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Introduction

Water soluble biomolecular templates such as cyclodextrins (CDs) have recently emerged as excellent potential tools for the preparation of metal or metal oxide materials.¹⁻³ CDs are water soluble cyclic oligosaccharides formed of 6 (α -), 7 (β -) or 8 (γ -) glucopyranose units that exhibit multifunctional properties, such as the formation of host-guest inclusion complexes,4-9 and the stabilization of metallic nanoparticles10-12 and molecule-ion adducts with inorganic metal salts.13,14 In addition, recent studies of our group have revealed that transformations in valence states of transition metal ions could occur during sintering intimate mixtures of a metal salt with β -CD. For example, it has been demonstrated that the valence of copper can be easily modulated from Cu(II) to Cu(I) by changing the initial molar ratio of copper chloride dihydrate to β-CD in the sintering process in ambient atmosphere.15 These results encouraged us to further investigate the formation mechanism of metal-based composites.

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A new route to produce Ru-based nanocomposites with mixed valence states of ruthenium is reported in this paper via a solid-phase sintering process. Precursor particles were prepared by an intimate mixing of RuCl₃ and native β -cyclodextrin (β -CD) with a molar ratio of 1 : 1, followed by a sintering process at various temperatures ranging from 573 to 1173 K in ambient atmosphere. The so-obtained composite nanomaterials have been characterized by X-ray diffraction and notably the results show that an adjustment of the temperature enabled us to obtain Ru-based nanoparticles with controllable compositions. The surface-enhanced Raman scattering performances of the obtained nanomaterials have been analyzed using Rhodamine 6G (R6G) as the Raman probe. Their magnetic behaviors have been investigated as a function of the field strengths. The present work provides a significant advance in the development of both transformation in valence states of transition metals and *in situ* nanocomposites of metal/metal oxide combinations.

> Metal/metal oxide nanocomposite materials have attracted wide interest because they have improved multifunctional properties and potential wide-ranging applications in many fileds.16 For example, composites consisting of nanostructured ruthenium (Ru) and its oxides (e.g., RuO₂) have shown promising results in experimental studies.17-19 Usually, Ru-based materials are initially prepared in solution by chemical reduction of ruthenium salts,²⁰ complexes^{17a} or oxides.²¹ Thus, the use of reducing agents [e.g., hydroxylamine, hydrazine, sodium borohydride or polyols] is the most common method employed. Recently, Zhang and co-workers reported the preparation of Ru@RuO2 composites using an electrochemical method.22 In general, the procedure requires drastic conditions, such as high reflux temperatures and the use of toxic or expensive organic reagents. Thus, it was found that, after their direct deposition onto inorganic oxide supports, 1 wt% Ru-based supported nanocatalysts were highly active and stable in the catalytic conversion of ethanol to CO₂. Surprisingly, despite these promising effects, the preparation of Ru-based composites has not been the subject of further investigations, and in particular, their synthesis in the presence of molecular templates by solidphase sintering in ambient atmosphere has never been explored. The interest of the procedure is to perform the solidphase reaction without adding any strong reducing agents, neither in solution nor in the gas phase and so to avoid the use of liquid organic media.

> The present work describes for the first time the effect of β -CD on the temperature dependence of transformation in ruthenium valence states, starting from a molecule-ion solution of RuCl₃ and β -CD with an initial molar ratio of 1 : 1. After

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Temperature-dependent formation of Ru-based nanocomposites: structures and properties†

evaporation of the solvent, the sintering experiments of the resulting solid mixture have been performed under ambient atmosphere in a muffle furnace at different temperatures, ranging from 573 to 1173 K. A series of Ru-based composites (SP-a to SP-g) have been obtained and characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman and electron microscopy. Several control materials formed by the same solid-state method but from different carbon sources (α-CD, γ-CD and activated carbon) were conducted to have a better insight into the role of the organic templates during the sintering process. Unexpectedly, we have found that the ability of the CDs to modulate the valence transformation of ruthenium [from Ru(III) to Ru(0) and Ru(IV)] and stabilize the Ru-based nanocomposites depended both on the temperature of sintering and chemical nature of the oligosaccharides. A possible formation mechanism of the Ru-based composites was proposed. Further, we found that these composite materials exhibit different surface-enhanced Raman scattering (SERS) properties. Finally, field dependences of the Ru-based materials have been determined to be highly related to the composite ratios of Ru(0) to RuO_2 .

