + 1/\pi t$, where $t$ is the thickness of the NSs.

![Fig. 3](image-url) Devices and electrical conductivity at room temperature. (a) SEM image of the 4-terminal device based on a single-crystalline RuO$_2$ NS. (b) Conductivity of the pristine, Ag-acetate-treated, and Ag-doped RuO$_2$ NS. (c) Conductivity of the pristine RuO$_2$ NS as a function of the number of layers. (d) Ag-doping effect on conductivity. The enhancement of conductivity is presented as $(\sigma_{Ag-doped} - \sigma_{pristine}) / \sigma_{pristine}$ × 100. The inset shows Ag-acetate-treated effect on conductivity, which is plotted as $(\sigma_{Ag-acetate-treated} - \sigma_{pristine}) / \sigma_{pristine}$ × 100.
$t$ is the thickness of the NSs.\textsuperscript{27} From this relation, the conductivity of the NS can be represented as follows:

$$\frac{\sigma}{\sigma_b} = \frac{\pi}{t_b}$$

where $\sigma_b$ is the conductivity of the bulk crystal. If the conductivity of the NS is significantly lower than that of the bulk crystal, the conductivity of the NS is linearly proportional to the thickness (number of layers). In the RuO$_2$ bulk crystals, the conductivity (2.84 $\times$ 10$^4$ $\Omega^{-1}$ cm$^{-1}$) was found to be approximately 10 times higher than that measured in this study; thus, $\sigma_b$ was calculated to be approximately 1 $\mu$m.\textsuperscript{23,28} Our experimental results are thus in good agreement with the linear relation presented in eqn (1), as shown in Fig. 3c.

Note that the conductivity was enhanced by Ag doping (Fig. 3b). The conductivities of the Ag-doped NSs in particular dramatically increased by the NaBH$_4$ reduction process as compared to those of the pristine and Ag-acetate-treated NSs (red, orange, dark yellow, green, and blue lines). Furthermore, the change of electrical conductivities was not observed when the NaBH$_4$ reduction process was only carried out without Ag-acetate treatment, indicating that the doping effect was caused by the Ag NPs on the surface of the NSs (Table S1†). The doping effect on the conductivity via surface-treatment increased as the number of layers decreased, whereas the conductivity decreased as the number of layers decreased because of surface scattering. To obtain the layer number-dependent doping effect on conductivity, the mobility dependency due to the surface scattering was eliminated by normalization with the conductivity of the pristine NS, as shown in Fig. 3d. The enhancement of the conductivity dramatically increased with the decrease in the number of layers, reaching a maximum value of 3700% for the mono-layer RuO$_2$ NS. If the carrier density of the pristine NS and the doping effect are $n_i$ and $n_d$, respectively, the total number of carriers can be calculated as $N_i = wtL$ and $N_d = wt_cL$, respectively. Herein, $w$, $t$, $L$, and $t_c$ are the width, thickness, length, and critical thickness affected by the doping effect, respectively. From this relation, the overall carrier density can be determined as $n = n_i + (t_c/t)n_d$. The enhancement of conductivity was then obtained by

$$\frac{\Delta\sigma}{\sigma} = \frac{t_c}{n_i} \frac{1}{t},$$

which indicates that the enhancement of conductivity is reciprocally proportional to the thickness of the NS (number of layers). Speculating that $n_i$, $n_d$, and $t_c$ are constant in the RuO$_2$ NS, the enhancement of conductivity due to the doping effect was fitted with the number of layers according to eqn (2) (dashed line in Fig. 3d and inset). Because the critical thickness can be considered equal in both the Ag-acetate-treated and Ag-doped NSs, which was quantitatively confirmed via the Hall measurements, the induced carrier density in the Ag-doped NS was found to be more than 10 times of that in the Ag-acetate-treated NS. These interpretations based on the number of layers according to eqn (1) and (2) reveal that the mobility is dominated by the surface scattering and the surface treatment doping alters the carrier density.

These phenomena regarding the mobility and carrier density are consistent with the temperature-dependent conductivity, as shown in Fig. 4. Although the RuO$_2$ bulk crystals show metallic temperature-dependence of conductivity, RuO$_2$ NSs exhibit non-monotonic and semiconducting behaviors as the number of layers decreases, which can be observed in low-dimensional materials (Fig. 4a).\textsuperscript{23,28,29} In a bulk crystal, the temperature dependence of conductivity is dominated by that of the mobility, which depends on the carrier-acoustic phonon scattering.\textsuperscript{29} However, in a low-dimensional material such as a NS, the mobility is determined by the surface scattering rather than by the phonon scattering, as described in the interpretation using eqn (1). As a result, the thermal excitation of the carriers dominates the temperature dependence of the conductivity as a decrease of the dimension. For this reason, in the temperature range of 150–300 K, the metallic behavior clearly observed in the seven-layered NS was weakened in the four-layered NS, and the NSs with less than four-layers exhibited semiconducting behavior at all temperatures (inset of Fig. 4a). The exponentially reduced conductivity at temperatures below 100 K also revealed that the carrier...
density dominated the temperature dependence of the conductivity.

