

Rational Synthesis for a Noble Metal Carbide

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S Supporting Information

ABSTRACT: Transition metal carbides have attractive physical and chemical properties that are much different from their parent metals. Particularly, noble metal carbides are expected to be promising materials for a variety of applications, particularly as efficient catalysts. However, noble metal carbides have rarely been obtained because carbide phases do not appear in noble metal-carbon phase diagrams and a reasonable synthesis method to make noble metal carbides has not yet been established. Here, we propose a new synthesis method for noble metal carbides and describe the first synthesis of rhodium carbide using tetracyanoethylene



(TCNE). The rhodium carbide was synthesized without extreme conditions, such as the very high temperature and/or pressure typically required in conventional carbide syntheses. Moreover, we investigated the electronic structure and catalytic activity for the hydrogen evolution reaction (HER). We found that rhodium carbide has much higher catalytic activity for HER than pure Rh. Our study provides a feasible strategy to create new metal carbides to help advance the field of materials science.

INTRODUCTION

Transition metal carbides, such as WC_1^{1-4} Fe₃C₁^{5,6} and $Co_2C_1^{7,8}$ have attracted a great amount of attention for industrial applications, such as catalysts and hard materials,

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because they show fascinating physical, chemical, and mechanical properties. In general, transition metal carbides are synthesized by heating together a transition metal and a carbon source, such as graphite or hydrocarbons, to promote atomic diffusion of C atoms.^{9,10} Given the high temperatures required, the products synthesized by this method tend to form an equilibrium phase. However, it has not been reported that noble metal carbides are obtained by just heating noble metals with a carbon source because there is no noble-metal carbide phase in the equilibrium phase diagrams.¹¹ However, if noble metal carbides existed, then some of the important properties of the most expensive noble metal elements like their catalytic activity would be enhanced by atomic alloying with the cheapest element of C.

Recently, a new nonequilibrium synthesis method for solidsolution alloy nanoparticles that are unobtainable in the bulk states was reported.^{12,13} The solid-solution alloy nanoparticles were synthesized with a quick chemical reduction method in which constituent metal atoms were concurrently supplied by tuning the reduction rate of the metal ions, so they could immediately aggregate and form an alloy even if they are immiscible in the bulk states. However, these new alloys comprise transition metals, and although a noble metal and carbon or nitrogen also are immiscible in the bulk states, such noble metal carbides and nitrides have not yet been developed.

Here, we propose a new facile synthesis method to produce noble metal carbides. We hypothesized that a noble metal carbide would be obtained by a concurrent supply of noble metal and C atoms. The bottom-up approach, especially for a liquid-phase chemical reduction method, could be applicable to finely tune the supply rate of the metal atoms. However, C atoms cannot be supplied by a reduction process, like metal atoms. Therefore, we focused on an organic compound to supply C atoms following decomposition by heating it in the reducing liquid phase. In addition, for the concurrent supply of noble metal and C atoms, we utilized an organic oxidant. An organic oxidant would arrest the reduction process of noble metal ions and stop functioning as an inhibitor of the reduction process by its decomposition. Therefore, the decomposition of the organic oxidant would trigger the reduction of noble metal ions as well as a supply of C atoms. This would result in a concurrent supply of noble metal and C atoms, and thus noble metal carbide should be obtained. Moreover, a liquid-phase synthesis is more suitable for mass production than conventional carbide syntheses that require extreme conditions, such as a high temperature and/or pressure.

As a first demonstration for our hypothesis, we focused on the combination of Rh and C, which is an immiscible system,¹¹ and successfully synthesized rhodium carbide (Rh_2C) by a chemical reduction method using an organic oxidant, tetracyanoethylene (TCNE). The obtained Rh_2C was characterized by powder X-ray diffraction (PXRD), neutron powder diffraction (NPD) and scanning transmission electron microscopy (STEM) coupled with electron energy-loss spectroscopy (EELS) analysis. The electronic structure of the Rh_2C was investigated by hard X-ray photoelectron spectroscopy (HAXPES) and density functional theory (DFT) calculations. Moreover, we investigated catalytic activity in the hydrogen evolution reaction (HER) of Rh_2C , which showed much higher activity than Rh at reduced loading of the costly noble metal specie.

