

Plasma-Assisted Synthesis of Monodispersed and Robust Ruthenium Ultrafine Nanocatalysts for Organosilane Oxidation and Oxygen Evolution Reactions

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We report a facile and general approach for preparing ultrafine ruthenium nanocatalysts by using a plasma-assisted synthesis at $< 100^\circ\text{C}$. The resulting Ru nanoparticles are monodispersed (typical size 2 nm) and remain that way upon loading onto carbon and TiO_2 supports. This gives robust catalysts with excellent activities in both organosilane oxidation and the oxygen evolution reaction.

Heterogeneous catalysts often consist of small metal particles dispersed on supports.^[1–4] Although many methods have been proposed for their synthesis,^[5–7] the most common approach involves impregnating the support with a metal precursor solution, followed by thermal decomposition and reduction at a relatively high temperature.^[8–10] The problem is that these steps often cause sintering and/or agglomeration.^[2–4, 11] Moreover, many “too-small-to-be-stable” nanoparticles form through the Ostwald ripening mechanism.^[12] The result is a broad particle-size distribution, which lowers catalyst performance.^[10, 13–15] Alternatively, one can use strong reducing agents, such as sodium borohydride and hydrazine, to convert the precursors into the corresponding metals, but many of these reductants are corrosive and/or toxic and can cause further problems downstream.^[16, 17] Hence, most of today’s syntheses of monodispersed nanocrystals are based on colloidal chemical synthetic procedures involving the use of capping agents and spacers, which hamper large-scale applications.

One way to avoid these problems is by using plasma-assisted synthesis.^[18, 19] This method produces nanoparticles and metal-supported catalysts from metal precursors.^[18, 20, 21] Some of the supported catalysts prepared by the plasma-assisted synthesis method are Au/Y-zeolite,^[22] Pt/Y-zeolite,^[22] Pt/ γ - Al_2O_3 ,^[23] Co/ γ - Al_2O_3 ,^[23] Ni/ γ - Al_2O_3 ,^[24] Pt/ Al_2O_3 - CeO_2 ,^[25] Co/C,^[26] and Fe/C.^[26] This method is simple, quick, and compatible with impregnation processes.^[27] However, these thermal plasma techniques do not always give good control of the particle size.^[28] In these processes, the nanoparticles undergo rapid agglomeration because of the high temperatures, which may result in broad particle-size distributions.^[28]

Herein, we report a cold plasma-assisted approach for the preparation of supported ruthenium catalysts.^[27–30] This method has excellent support compatibility (we used carbon as well as titania supports), which enables the synthesis of monodispersed and ultrafine Ru nanoparticles. Cold plasma synthesis is solvent-free and ligand-free, giving high-purity nanoparticles. We tested these catalysts in two representative yet different reactions: organosilane oxidation and the oxygen evolution reaction (OER). Previous organosilane oxidations were performed mainly by using metals such as gold,^[31–36] palladium,^[8, 32] platinum,^[37] and rhodium.^[38] The costs of these metals are 38, 24, 31, and 285 $\text{\$ g}^{-1}$, respectively (January 2017).^[39] Although ruthenium is much cheaper (1.3 $\text{\$ OZT}^{-1}$), it has rarely been used for silane oxidation. The OER is the rate-determining step in many important energy-related processes such as water splitting, reversible metal–air batteries, and fuel cells.^[40, 41] Ruthenium oxide (RuO_2) is one of the best-performing OER catalysts to date.^[42–44] Thus, we decided to focus on Ru catalysts, and in both reactions the catalysts showed high activity and stability.

Figure 1 illustrates the facile preparation procedures for the carbon-supported 5 wt% Ru catalyst (denoted hereafter as Ru-Plasma) by a cold plasma synthesis (detailed experimental procedures are included in the Supporting Information). The low-temperature process ($< 100^\circ\text{C}$) gave ultrafine and monodispersed Ru nanoparticles on the support. Conversely, conventional calcination requires at least 400°C to decompose the RuCl_3 precursor (see the coupled thermogravimetric and differential scanning calorimetric analyses in Figure S2 in the Supporting Information). Combined with sequential reduction in H_2 , it causes the agglomeration of the Ru nanoparticles.

