

Supporting Information

Nanostructured Trimetallic Pt/FeRuC, Pt/NiRuC, and Pt/CoRuC

Catalysts for Methanol Electrooxidation

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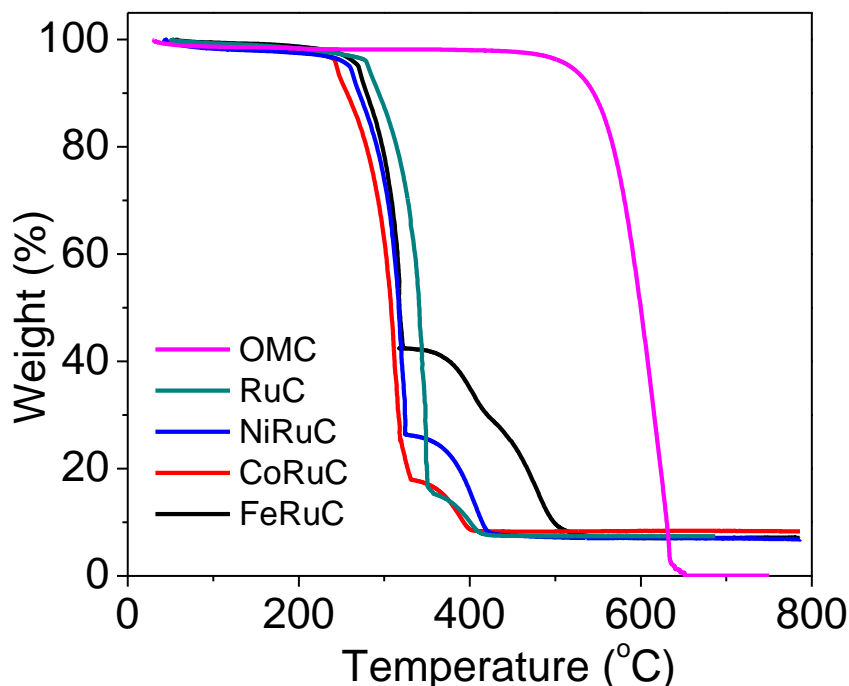


Figure S1. TG curves of all the supports.

Figure S1 shows the TG plots of all the supports. It is seen that complete combustion of supports containing Ru for FeRuC, CoRuC, NiRuC, and RuC mainly took place in the temperature range of 240–500 °C. The residual weight for FeRuC, CoRuC, NiRuC, and RuC is 7.1, 8.3, 7.2, and 7.5 wt%, respectively. The major weight loss for OMC occurs in the temperature range from 500 to 650°C and its residue is negligible, suggesting the complete removal of silica template using our method. The lower temperature range of weight loss for Ru-containing supports compared to OMC is due to the catalytic oxidation effect of metal species.¹ The detection of these supports with ICP method found that metal content is 7.0 wt% Ru for RuC, 3.0 wt% Fe and 3.5 wt% Ru for FeRuC, 3.8 wt% Co and 3.6 wt% Ru for CoRuC, and 3.5 wt% Ni and 3.4 wt % Ru for NiRuC, revealing that the total metal loading for these supports is within the similar level (6.5–7.4 wt%).