Fig. 4b and inset show the variation in the temperature dependence of the conductivity in pristine, Ag acetate-treated, and Ag-doped RuO₂ NSs. The carriers doped via Ag doping not only increased the conductivity but also reduced its temperature dependency, which indicated that the doped carrier density was retained even at low temperatures. In practice, the conductivity of the Ag-doped NS at 8.5 K is larger than that of the pristine NS at room temperature. The conductivity of NS before and after Ag doping can be expressed according to the carrier density as \( \sigma = e\mu n \) and \( \sigma = e(n_i + n_d)\mu \), respectively. Using these relations and speculating that the change of the carrier mobility according to the doping process is negligible, the doped carrier density ratio between the change of the carrier mobility according to the doping of RuO₂ should be reduced to Ag NPs to considerably enhance the electrical conductivity.

To interpret the enhancement of electrical conductivity obtained by doping, Hall measurements were carried out using additional NS devices. Fig. 5a shows the variation of Hall coefficient in a four-layered pristine NS as a function of temperature. The variation ranging from negative to positive values indicates the ambipolar transport characteristics of the RuO₂ NS. For the two-band system, in which electrons and holes coexist, the Hall coefficient \( (R_H) \) is determined by the partial Hall coefficients of each carrier weighted by the square of their partial conductivities. Therefore, for the pristine RuO₂ NS, the total Hall coefficient is given by

\[
R_H = \frac{\sigma_h^2 R_{H,h} + \sigma_e^2 R_{H,e}}{(\sigma_h + \sigma_e)^2} = \frac{\mu_h^2 p - \mu_e^2 n}{e(\mu_h p + \mu_e n)^2},
\]

where the subscripts h and e mean holes and electron, respectively. Because the partial Hall coefficients of electrons and holes exhibit opposite signs, the total Hall coefficient of the two-band system is significantly smaller than the partial Hall coefficients. Moreover, it is difficult to obtain the carrier density from the measured total Hall coefficient due to this offset. On the other hand, for a Ag-doped RuO₂ NS, in which the major carrier is electrons, the carrier density can be obtained using a simple relation, \( R_H = -1/ne \). In the Ag-doped NS, the carrier density and mobility were found to be \( 2.56 \times 10^{21} \) cm⁻³ and \( 17.7 \) cm² V⁻¹ s⁻¹, respectively, which are reasonable values as compared to those reported in a previous study. The small mobility of RuO₂ NSs can be attributed to the surface scattering caused by the significant spatial confinement of the NS structure, as shown in Fig. 3c. From the Matthiessen’s rule, the mean free path of the four-layered NSs was found to be 13.6 nm, which was two orders of magnitude smaller than that of the bulk. Therefore, it can be considered that the carrier mobility, which is significantly restricted by the NS structure, cannot be affected by doping. If we consider that the mobility of holes is similar to that of the electrons, it is possible to find the variation of carrier density in both the holes and electrons using the two equations \( \sigma = e(\mu_h p + \mu_e n) \) and eqn (3). Table 1 summarizes the obtained transport properties. The Ag doping increases the electron density and decreases the hole density. From the obtained variation of carrier density, the critical thickness affected by doping was found to be approximately 1 nm in the case of both the Ag-acetate-treated and Ag-doped NSs according to eqn (2).

Similarly, the temperature dependency of the carrier density can be estimated using the measured Hall coefficients.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Pristine</th>
<th>Ag-acetate-treated</th>
<th>Ag-doped</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_H (\text{cm}^2 \text{c}^{-1}) )</td>
<td>(-2.93 \times 10^{-3})</td>
<td>(-3.89 \times 10^{-3})</td>
<td>(-2.44 \times 10^{-4})</td>
</tr>
<tr>
<td>( \sigma (\Omega \text{cm}) )</td>
<td>3240</td>
<td>3540</td>
<td>7260</td>
</tr>
<tr>
<td>( p (\text{cm}^{-3}) )</td>
<td>(2.65 \times 10^{20})</td>
<td>(1.38 \times 10^{20})</td>
<td>—</td>
</tr>
<tr>
<td>( n (\text{cm}^{-3}) )</td>
<td>(8.79 \times 10^{20})</td>
<td>(1.11 \times 10^{21})</td>
<td>(2.56 \times 10^{21})</td>
</tr>
</tbody>
</table>
(Fig. 5b). The densities of the electrons and holes were determined by the relations