The powder X-ray diffraction (XRD) pattern of Ru-Plasma in Figure 2a confirms the complete decomposition of RuCl_3 and

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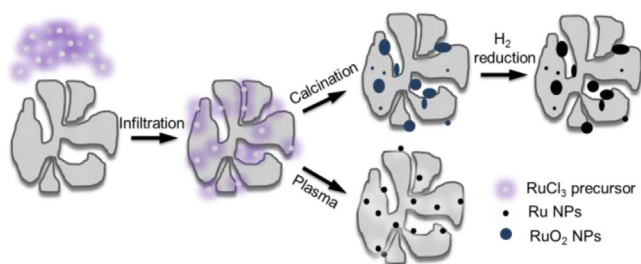


Figure 1. A comparison of the workflows for the preparation of supported Ru catalysts by conventional calcination–reduction and plasma-assisted synthesis.

the formation of metallic Ru after plasma treatment. By comparing with the pattern of commercial 5 wt% Ru on carbon (denoted hereafter as Ru-Conv), we attribute the broad peaks at $2\theta = 24.0$ and 43.5° to carbon (graphite) and the tiny peaks from $2\theta = 38.4$ to 44° to metallic Ru.^[45] X-ray photoelectron spectroscopy (XPS) also reveals the effectiveness of the plasma synthesis. Indeed, overlapping of the C 1s and Ru 3d core levels poses a challenge upon analyzing the spectrum in Figure 2b, particularly at low Ru loadings. Nonetheless, there is a clear binding-energy shift in the Ru 3d_{5/2} peak relative to its position in the sample before plasma treatment, which implies a decrease in the Ru oxidation state (see inset).^[46,47] We also studied the crystal structure of Ru-Plasma through high-resolution transmission electron microscopy (HRTEM). Figure 2c shows the atom-resolved micrographs of two Ru compound particles; the 2.3 Å *d* spacing indicates the (100) plane of metallic Ru crystal.^[48,49]

Thanks to the plasma treatment, Ru-Plasma has a highly uniform particle-size distribution. Figure 2d,e shows that nearly all of the Ru nanoparticles have dimensions between 1 and 2 nm. In contrast, the Ru particle-size distribution in commercial Ru-Conv is much wider (see Figure 2f,g). There are many too-small (< 1 nm, blue arrow) and too-large (> 5 nm, yellow arrow) Ru nanoparticles that reduce performance (more TEM results of Ru-Plasma are included in the Supporting Information). This confirms the hypothesis of sintering by Ostwald ripening: the small particles become even smaller as the big ones grow bigger, a “big-fish-eat-small-fish” effect.^[12] In addition, Ru-Plasma has a higher specific surface area ($1298 \text{ m}^2 \text{ g}^{-1}$) than Ru-Conv ($713 \text{ m}^2 \text{ g}^{-1}$) according to standard N_2 adsorption measurements, due to its finer nanostructure.

Ru-Plasma showed excellent activity and stability in a number of chemical and electrochemical reactions. We initially performed organosilane oxidation to organosilanol by using water as an oxidant under ambient conditions (see Scheme 1 and Table 1). Our catalyst produced organosilanols selectively. H_2 gas was the sole byproduct, and no disiloxanes were observed, unlike conventional approaches.^[31–38,50–53] The reported reactions were conducted at high temperature and/or under an O_2 atmosphere, and the turnover number (TON) was not usually higher than 20.^[32,36] With dimethylphenylsilane as the model substrate, our Ru-Plasma catalyst showed a turnover frequency (TOF) of 29 min^{-1} at room temperature. Conversely, Ru-Conv showed a TOF of only 6 min^{-1} (see Table 1, entry 4), which reflects the presence of less-active sites. At 40°C , the TOF increased to 44 min^{-1} with the Ru-Plasma catalyst, even though we doubled the silane/Ru molar ratio to 2637 (Table 1,