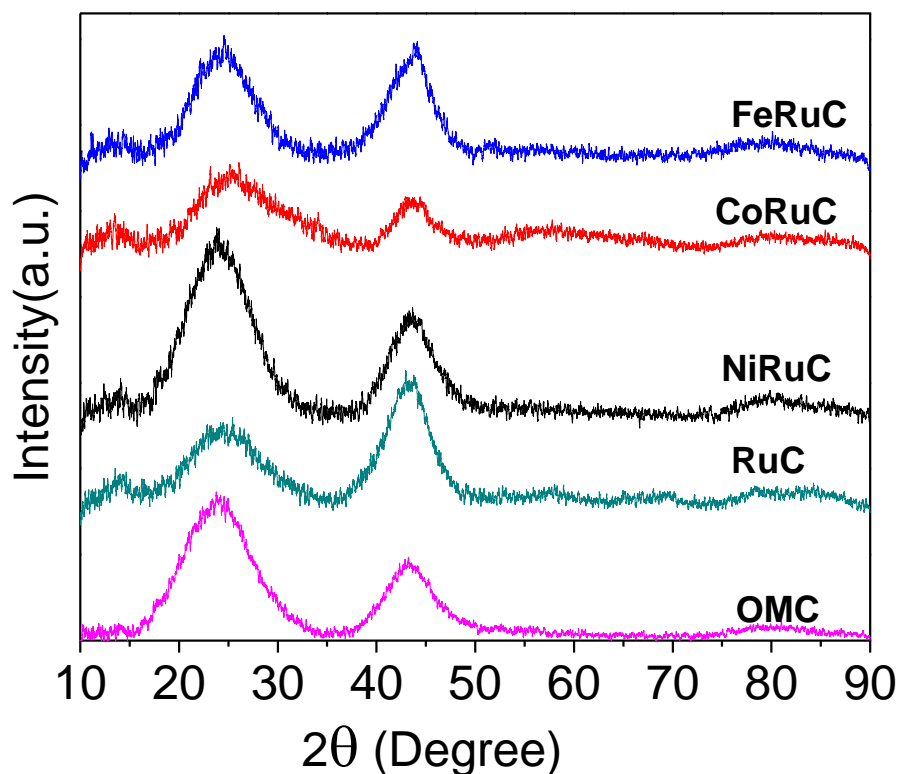
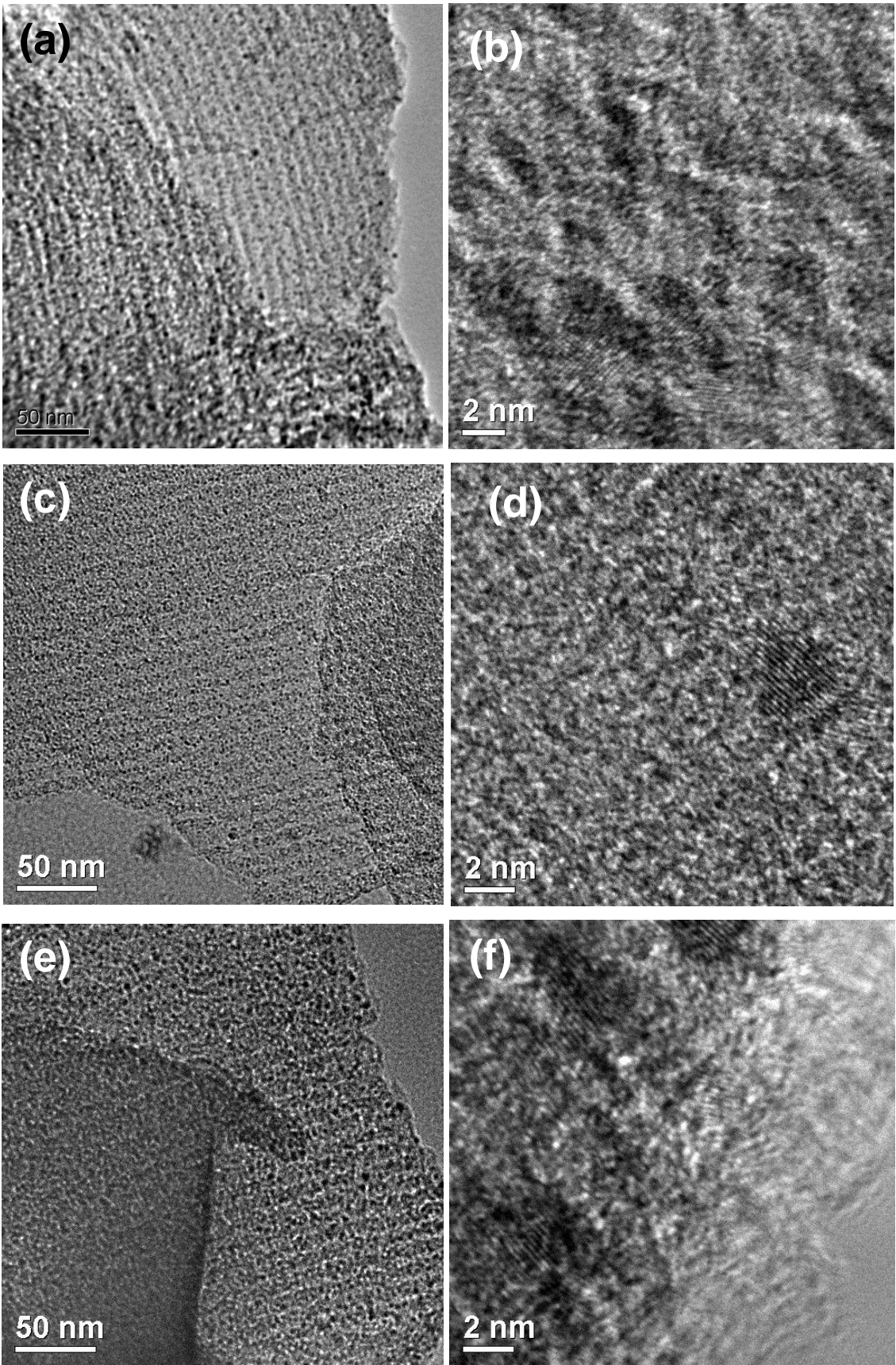