Experimental section

Materials

 β -CD was purchased from Shanghai Chemical Reagent Company and recrystallized twice from deionized water. RuCl₃·3H₂O was from Aladdin Chemistry Co. Ltd. Commercial activated carbon was from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). α - and γ -CD were purchased from Aldrich. Rhodamine 6G (R6G) was purchased from Sigma-Aldrich. All other chemicals were of general-purpose reagent grade, unless otherwise stated.

Preparation of intimate mixtures

The intimate mixture of RuCl₃ and β -CD was prepared by the follow method. Initially, 1 mmol RuCl₃ (207 mg) and 1 mmol β -CD (1134 mg) were mixed into a round-bottom flask with deionized distilled water of 100 mL and magnetically stirred at 298 K for 4 h. Then, the distilled water was drawn off by rotary evaporation under vacuum at 323 K. Finally, a brown residue was obtained and dried in vacuum to a constant weight. Note that, in addition, intimate mixtures of RuCl₃ with other CDs (α - and γ -CD) and material (activated carbon) were prepared by the same procedure.

Sintering experiments of intimate mixtures

Sintering experiments of the intimate mixture of β -CD with RuCl₃ were carried out in a muffle furnace at 573, 673, 773, 873, 973, 1073 and 1173 K for 4 h. After sintering, the products were cooled under a vacuum, and weighted at room temperature, hereafter denoted as SP-**a** to SP-**g**, respectively. Their color changes were uniform, all from brown to black.

Also, the sintering products of intimate mixtures of RuCl₃ with activated carbon, α - and γ -CD were obtained at 573, 773, 873 and 1173 K for 4 h in ambient atmosphere.

SERS measurements

SP-a, c, d and g were dispersed on a silica substrate (1 cm \times 1 cm) after suspended in alcohol. Then, the R6G reagent (used as probe molecule) was dissolved into pure water. Finally, 20 μ L of the probe solution (10⁻³ M) was dropped onto the silica substrate.

Instruments and methods

XRD analyses of solid samples were carried out in a Philips X'Pert Pro X-ray diffractometer. Samples were irradiated with monochromatized Cu K α and analyzed in the 2θ range from 20 to 60°. Elemental analysis was done on an Elementar Vario EL III elemental analyzer. XPS was performed at Photoemission Station of National Synchrotron Radiation Laboratory of Hefei with a VG Scienta R3000 electron energy analyzer, using Al K α radiation (1486.6 eV) in ultra-high vacuum (2.00×10^{-9} torr) at room temperature. The energy resolution of the instrument is 0.16 eV. The C 1s peak (284.8 eV) was used as the internal standard for binding-energy calibration. Raman spectra were collected at room temperature with a LABRAM-HR Confocal Laser MicroRaman spectrometer with a resolution of 0.6 cm⁻¹ in the range 100–2000 cm⁻¹.

Field emission scanning electron microscope (FE-SEM) images were recorded on a JEOL-JSM-6700F field-emitting microscope. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images were carried out with a JEOL-2010 field-emission transmission electron microscope using an accelerating voltage of 200 kV. STEM (scanning transmission electron microscopy) and EDS (energy dispersive X-ray spectroscopy) mappings were obtained on a JEM 2010F field-emission TEM at 200 kV, equipped with an X-ray energy dispersive spectrometer (EDS). Magnetic properties of solid samples were investigated using a quantum design magnetic property measurement system superconducting quantum interference device (SQUID) magnetometer.