\[ n = N_c \exp \left( -\frac{E_c - E_F}{kT} \right) \]

and

\[ p = N_v \exp \left( -\frac{E_F - E_v}{kT} \right), \]

respectively.\(^{27}\) Herein, \( N, E, \) and \( k \) indicate the effective densities of state, band energy, and Boltzmann constant, respectively, and the subscripts \( c, v, \) and \( F \) represent the conduction and valence band edges and Fermi energy, respectively. The estimated electron and hole densities were fitted using eqn (4) and (5), and the effective densities of state of electrons and holes were found to be \( 1.33 \times 10^{21} \text{ cm}^{-3} \) and \( 1.09 \times 10^{21} \text{ cm}^{-3} \), respectively. From the fitting, the overlap energy between the conduction and valence bands was found to be approximately 12.0 meV. This small band overlap energy indicates semi-metallic characteristics in the RuO\(_2\) NSs.

**Flexible transparent electrode films of the Ag-doped RuO\(_2\) NSs**

The Langmuir–Blodgett (LB) method, which had advantages in the deposition of self-assembled monolayer films, was employed for the fabrication of the flexible transparent electrode on polycarbonate (PC) substrates. A diluted RuO\(_2\) NSs colloidal suspension with a density of 5 \( \mu \text{g cm}^{-3} \) was utilized, and the surface pressure of the air–water interface was controlled to increase the packing density of RuO\(_2\) NSs. The detailed condition of the LB deposition has been discussed in the experimental methods. Prior to doping Ag NPs on the RuO\(_2\) NSs, the pristine RuO\(_2\) NSs were deposited. Fig. 6a shows that the pristine RuO\(_2\) NSs were deposited in a monolayer, such that the packing density of the pristine RuO\(_2\) NSs was calculated to be about 89% from the SEM image (inset of Fig. 6a). Therefore, to obtain sufficient electrical path in the films, the LB deposition process should be adequately repeated for good coverage of the films. After the LB deposition, ultra-violet (UV) irradiation cleaning was carried out to remove tetrabutylammonium ions and make the surface hydrophilic. For enhancing the electrical conductivity of the LB-deposited films, Ag doping on the RuO\(_2\) NSs was utilized by dipping pristine RuO\(_2\) NSs in 0.05 M Ag-acetate solution and 0.05 M NaBH\(_4\) solution in sequence as abovementioned. Ag NPs were successfully formed on the LB-deposited film, as verified in Fig. 6b. To investigate the cross-sectional nanoscale structure of the multilayer films, LB deposition of the Ag-doped RuO\(_2\) NSs was carried out on the Si substrate using the same process. HR-TEM image, as shown in Fig. 6c, indicated that the LB-deposited Ag-doped RuO\(_2\) films have a relatively uniform structure with a total thickness of \( \sim 7 \) nm.

For revealing the layer number-dependent doping effect in the RuO\(_2\) NSs films, the electrical and optical properties of the LB-deposited films with various number of LB depositions and Ag doping conditions were investigated. Table 2 shows the LB-deposition and Ag doping conditions of the samples. It was not possible to measure the electrical properties of the two-layer film since the electrical path was not established due to the voids between NSs (Fig. S2†). As shown Fig. 6d, the sheet

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**Fig. 6** LB-deposited RuO\(_2\) NSs films on a PC film. (a) SEM image of the pristine RuO\(_2\) NSs monolayer film by LB-deposition. The packing density of the RuO\(_2\) NSs was calculated from the SEM image of the inset. (b) SEM image of the Ag-doped RuO\(_2\) NSs monolayer film. (c) The cross-sectional TEM image of the nanoscale lamellar structure in the LB-deposited RuO\(_2\) NSs multilayer film (4-layer). The sheet resistance and optical transmittance of the RuO\(_2\) NSs multilayer films as a function of (d), (e) Ag doping condition, and (f) the number of the LB-layer.
Resistance and optical transmittance of the Ag-doped RuO₂ NS four-layer films were measured to be $\sim 1.1 \, \text{kΩ} \, \text{sq}^{-1}$ and $\sim 92.2\%$ in the visible region. Considering that the sheet resistance and optical transmittance of the pristine RuO₂ NSs multilayer films with the same number of layers were found to be $\sim 3.2 \, \text{kΩ} \, \text{sq}^{-1}$ and $\sim 93.4\%$, it was proven that the Ag doping was effective for enhancing the electrical transport of the pristine RuO₂ NS multilayer films. This result obtained for the LB-deposited RuO₂ films is consistent with that obtained for an individual NS, as shown in Fig. 4b. Note that the change in optical transmittance was almost negligible before and after Ag-doping, whereas the reduction of sheet resistance was remarkably high. The negligible degradation of the optical transmittance in Ag-doped RuO₂ NSs multilayer films can be attributed to the extremely small diameter of the Ag NPs ($\sim 2$ nm), which is too small to scatter the light of the visible region.