EXPERIMENTAL SECTION

Synthesis of Rhodium Carbide. To synthesize rhodium carbide, we chose Rh(III) acetylacetonate, ethylene glycol (EG) and TCNE as a precursor, a reducing agent, and an organic oxidant,¹⁴ respectively. Rh(III) acetylacetonate (0.1 mmol, Strem Chemicals) and TCNE (0.03 mmol, TCI) were added to EG (50 mL, Wako Chemicals), and the solution was heated in an eggplant flask in an oil bath at 200 °C for 6 h. After the reaction was completed, the product was separated by centrifugation. The details of the synthesis conditions for other samples are described in the Supporting Information (SI).

Characterization. The structure of rhodium carbide was determined by synchrotron PXRD measurement ($\lambda = 0.5807$ Å (Figures 1a and S1) and $\lambda = 0.5791$ Å (see below) at SPring-8



Figure 1. (a) The synchrotron PXRD patterns of the obtained compound (red) and bulk fcc Rh (black). (b) The NPD pattern of the obtaind compound (red dots) and the results of the Rietveld refinement (the blue line is calculated pattern; the gray line is the background; and the black line is the residual). (c) The structural model obtained from the Rietveld refinement of the synchrotron PXRD pattern. The red spheres are Rh atoms, and the black spheres are C atoms. (d) The MEM electron density map for Rh₂C. The yellow surface is the electron density surface (0.65 electrons per Å³).

beamline BL02B2¹⁵ and NPD measurement using a time-of-flight high intensity total diffractometer (NOVA) installed at the Materials and Life Science Experimental Facility (MLF) at the Japan Proton Accelerator Research Complex (J-PARC). Rietveld refinement of the PXRD pattern and the calculation of the electron density map with the maximum entropy method (MEM) were performed using ENIGMA,¹⁶ and refinement for the NPD pattern was performed using Z-Code developed by KEK. High-angle annular dark-field (HAADF)-/annular bright-field (ABF)-STEM observation and STEM-EELS analysis were performed using an aberration-corrected electron microscope JEOL JEM-ARM 200F operated at 200 kV at The Ultramicroscopy Research Center, Kyushu University. The 3D tomographic images were reconstructed from the HAADF-STEM tilt image series recorded over an angle range from -70° to 65° by simultaneous iterative reconstruction technique (SIRT)17 implemented in the TEMograpy software (System in Frontier, Inc.)

Investigation of the Electronic Structure. The HAXPES spectra were recorded at SPring-8 beamline BL15XU at the incident photon energy of 5.95 keV. The DFT calculations were carried out

using the Vienna ab initio simulation package (VASP)^{18–21} within the generalized gradient approximation based on the Perdew–Burke– Ernzerhof (GGA-PBE)^{22–25} functional with the projector augmentedwave method (PAW).^{26,27} A cutoff energy of 700 eV and $9 \times 9 \times 9$ kpoint grid were employed.

Catalyst Preparation. The Rh reference material was prepared from Rh₂C by heating Rh₂C at 150 °C for 2 h under a 1 atm hydrogen atmosphere to prepare Rh with the same shape as the Rh₂C (Figure S2). The Rh₂C and Rh dispersed in 7 mL of ethanol were sonicated for 1 h and mixed with Vulcan XC 72R carbon and 23 mL of isopropanol. After sonicating for 4 h, the products were centrifuged and dried. Then, 5 mg of the catalysts were suspended and sonicated in a mixture of 300 μ L water, 600 μ L isopropanol and 100 μ L Nafion. Ten microliters of the catalyst ink was deposited on a grassy carbon working electrode (5 mm diameter) (Pine Instruments).

Electrochemical Measurements. All electrochemical measurements were performed at room temperature on a CHI 760E electrochemical analyzer (CH Instruments) in a standard three-electrode system using a gold mesh electrode and a Hg/HgO electrode as the counter and reference electrodes, respectively. The electrolyte was Ar-saturated 1.0 M KOH. The potential was converted to the reversible hydrogen electrode (RHE). The polarization curves were obtained at a scan rate of 50 mVs⁻¹ with 85% *iR* compensation.