Thermal gravimetric (TG) analyses were obtained on a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of 10.0 K min^{-1} in ambient atmosphere with a gas flow of 25 mL min⁻¹. All solid samples were ground to fine powder by mortar and pestle before analysis. The weight of the solid samples analyzed was in the range of 5 mg to 7 mg.

Results and discussion

Formation and composition of a series of Ru-based nanocomposites

Fig. 1 shows the XRD patterns of the seven materials (SP-**a**–**g**) prepared from RuCl₃ and β -CD. Clearly, the five characteristic diffraction peaks at 2θ angles of 28.3, 35.1, 40.3, 54.5 and 58.1° (indicated by red asterisks) are attributable to the (110), (101), (111), (211) and (220) phases of crystal structure of RuO₂ (tetragonal system), respectively (JCPDS 88-0322).²³ At the same time, the characteristic diffraction peaks of metallic Ru at 38.5 (100), 42.3 (002) and 44.0° (101) (hexagonal system, JCPDS 89-



Fig. 1 (A) XRD patterns of SP-a-g, (B) XPS-(Ru 3p) spectra of SP-a, c, d and g, and (C) molar percentages (%) of Ru(0) and RuO₂. The peaks and percentages of RuO₂ and Ru are marked by red and blue, respectively.

4903)²⁴ (indicated by blue asterisks), were also detected in SP-a-f.

The change of the molar percentages of Ru(0) and RuO_2 in the series of composites is further illustrated by XPS measurements as shown in Fig. 1. At lower sintering temperatures (573– 773 K), the relative content of metallic Ru becomes higher with the increase of temperature (indicated by the green arrow). Contrarily, at higher sintering temperatures (873–1173 K), the relative content of metallic Ru decreases with the increase of temperature and finally the metallic Ru phase disappears completely to give pure RuO_2 phase in SP-g (indicated by the black arrow). This result, which shows that the content of metallic Ru passes through a maximum at a temperature of about 773 K, strongly suggests two significant points regarding the redox properties of $RuCl_3$ in the presence of β -CD.

First, the reduction of $RuCl_3$ to Ru(0) is likely to be associated with the generation of graphite particles during the decomposition process of β -CD. In addition, it can be mentioned that besides the RuO_2 diffraction lines, no signal assigned to a Ru(0)phase was ever detected in the sintering products of free $RuCl_3$ under the same conditions (Fig. S1, ESI[†]).

Second, the formation and constitution of the composites consisting of metallic Ru and RuO_2 is highly dependent on, and can be manipulated by, changes in sintering temperatures.

The Ru-based nanocomposites: SP-**a** (RuO₂ is dominant, *i.e.*, the molar ratio of Ru(0) to RuO₂ is about 1 : 9), SP-**c** (metallic Ru

is dominant, *i.e.*, the molar ratio of Ru(0) to RuO_2 is about 5 : 1), SP-d (RuO₂ and metallic Ru are almost equivalent) and SP-g (only RuO₂) have been further characterized by FE-SEM and TEM analyses in order to show the differences in their morphology or surface structure. Fig. 2a-d shows surface structures of the four Ru-based materials. Obviously, SP-a, SP-c and SP-d have analogous ordered three-dimensional structures shaped like doughnuts comprising nanoparticles with a mean diameter of 50-70 nm. In contrast, a large agglomerate diameter (>200 nm) and a relative large mean diameter (about 120 nm) of particles are observed in the pure RuO_2 (SP-g). The HR-TEM image of SP-g shows that the interplanar spacing is 0.255 nm (Fig. S2, ESI[†]), corresponding to the (101) plane of tetragonal RuO₂. The selected area electron diffraction (SAED) pattern recorded indicates the single crystallinity of the RuO₂ crystal and can be indexed to the tetragonal RuO₂ structure along the [010] zone axis, corresponding to the nanocrystal grown along [101] direction (Fig. S2, ESI[†]).