Figure S2. XRD patterns of all supports.

Figure S2 presents the XRD patterns of all the support materials. Two diffraction peaks located at around 25.4 and 43.5° , corresponding to (002) and (101) diffractions of carbon, can be observed for all samples. For OMC, the intensity of first peak is much larger than that of second peak, an indicative of a common characteristic of carbon materials. There are no visible peaks for the presence of Fe, Co, and Ni species, indicating that these metal nanoparticles are too small to be detected with XRD (see below TEM images). For RuC support, the higher intensity of the peak at around 43.5° than that at about 25.4° indicates the presence of Ru due to the overlapping of the (101) diffraction peak of pure carbon with the peak of (101) diffraction of hexagonal Ru metal (ICDD-JCPDS Card No. 06-0663), which is located at around 43.8° . It has been known that Ru species can be thermally reduced by carbon at high temperature.¹ Therefore, we may infer that the metals present in the supports existed in the metallic form, especially for Ru, although it is hard to know whether the metals are alloyed.



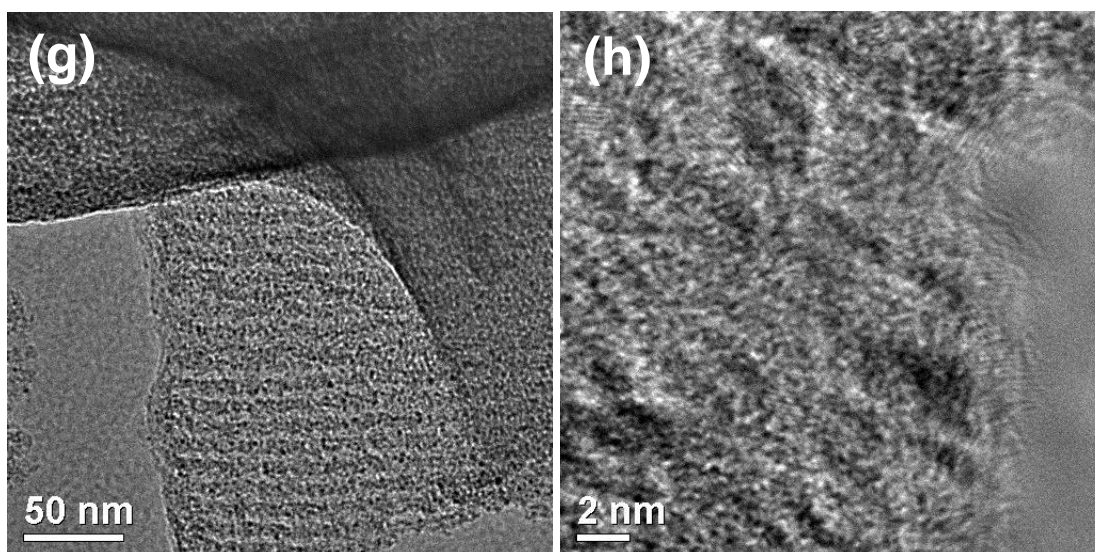


Figure S3. TEM images of RuC (a and b), FeRuC (c and d), CoRuC (e and f), and NiRuC (g and h).

Figure S3 shows the TEM images of all the metal-containing supports. TEM image of FeRuC sample in Figure S3a is taken along [001] directions for better observation, showing highly ordered structure with an interplanar distance of around 10 nm, consistent with previous reports.²⁻⁴ The small black dots indicate the presence of metal nanoparticles with a size of around 2–3 nm, which are highly dispersed within the carbon matrix. Figure S3b shows its HRTEM image, in which, the crystal lattice of a metal nanoparticle can be clearly seen and the particles size is about 2–3 nm. The similar ordered pore structure and metal nanoparticle morphology can be seen for CoRuC (Figures S3c and S3d), NiRuC (Figures S3e and S3f), and RuC (Figures S3g and S3h). It can be concluded that all the metal nanoparticles are deposited into the carbon support matrix not in pore channels, which are accessible for deposition of Pt nanoparticles.