RESULTS AND DISCUSSION

Figure 1a shows synchrotron PXRD patterns of the obtained compound and bulk Rh. The pattern of the obtained compound is totally different from the patterns of Rh or the Rh precursor (Figures 1a and S1). Although this PXRD pattern has not been observed in any other Rh compound, we found that the pattern is similar to that of cobalt carbide (Co_2C) .²⁸ To investigate the crystal structure, we performed Rietveld refinement using a hypothetical model of Rh₂C with the space group of *Pmnn* that refers to Co_2C and obtained a good fit with the lattice parameters of a = 3.07667(5) Å, b = 4.76708(9) Å, and c = 4.72274(8) Å (Figure S1b and Table S1a,b). The obtained compound was stable until 523 K (Figure S3). Furthermore, to confirm the position of C atoms and the ratio of Rh to C, we performed an NPD measurement and Rietveld refinement (Figure 1b, Table S1c,d). The NPD pattern also fit well with the same model. These results indicated that the obtained compound was Rh₂C (Figure 1c). In the structure of Rh₂C, the ABAB stacking sequence of the Rh planes can be seen and is similar to a hexagonal close-packed structure along the [001] zone axis (Figure S4a); a C atom is located at a distorted octahedral site among the Rh atoms (Figure S4b), whereas the bulk Rh adopts a face-centered cubic (fcc) structure with the close-packed planes stacked in the ABCABC sequence. Figures 1d and S4c,d show the electron density map obtained using the MEM for Rh₂C, suggesting that there are bonds between the Rh and C atoms.

Microscopic analysis also confirmed the model structure obtained by the X-ray and neutron diffraction studies. The bright-field (BF)-STEM images show that the average size of the obtained Rh₂C is 99.3 \pm 23.5 nm, and the particle consists of small tabular nanocrystals, which was confirmed by 3D electron tomography (Figures 2a and S5). Figure 2b is a HAADF-STEM image viewed from the flat side of the crystal, and it shows an ABAB stacking sequence of Rh atoms with the (002) lattice spacing of 2.3 Å. This image and its Fourier-transform (FT) pattern are consistent with the structural model obtained from the Rietveld refinement corresponding to a view along the [100] zone axis (Figure S6a). The ABF-STEM image observed from a lateral side of the crystal and its FT pattern correspond to the structural model viewed along



Figure 2. (a) BF-STEM image of Rh_2C . (b, c) Atomic resolution in STEM images. (b) The HAADF-STEM image along the [100] zone axis. (c) the ABF-STEM image along the [001] zone axis and the structural models obtained from the Rietveld refinement (insets). The red spheres are Rh atoms, and the black spheres are C atoms. (d) HAADF-STEM image and STEM-EELS images of (e) Rh-M, (f) C-K, and (g) overlay of Rh and C (scale bar, 5 nm).

the [001] zone axis (Figures 2c and S6b). The ABF-STEM image contains clear black dots that indicate heavy Rh atoms and fuzzy black dots that imply light C atoms at the center of hexagons formed by the Rh atoms. STEM-EELS maps of Rh-M and C-K show that the Rh and C atoms are distributed homogeneously over the whole particle (Figure 2d–g). In addition, the EELS spectrum does not show an obvious N-K edge around 401 eV, even though C-K and Rh- M_3 edges were clearly observed around at 284 and 496 eV, respectively (Figure S7). Therefore, the obtained compound was not Rh nitride, but Rh₂C.

The electronic structures of the Rh_2C were investigated by HAXPES and a DFT calculation using the structural model obtained from the Rietveld refinement. The valence-band (VB) HAXPES spectra of Rh_2C and Rh (Figure 3a,b, respectively) clearly show four and three peaks, respectively,



Figure 3. (a) The HAXPES spectrum of Rh_2C and (b) Rh. (c) The calculated total density of sates of Rh_2C and (d) Rh. In the spectrum of Rh_2C , four main peaks are denoted, whereas in that of Rh, three main peaks are denoted.



Figure 4. (a) The PXRD patterns of the products synthesized with different amounts of TCNE. The open circles indicate the peaks of Rh₂C and the closed squares indicate the peaks of Rh. (b) Photographs of the synthesis solutions at increasing reaction times. From left to right: 5 min, 10 min, 20 min, 30 min, 40 min, 50 min, 1 h, 2 h, 3 h, 4 h, 5 h, and 6 h. (c) The TEM images of the synthesis solutions with TCNE (upper) and without TCNE (lower) (scale bar, 50 nm). (d) The consumption percentage of the Rh precursor during the synthesis. These data were obtained by the normalized absorbance of the peak at 324 nm in the UV–vis spectra of the solutions with TCNE (red) and without TCNE (blue) as written in the Experimental Section. (e) The PXRD patterns of the products synthesized with the different electron acceptors. ($\lambda = 0.5791$ Å)

which correspond to the calculation results (Figure 3c,d). According to the partial densities of states (PDOS) of Rh_2C (Figure S8), peaks 3 and 4 are formed by the hybridization of Rh and C orbitals, which is consistent with the existence of the bonds suggested in the MEM electron density map (Figures 1d and S4). In addition, no energy gap at the Fermi level was observed in Rh_2C , indicating a metallic nature. The core-level HAXPES spectra indicate that the valence state of Rh in Rh_2C is 0 (Figure S9).