Fig. 2 FE-SEM and TEM (insets) images of (a) SP-**a**, (b) SP-**c**, (c) SP-**d** and (d) SP-**g**. Size distributions of particles of (e) SP-**a**, (f) SP-**c**, (g) SP-**d** and (h) SP-**g** based on the TEM images.

STEM and EDS analyses were performed to further characterize the detail structure of the nanoparticles in SP-c. Result indicates that a low content of oxygen but a high content of ruthenium appear at the center of some nanoparticles (Fig. S3, ESI†). This is a strong indication that the Ru phase within the nanoparticles is not homogeneously distributed, showing a native oxide shell in combination with an underlying Ru core. However, we also notice that not all the nanoparticles display such a core–shell structure. We speculate that this phenomenon may be related to two factors (i) incomplete dispersion of the RuCl₃ in its mixture of β -CD, and (ii) the growth of the nanocomposites with more kinetically controlled than thermodynamically controlled process, *e.g.*, the effect of the size of the nanoparticles on the oxidation rate of Ru(0).

In conclusion, the temperature dependence of transformation in valence states of Ru gives a strong impression that β -CD seems to play an important role as the composite particle precursor.

Formation process of the Ru-based nanocomposites

Raman spectra of the Ru-based materials in Fig. 3 provide further information about the structural nature of the composites, allowing us to speculate the role of β -CD. As shown in Fig. 3, in the case of SP-**a**, the occurrence of a band at 1589 cm⁻¹ (G band of the C–C vibration of graphite layers²⁵) indicates the existence of graphite (mass percentage: 0.36%, based on elemental analysis) in this material. Undoubtedly, the graphite particles were originated from the decomposition process of β -CD. The very low value of the relative content of graphite should be a reason for the absence of the X-ray diffraction lines of graphite.²⁶ Nevertheless, in SP-**c**, SP-**d** and SP-**g**, the G band disappears completely. One reason is the presence of an interaction between graphite and RuCl₃, and the other is the oxidation of graphite particles with the increase of temperature. Instead, several bands at 513, 626 and 704 cm⁻¹, belonging to



Fig. 3 Raman spectra of SP-a, c, d and g. Relative signal intensity was normalized to the intensity of the peak at 1026 cm^{-1} in SP-c.

Raman-active modes (E_g , A_{1g} and B_{2g}) of RuO₂,²⁷ appear clearly. Additionally, there are two bands at 1026 and 1252 cm⁻¹, which are the overtones of 513 and 626 cm⁻¹ Raman bands. The results of Raman spectra suggest that the graphite carbon generated in this carbonization process of β-CD may act as a reduction agent of Ru(m) to Ru(0).

The thermal decomposition of β -CD has already been the subject of several investigations in the literatures.28,29 Thus authors have reported that the process occurred in three stages: (i) the release of physically absorbed and crystallized water below 110 K, (ii) the dissociation of cyclodextrin rings to form saturated or unsaturated organic compounds below 573 K, and (iii) the formation and oxidation of graphite carbon at high temperatures (>573 K). A comparison of the TG curves between free β -CD and the mixture (1 : 1, molar ratio) of β -CD and RuCl₃ at the entire temperature range reveals significant decomposition differences (see Fig. S4, ESI⁺). The β -CD in the mixture completely decomposes much earlier (710 K) when compared to free β -CD (850 K), implying that the presence of RuCl₃ favors the cleavage of glycosidic bonds. TG data is in accordance with the results of XRD and XPS. For example, when the decomposition of β -CD ends, a solid product with a residual mass of 7.8% at 773 K was collected. Notably, this experimental value is in well-agreement with the ratio of Ru(0) to RuO₂ previously estimated by XPS analysis (i.e. 5 : 1 corresponding to 78.8 wt% metallic Ru).

Several control experiments using different oligosaccharides were performed in parallel for comparison. The XRD patterns of sintering products of the mixtures of RuCl₃ with α - and γ -CD at the same sintering temperatures as those used in the case of β -CD indicate that although the Ru-based composites can be produced in the presence of each of the CDs, there are two significant characteristics that need to be pointed out (Fig. S5, ESI†).