Fig. 6e shows the Ag doping condition dependences in the four-layer films. On increasing the number of doping processes, the sheet resistance was considerably reduced, whereas the transmittance was negligibly reduced. On the other hand, the optical transmittance was significantly decreased with the increasing number of the LB layer (Fig. 6f).

Since the main objective of using a flexible electrode is to realize the reliable performance from the continuous mechanical deformation, the mechanical stability was tested using the fabricated Ag-doped RuO₂ NS multilayer films (Sample 2, 4, and 6). Fig. 7a shows the schematic of the continuous bending test. The bending angle and bending radius were set at 180 degrees and 1 mm, respectively. The resistance of the films was measured in situ when the bending test was carried out. The Ag-doped RuO₂ NSs multilayer films (Sample 2) demonstrated extraordinarily high bending stability, showing that the change of the resistance ($\Delta R/R_0$) was less than 1% over 50,000 cycles. Moreover, $\Delta R/R_0$ of Sample 4 has a value similar to that of Sample 2, whereas the $\Delta R/R_0$ of Sample 6 shows a higher change in the resistance of $\sim 12\%$. Considering that the $\Delta R/R_0$ of the Ag nanowires, which are very commercial materials for transparent flexible electrodes, is $\sim 50\%$ at 2000 cycles in the bending radius of 1 mm, it is clear that RuO₂ NSs films could improve the bending stability because of the thinner film thickness of the Ag-doped RuO₂ NS multilayer films. As shown in Fig. S3,† the Ag-doped RuO₂ NSs multilayer films were not delaminated from the substrate although small degradation was observed. To examine the foldability and the electrical connectivity, light emitting diode (LED) bulbs were connected to the Ag-doped

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>LB-deposition and Ag doping</th>
<th>Layer no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>LB-deposition × 4</td>
<td>4</td>
</tr>
<tr>
<td>Sample 2</td>
<td>(LB-deposition + Ag doping) × 4</td>
<td>4</td>
</tr>
<tr>
<td>Sample 3</td>
<td>LB-deposition × 2 + Ag doping</td>
<td>2</td>
</tr>
<tr>
<td>Sample 4</td>
<td>(LB-deposition × 2 + Ag doping) × 2</td>
<td>4</td>
</tr>
<tr>
<td>Sample 5</td>
<td>LB-deposition × 4 + Ag doping</td>
<td>4</td>
</tr>
<tr>
<td>Sample 6</td>
<td>LB-deposition × 6 + Ag doping</td>
<td>6</td>
</tr>
</tbody>
</table>

Fig. 7 (a) Schematic of the continuous bending test (bending radius = 1 mm). (b) The change in the resistance for Ag-doped RuO₂ NS multilayer films on a PC substrate during the cyclic bending test. (c) and (d) Images of the blue LED connected to the Ag-doped RuO₂ NS multilayer films on a PC substrate under the condition of flattening and folding, respectively.
RuO$_2$ NS multilayer films on a PC substrate. The light of the LED remained turned on, as shown in Fig. 7c, when the Ag-doped RuO$_2$ NSs multilayer films were folded.

Conclusions

In summary, we systemically investigated the electrical transport properties in the exfoliated individual RuO$_2$ NSs. It was revealed that Ag doping by the decoration of Ag NPs on the surface of the RuO$_2$ NSs was effective to enhance the electrical conductivity of the RuO$_2$ NSs. In particular, the electrical conductivity of a monolayer RuO$_2$ NS was increased by up to 3700%. The enhanced electrical conductivity via Ag doping increased with the decreasing number of layers, indicating the clear layer-number dependence. This result obviously shows that the mobility is dominated by surface scattering and the carrier density of RuO$_2$ NSs is increased via Ag doping. Our results demonstrate that the Ag NP doping and layer number of NS play very significant roles in the charge transport of the RuO$_2$ NSs. Furthermore, the Ag-doped RuO$_2$ NS multilayer films show an extraordinarily high bending stability that the change in the resistance is less than 1% over 50,000 cycles, with a reduced sheet resistance of one-third. These enhanced electrical properties and mechanical stability of the Ag-doped RuO$_2$ NSs multilayer films suggest the application of 2D oxide materials as nanoscale transparent electrodes for the flexible electronics and optoelectronics.

Author contributions


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References