To verify our hypothesis that the decomposition of an organic oxidant, TCNE, would trigger a concurrent supply of noble metal and C atoms, the roles of TCNE as a carbon source and an inhibitor of the reduction were studied. First, the hypothesized role as a carbon source was confirmed by decreasing the amount of TCNE for syntheses (Figure 4a). In the synthesis of Rh_2C , we used 0.03 mmol TCNE and obtained only the Rh_2C phase (Figure S1). However, in the case without TCNE, the fcc Rh phase was obtained as usual, and the mixture of Rh_2C and Rh was synthesized using 0.01 mmol TCNE. Therefore, the amount of TCNE plays a key role in the formation of Rh_2C . In addition, to investigate the change

in the TCNE during the synthesis process, ultraviolet-visible (UV-vis) absorption spectroscopy was performed with a TCNE solution (Figure S10). The absorption peak of the TCNE at approximately 240 nm gradually disappeared, indicating that TCNE is decomposed by heating in EG. This suggests that C atoms are gradually supplied by the TCNE following its decomposition during the synthesis process. These results revealed that TCNE works as a carbon source and is essential for the synthesis of Rh₂C.

Second, the role of TCNE as an inhibitor of the reduction of Rh ions was investigated. During synthesis, the color of the solution with TCNE changed from transparent to black, implying that the formation of nanoparticles, was slower than that of the solution without TCNE (Figure 4b). TCNE is one of the most well-known electron acceptors.¹⁴ Since an electron acceptor attracts electrons and works as an oxidant, it is expected that TCNE can work as an inhibitor of the reduction of Rh ions in the reaction. We observed the particle growth process in the synthesis solutions with/without TCNE by TEM (Figure 4c). In the solution without TCNE, particles were clearly observed starting at 10 min (Figure S11), rapidly

grew and formed agglomerates until 20 min elapsed. In contrast, in the solution with TCNE, small particles were sparsely observed at 20 min, and they gradually grew for more than 2 h. These results imply that TCNE acts as an inhibitor for the reduction of Rh ions. The heating time dependence of the consumption percentage of Rh precursor was estimated by the intensity of the UV-vis absorption peak of Rh acetylacetonate²⁹ during the synthesis process (Figures 4d and \$12). The consumption percentage of Rh precursor in the solution with TCNE increased at slower rate with increasing time than that in the solution without TCNE. In the UV-vis spectra of the TCNE solution (Figure S10), the main TCNE peak decreased for the first 20 min, which means that the TCNE started to decompose in the first 20 min. The start of the nucleation observed by TEM coincides with the start of the decomposition of TCNE observed by the UV-vis analysis. These results suggest that TCNE acts as an inhibitor and that its decomposition induces the reduction of Rh ions. Given that TCNE works as a carbon source, both the supply of C atoms and the reduction of Rh ions were accompanied by the decomposition of TCNE, and Rh₂C was formed by the concurrent supply of Rh and C atoms. To further investigate the correlation between the redox potential of an organic oxidant and the formation of Rh₂C, we examined other organic oxidants with different redox potentials to synthesize Rh₂C (Figures 4e, S13, and S14). Rh₂C was obtained using 7,7,8,8tetracyanoquinodimethane (TCNQ) or 2,3,5,6-tetrafluoro-TCNQ (F₄TCNQ) but not using 1,4-benzoquinone, chloranil, or 1,2,4,5-tetracyanobenzene (TCNB). This tendency follows the order of the redox potential of the organic oxidants.³⁰ F₄TCNQ, TCNE, and TCNQ have high redox potentials $(+0.60 \text{ V},^{31,33} + 0.29 \text{ V},^{31,32} \text{ and } +0.22 \text{ V},^{31-33} \text{ respectively}),$ whereas chloranil, 1,4-benzoquinone, and TCNB have low redox potentials (+0.05 V, $^{31-33}$ –0.46 V, 32 and –0.65 V, 32 respectively). Therefore, it is concluded that novel Rh₂C can be successfully synthesized by choosing organic oxidants with an optimum redox potential to tune the reduction of Rh for a concurrent supply of Rh and C atoms.