First, the relative contents of metallic Ru in the composites are quite different even at the same sintering temperatures. For example, at 573 K, while the treatment with α -CD leads to the highest content of Ru, by treatment with β -CD, RuO₂ is clearly the dominant phase. Interestingly, at this temperature, the use of γ -CD results in almost equivalent amounts of Ru(0) and RuO₂. Second, in the presence of α - or γ -CD, with the increase of temperature from 573 to 873 K, the relative content of Ru(0) decreases while the content of RuO₂ increases gradually.

These observations reveal that the generation of the Rubased nanocomposites by means of *in situ* chemical processes is highly dependent on the chemical nature of the oligosaccharides. On the one hand, this finding suggests that there are different ways, in which RuCl₃ can interact with the oligosaccharides in aqueous solution, causing each molecule-ion system to generate a characteristic compositing process of the Ru-based crystallite nanoparticles formed during the thermal process. On the other hand, different thermal decomposition processes (Fig. S6, ESI†) of the oligosaccharides may be an important reason for different formation rates of graphite carbon, leading to a difference in compositions of the composites.³⁰

In addition, we performed control experiments by using activated carbon instead of β -CD. Our data (Fig. S7, ESI[†])

indicate that the introduction of activated carbon causes the generation of metallic Ru at 573 K, and subsequently the Ru disappears with the increase of sintering temperature. The result is due to the well-known rapid oxidation of activated carbons by oxygen in air and suggests indirectly that the interactions between RuCl₃ and the activated carbon are not of the same type as those occurring the metal precursor and β -CD.

Starting from this observation, a process for the valence transformation of Ru can be therefore proposed, as illustrated in Fig. 4. Initially, an intimate mixture of β -CD and RuCl₃ was prepared as a precursor. Subsequently, several basic reactions (eqn (1)-(5)) occurred during the sintering process of the mixture. The oxidation of RuCl₃ by oxygen in air to form RuO₂ (eqn (1)) is simultaneous with the reduction of the RuO_2 to Ru(0) (eqn (4)) by graphite carbon derived from the slow release in the decomposition process of β -CD (eqn (2)). At the same time, the oxidation of the Ru(0) to RuO_2 occurs in this process at higher temperatures (eqn (5)). Our data indicate that the release rate of the graphite carbon from β-CD is relatively low particularly at lower temperatures such as 573 K, which results in that the oxidation of RuCl₃ is dominant at this temperature. As temperature increases from 573 to 773 K, the release of carbon accelerates, causing the content increase of Ru in the composites. For example, after sintering for 2 h at 773 K, a higher intensity of the Ru(0) XRD peaks was obtained because of the quick release of carbon (Fig. S8, ESI†) and the as-obtained Ru could be maintained after another 2 h. Moreover, when temperature is higher than 773 K, the Ru is gradually oxidized to RuO₂, and finally completely disappears at 1173 K when carbon disappears (eqn (3)). Therefore, this result should be a reflection of an earlier and easier oxidation of activated Ru species since in general metallic Ru does not oxidize in air at temperatures below 1073 K.31

We performed additional sintering experiments using intimate mixtures of β -CD and RuCl₃ with molar ratios of 1 : 2 and 2 : 1. XRD analysis (Fig. 5) provides very interesting findings with regard to the composition of the final products by changing the sintering temperature. We noticed that all the products obtained by changing the sintering temperature are proved to be RuO₂. Therefore, it does not follow the same trend



Fig. 4 Formation process of the Ru-based nanocomposites.