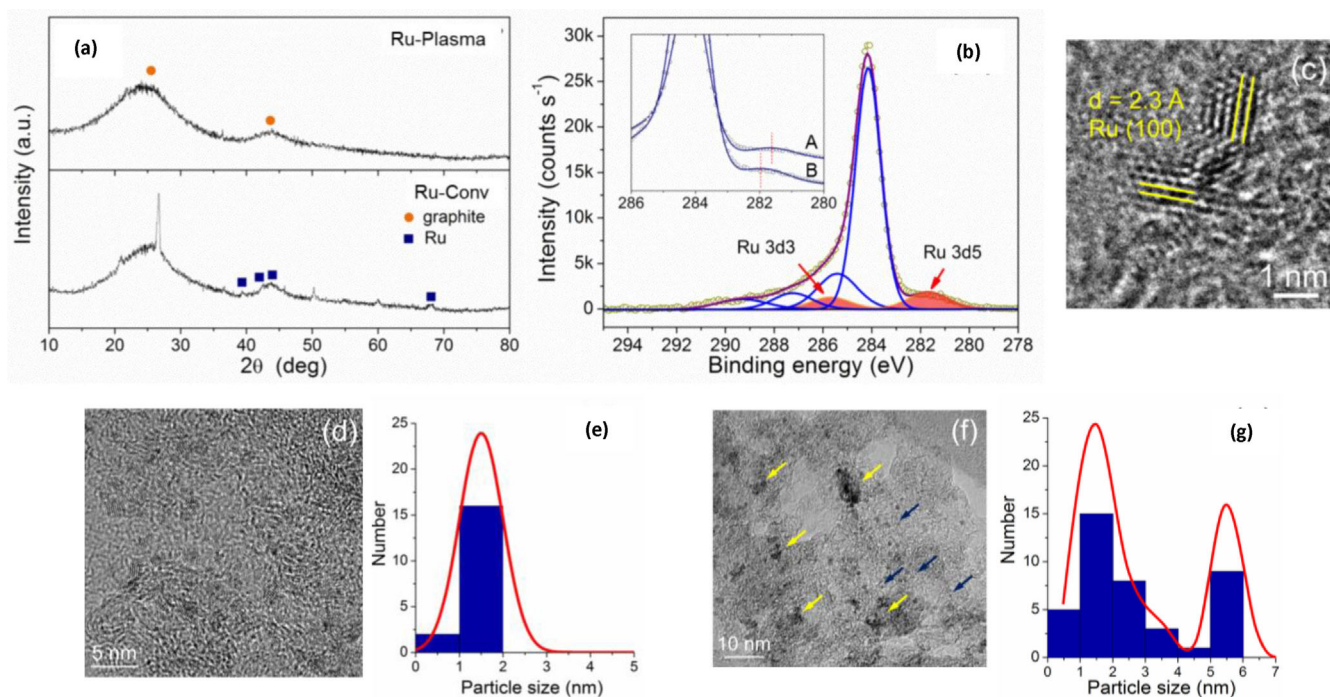


Figure 2. a) XRD patterns of Ru-Plasma and Ru-Conv. b) Deconvoluted X-ray photoelectron spectra of the C 1s and Ru 3d core levels. A and B in the inset compare the fitted envelopes in the region of Ru 3d₅ for Ru-Plasma before and after plasma treatment. c) HRTEM micrograph of Ru nanoparticles on carbon. TEM images of the d) Ru-Plasma and f) Ru-Conv catalysts and e, g) the corresponding particle-size distribution plots.

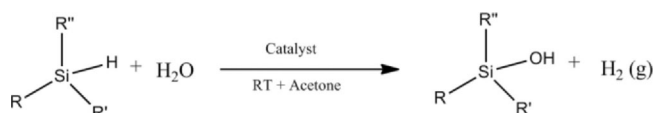
**1a** R, R' = CH₃, R'' = C₆H₅**1d** R = H, R' = CH₃, R'' = C₆H₅**1b** R, R' = C₆H₅**1e** R, R', R'' = C₂H₅**1c** R, R' = C₆H₅, R'' = CH₃**1f** R = H, R', R'' = C₆H₅**Scheme 1.** Oxidation of organosilane to silanol with water by using supported Ru catalysts.