Rh₂C is expected to show unique properties because its electronic and surface structures are different from those of Rh. As a first demonstration, we investigated the catalytic activity for an alkaline HER, which has become one of most required reactions in the past few years.³⁴⁻³⁸ This reaction is a crucial step in electrochemical water splitting and plays an important role in energy conversion for the development of hydrogenbased energy resources. The catalytic performance was investigated with a standard three-electrode system in 1.0 M KOH aqueous solution. We performed linear sweep voltammetry about 20 wt % Rh₂C/C (Figure 5a). The 20 wt % Pt/C and Rh/C were also investigated as references, and Pt is well-known as the best catalyst for HER. We compared the activities by overpotentials and Tafel plots (Figure 5b,c). The overpotentials at -5 mA cm^{-2} are 13.0 mV (Rh₂C/C), 13.4 mV (Pt/C) and 31.6 mV (Rh/C) (Figure 5b). The Tafel slopes of Rh₂C/C, Pt/C and Rh/C are 74.5 mV dec⁻¹, 73.4 $mV dec^{-1}$ and 114.5 mV dec⁻¹, respectively (Figure 5c). These results suggest that the catalytic activity of Rh is enhanced by alloving with C, resulting in Rh₂C exhibiting a comparable HER activity to Pt. In addition, Rh₂C showed high stability during HER and higher conductivity than Rh (Figures S15 and S16). To clarify the mechanism of the enhancement, theoretical studies were performed on the (001), (111), and (021) surfaces of Rh_2C , which were confirmed by microscopic



Figure 5. (a) The HER polarization curves of 20 wt % Rh_2C/C (red), Pt/C (black), and Rh/C (blue). The data were recorded in a 1.0 M KOH electrolyte with a scan rate of 50 mV s⁻¹. (b) The overpotentials at -5 mA cm⁻¹. (c) The Tafel plots and fitting lines to obtain the Tafel slopes for 20 wt % Rh_2C/C (red), Pt/C (black overlapped with red) and Rh/C (blue). (d) The 3-state free energy diagram for HER. The structural models show the OH* precovered surfaces used for calculations. The blue spheres are hydrogen atoms, and the gray spheres are oxygen atoms.

analysis (Figure S5). Among these surfaces, the C-terminated surfaces are more stable than the Rh-terminated surfaces and low indexed surfaces such as (100) and (010) (Figure S17a). Although the hydrogen adsorption free energy (ΔG_{H^*}) is wellknown as a reasonable descriptor to discuss the HER activity of a catalyst,³⁹ the effect of hydroxyl species adsorbed on the surface (OH*) must be considered because the HER activity in alkaline solution is strongly affected by OH*.^{40–43} Given the pH of the test conditions, the C sites of the Rh₂C surfaces are covered with OH* under the reaction potential (Figure S17c). Therefore, we calculated the free energy of H* on the OH* precovered C-terminated $Rh_2C(001)$, (111), and (021) surfaces (Figure S17d). While a hydrogen atom adsorbs on an hcp hollow site on the Rh(111) surface, a hydrogen atom adsorbs on the bridge site of Rh atoms of the C-terminated $Rh_2C(001)$ surface. Figure 5d shows the free energy diagram of H* on OH* precovered surfaces. A catalyst with a free

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energy of H* close to zero is considered to show a high activity. The diagram indicates that the C-terminated Rh_2C -(001) surface is the most active for HER. These theoretical studies revealed that alloying with C leads the different hydrogen adsorption sites to provide suitable adsorption energy for HER.

CONCLUSIONS

Noble metal carbides have rarely been investigated. Our results demonstrated the first rational and facile synthesis of a noble metal carbide that did not use special conditions, such as a high temperature or high pressure. A concurrent supply of metal and carbon atoms, which is crucial for the new synthesis method for noble metal carbides presented here, was realized by adding an effective organic oxidant to the reduction reaction. Moreover, the catalytic activity of Rh_2C for HER is higher than that of Rh. This new synthesis strategy could be applied to other metal carbides by choosing an optimum organic oxidant and create novel metal carbides.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b09219.

Reaction conditions for the syntheses of the samples, measurements conditions of UV-vis absorption measurements and TEM images of the synthesis condition, calculation conditions for catalytic activities, supporting figures, and tables (PDF)

3D tomographic reconstruction movie (MP4)

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Notes

The authors declare no competing financial interest.

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