Fig. 5 XRD patterns of the sintering products of the intimated mixtures of β -CD and RuCl₃ with molar ratios of 2 : 1 (A) and 1 : 2 (B) at 573 (a), 773 (b), 873 (c), 973 K (d).

when the initial molar ratio of RuCl₃: β -CD is not fixed at 1 : 1, like more RuCl₃ or more β -CD. It can be explained by the formation process of the Ru-based nanocomposites as described in Fig. 4. On the one hand, when the amount of β -CD is relatively large, extra water molecules were produced in the sintering process (see eqn (2)). The presence of the water molecules will promote the formation reactions (eg, eqn (1)) of RuO₂. On the other hand, when the amount of β -CD is relatively small, the formation reaction (eqn (4)) of Ru will be difficult to occur because of the lack of released carbon from the decomposition of β -CD. This observation not only suggests that the composition of the final products of the mixtures of β -CD and RuCl₃ is strongly associated with the mixed ratios, but also further supports the proposal of the formation process of the Ru-based nanocomposites.

The remarkable difference in compositions of the Ru-based nanocomposites allows us to characterize the relationship between the compositions and physical properties. Two independent experimental techniques, *i.e.* SERS and magnetic enrichment effects, were employed to evaluate this question.

SERS properties of the Ru-based nanocomposites

SERS is a very useful technique causing strongly increased Raman signals from compounds, which have been attached to nanofilms, nano-sized structures, architectures, assemblies.³² A large number of studies have reported on applications of metallic nanomaterials, such as gold and silver, in SERS.³³ However, not enough concern was given to the application potential of metallic oxide nanomaterials in SERS. Therefore, we performed a series of SERS experiments with the use of the Ru-based composites.

Fig. 6 depicts the Raman spectra of the probe molecule R6G on the Ru-based composites deposited onto a silica glass substrate. No Raman signal is observed from the R6G on the silica substrate. However in the presence of the composites, there are several clear signals at 612, 771, 1361 and 1648 cm⁻¹, due to the carbon–oxygen stretch, ethylamine group wag and

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Fig. 6 SERS spectra of R6G on a silica substrate, and SP-a, c, d and g.

xanthene ring stretch of R6G, revealing the SERS properties of the Ru-based nanocomposites. This property was reported previously, but only for pure metallic Ru phase.³⁴ In particular, the two composites: SP-a and SP-c, have stronger SERS activity relative to the other two: SP-d and SP-g. It suggests that the ratio of RuO₂ to Ru(0) in the nanocomposites has an important effect on the Raman scattering. This is a very interesting phenomenon: when the content of metallic Ru is much higher or much lower than RuO₂, the composites show better SERS activity. Taken this together with the structural features of the composites, it can be suggested that such a Raman enhancement effect may be attributed to the enhanced localized electromagnetic field, which is affected by two factors: the interaction between Ru(0) and RuO2, and the small size and large surface area per unit mass of the nanocomposites.35 Although the SERS effect in the Ru/RuO₂ composites is relatively small compared to that generally reported for noble metals, understanding the relationship between the compositions of the nanocomposites and their SERS effects is significant because it could lead to a strategy for improvement. Our result may provide a clue to further modify the SERS properties of metal/metal oxide nanocomposites.

Magnetic properties and electronic structures of the Ru-based nanocomposites

Magnetic properties of SP-**a**, **c**, **d** and **g** were measured by a SQUID. Fig. 7 depicts the field dependences of magnetizations of the four nanomaterials at 298 K. Two interesting phenomena are observed from this figure. First, all the four Ru-based nanocomposites exhibit superparamagnetism. Second, the crystallites have very low, but different, magnetizations in fields up to the maximum applied magnetic field (10 kOe). For example, the saturation magnetizations (M_s) of SP-**a**, **c**, **d** and **g** at 298 K are 0.85×10^{-2} , 2.8×10^{-2} , 0.56×10^{-2} and 1.4×10^{-2} emu g⁻¹, respectively. It is known that the magnetic susceptibility of RuO₂ is much higher than that of metallic Ru. However, in the present case, this relation is reversed and is abnormal. For example, SP-**c** with a large amount of Ru(0) exhibits a much higher M_s , when compared to pure RuO₂ (SP-**g**). We believe that the reason for this difference may be that the *in situ* composite



Fig. 7 Field dependences of magnetizations of SP-**a**, **c**, **d** and **g** at 298 K. The inset is the magnified version of the hysteresis loop in the field range of 300 Oe.

interaction between metallic Ru and RuO_2 has induced a change in the distribution of electronic density in the crystals. Therefore, it seems tempting to speculate on the possibility whether inner electronic structures of Ru core levels vary with the formation of composites.