Table 1. Organosilane oxidation to silanol by using supported Ru catalysts. ^[a]						
Entry	Catalyst	Substrate	Conv. [%]	T [min]	TON	TOF [min ⁻¹]
1	Ru-Plasma	Me ₂ PhSiH (1a)	> 99	45	1318	29
2	Ru-Plasma	Me ₂ PhSiH (1a)	> 99 ^[b]	60	2637	44
3	Ru-Plasma	Me ₂ PhSiH (1a)	> 99 ^[b]	140	5274	38
4	Ru-Conv	Me ₂ PhSiH (1a)	> 99	210	1318	6
5	Ru-Plasma	Ph ₃ SiH (1b)	> 99	30	500	17
6	Ru-Plasma	MePh ₂ SiH (1c)	> 99	50	500	10
7	Ru-Plasma	PhMeSiH ₂ (1d)	> 99	25	500	20
8	Ru-Plasma	Et ₃ SiH (1e)	> 99	20	500	25
9	Ru-Plasma	Ph ₂ SiH ₂ (1f)	> 99	35	500	14.3
10	none	Me ₂ PhSiH (1a)	0	180	100	0

[a] Reaction conditions: catalyst (25 mg), H₂O (2 mL, as oxidant), acetone (5 mL), 25 °C. [b] Reaction was performed at 40 °C.

entry 2). The reaction proceeded to complete conversion even at a higher silane/Ru ratio of 5274 with a TOF of 37.7 min⁻¹ (Table 1, entry 3).

Ru-Plasma was also active for the oxidation of other organosilanes (Table 1, entries 5–9). Control experiments confirmed that no reaction took place in the absence of the catalyst or only with the carbon support. The selectivity to silanol was > 99%. No disiloxane was detected, ruling out silanol condensation. Interestingly, the spent Ru-Plasma catalyst retained high activity and selectivity after three consecutive runs, indicating its stability (see the TEM image of the spent catalyst in the Supporting Information). We then prepared titania-supported Ru catalysts by the same synthesis route. These also had monodispersed Ru nanoparticles and showed excellent activity in organosilane oxidation reactions (see the Supporting Information for details), which suggests good support compatibility of the new synthesis approach.

A new catalyst synthesis protocol is much more useful if it can be applied to different reaction scenarios. We therefore examined the performance of the Ru-Plasma catalyst in the electrochemical oxygen evolution reaction. However, the “too-small” Ru nanoparticles corroded if the OER potential was applied (RuO₄²⁻ was soluble in the reaction medium).^[42,54] Thus, careful control of the nanostructure of the catalyst is important. Figure S6 shows the cyclic voltammetry (CV) curve of Ru-Plasma in 0.05 M deoxygenated H₂SO₄. The redox peaks were

attributed to the hydrolysis of Ru [Eq. (1)],^[55] in agreement with the formation of metallic Ru after plasma treatment.



Figure 3 shows the 20 cycle CV curves of Ru-Plasma and Ru-Conv in oxygen-saturated electrolyte from 0.8 to 1.58 V versus the reversible hydrogen electrode (RHE) (overpotential, $\eta = 0.3$ V). Apparently, Ru-Conv suffered instant oxidation at approximately 1.51 V versus RHE in the first cycle (see the anodic