In line with this, the Ru 3p XPS spectra for SP-**a**, **c**, **d** and **g**, which are shown in Fig. 1, exhibit significant shifts in the binding energy of Ru(v) and Ru(0). The Ru 3p region of SP-**a** was separated into two components: one having higher binding energies of about 462.2 (3p_{5/2}) and 484.3 (3p_{3/2}) eV due to Ru(v) in RuO₂,³⁶ and the other having lower binding energies of about 461.1 (3p_{5/2}) and 482.7 (3p_{3/2}) eV due to Ru (0).³⁷

However, we find that a shift in binding energies for Ru 3p core level has occurred from one composite to another and especially from one composite to the pure RuO₂. For example, in the SP-d, the binding energies of Ru(IV) 3p_{5/2} and 3p_{3/2} increase largely to 463.3 and 485.7 eV, respectively, when compared to those of SP-a. We speculate that it is due to substantially more electron transfer from Ru atoms to oxygen atoms while the materials were synthesized at higher temperatures. This electron transfer effect is also in line with the decrease in the O 1s binding energy that is measured in the samples prepared at 573 and 873 K (Fig. S9, ESI[†]). It should be noted that the O 1s line shape is asymmetric in both SP-a and SP-d, probably as a result of the compositional heterogeneity of the oxide near-surface region.³⁸ In the pure RuO₂, the binding energies of Ru(IV) 3p_{5/2} and 3p_{3/2} increase dramatically to 464.5 and 486.4 eV, respectively. It is apparent that such a large shift is a reflection of significant differences in the electronic structure of Ru(IV) among the composites and especially between the pure RuO₂ phase and its composite materials. This provides evidence for our conclusion that the composite interaction between metallic Ru and RuO₂ leads to a change in inner electronic structures of Ru core levels.

These findings provide a basis for understanding the magnetic properties of Ru-based composite materials. The Rubased materials show magnetic behaviour even though neither ruthenium nor ruthenium dioxide is ferro-, ferri-, or antiferromagnetic. We consider that this is a very rare case of the composite materials between a metal and its oxides. In particular, the fact that the SP-c with a large amount of metallic Ru exhibits a much higher M_s , when compared to pure RuO₂ (SP-g), is especially interesting because this allows us to illustrate some important properties of the composite model. On the one hand, the composite interaction between Ru and RuO₂ has led to a change of electronic structure of Ru cores based on XPS analysis, suggesting that there might be a possibility of electronic transfer between the Ru(0) and the Ru(IV). This electronic transfer could be one reason for the change in the Ru local magnetic anisotropy, leading to a distribution of local Ru magnetic-moment orientations. On the other hand, the obtained composite powders had a crystallite size in the range of nanoscale (diameter, <50 nm). This is the other important reason why these composite materials show magnetic behaviour, because at the nanometer scale, each particle may contain only a single magnetic domain.

Conclusion

This work demonstrated for the first time the valence transformation of Ru(III) to Ru(IV) and Ru(0) via a modified combustion method based on ruthenium chloride and β -CD. The special interest of the method lies in the fact that it yields a series of Ru/RuO₂ nanocomposites with temperature-dependent composite ratios, but without adding any extra components such as inorganic reducing agents, organic solvents and surfactants. We believe that this method could be used for many different systems. Particularly, our results firstly revealed that the composite ratios have a crucial effect on the physical properties of the nanocomposites, including magnetizations and SERS effects. In addition, the size of the domains could also play a role in the physical properties. We consider that the description of the composition-property relationship provides a framework for designing and developing metal-metal oxide nanocomposite materials.

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