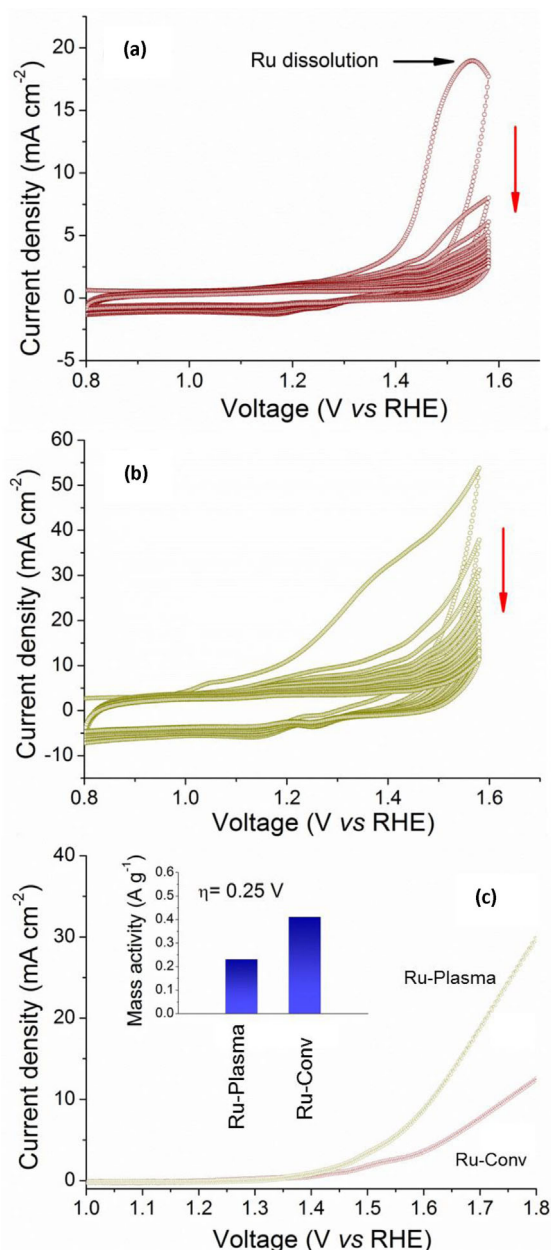


Figure 3. 20 cycle CV plots of the a) Ru-Conv and b) Ru-Plasma catalysts in O₂-saturated 0.05 M H₂SO₄ from 0.8 to 1.58 V vs. RHE. c) A comparison of the OER LSV curves for the Ru-Conv and Ru-Plasma catalysts after CV cycling. The scan rate was 10 mV s⁻¹, the rotating speed of the rotating disc electrode was 1600 rpm, and *iR* correction was applied; the inset shows the mass activity of both catalysts at $\eta = 0.25$ V.

peak indicated by the arrow), which has been widely documented as the sequence of Ru-nanoparticle dissolution.^[42,54] A large portion of Ru nanoparticles in Ru-Conv was less than 1 nm in size (see Figure 2) and was inherently more susceptible to deep oxidation to form soluble RuO_4^{2-} species.^[42,54] Conversely, this was not observed on Ru-Plasma; gradual current degradation was owing to the accumulation of oxygen bubbles that blocked the working electrode. We then ran linear sweep voltammetry (LSV) while rotating the electrode at a scan rate of 10 mV s^{-1} to study the OER activity as well as the stability of both catalysts (see Figure 3c). The OER onset potentials were essentially identical for both catalysts, as RuO_2 itself is an excellent OER catalyst. At $\eta = 0.25 \text{ V}$, the mass activity of Ru-Plasma reached 0.41 Ag^{-1} , which was nearly double that of Ru-Conv and better than that of most 5 wt% Ru catalysts previously reported.^[43] Though oxygen bubbles were removed, the Ru-Conv catalyst showed more significant performance loss than the Ru-Plasma catalyst. These observations reflect the good structural stability of Ru-Plasma, which can sustain more Ru nanoparticles (active sites) than Ru-Conv after applying OER potentials. A broad peak at approximately 1.54 V in the LSV curve of the Ru-Conv sample might be related to the oxidation of Ru nanoparticles. We also performed several cycles of LSV for the Ru-Plasma catalyst, which showed reproducibility and thus stability (see the Supporting Information).

In summary, our results show that plasma treatment effectively decomposes RuCl_3 to Ru nanoparticles under near-ambient conditions. The resulting metal particles on both carbon and TiO_2 supports were ultrafine and monodispersed. In particular, the Ru-Plasma catalyst demonstrated significantly higher activity and stability in both organosilane oxidation and the oxygen evolution reaction than the catalyst made by the conventional method. As we showed, the method could be applied successfully for multiple supports, indicating its general use.

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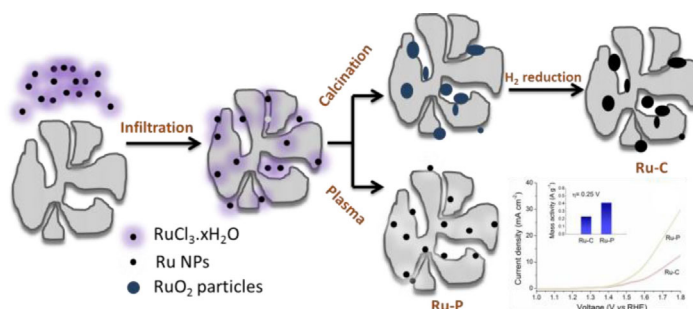
COMMUNICATIONS

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Out in the cold: Supported ruthenium catalysts prepared by a novel cold plasma-assisted approach show excel-

lent activity in two representative yet different reactions: organosilane oxidation and oxygen evolution.