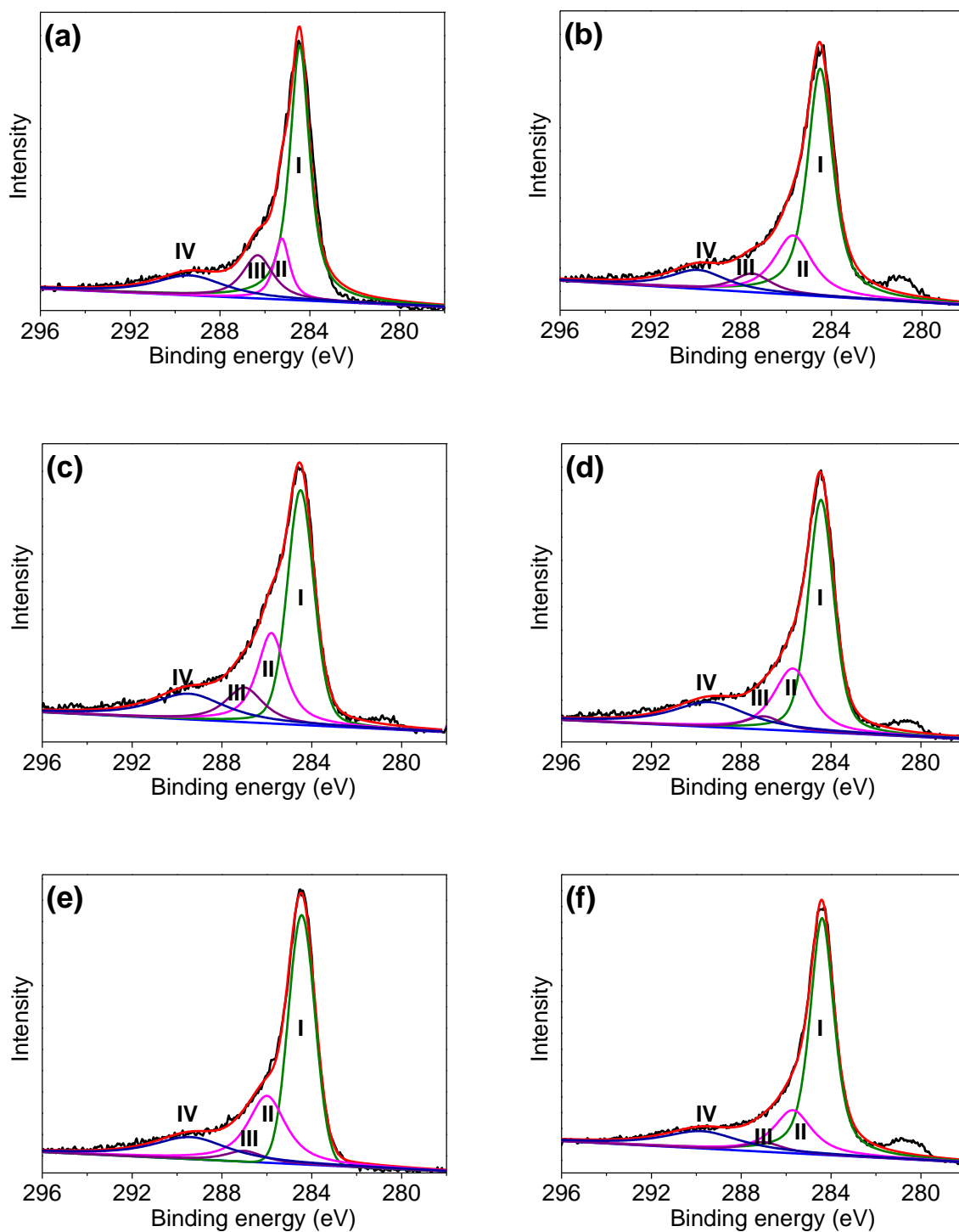


Figure S4. XPS survey spectra of the C1s: (a) Pt/FeRuC, (b) Pt/CoRuC, (c) PtNiRuC, (d) PtRuC, (e) Pt/OMC, and (f) JM.

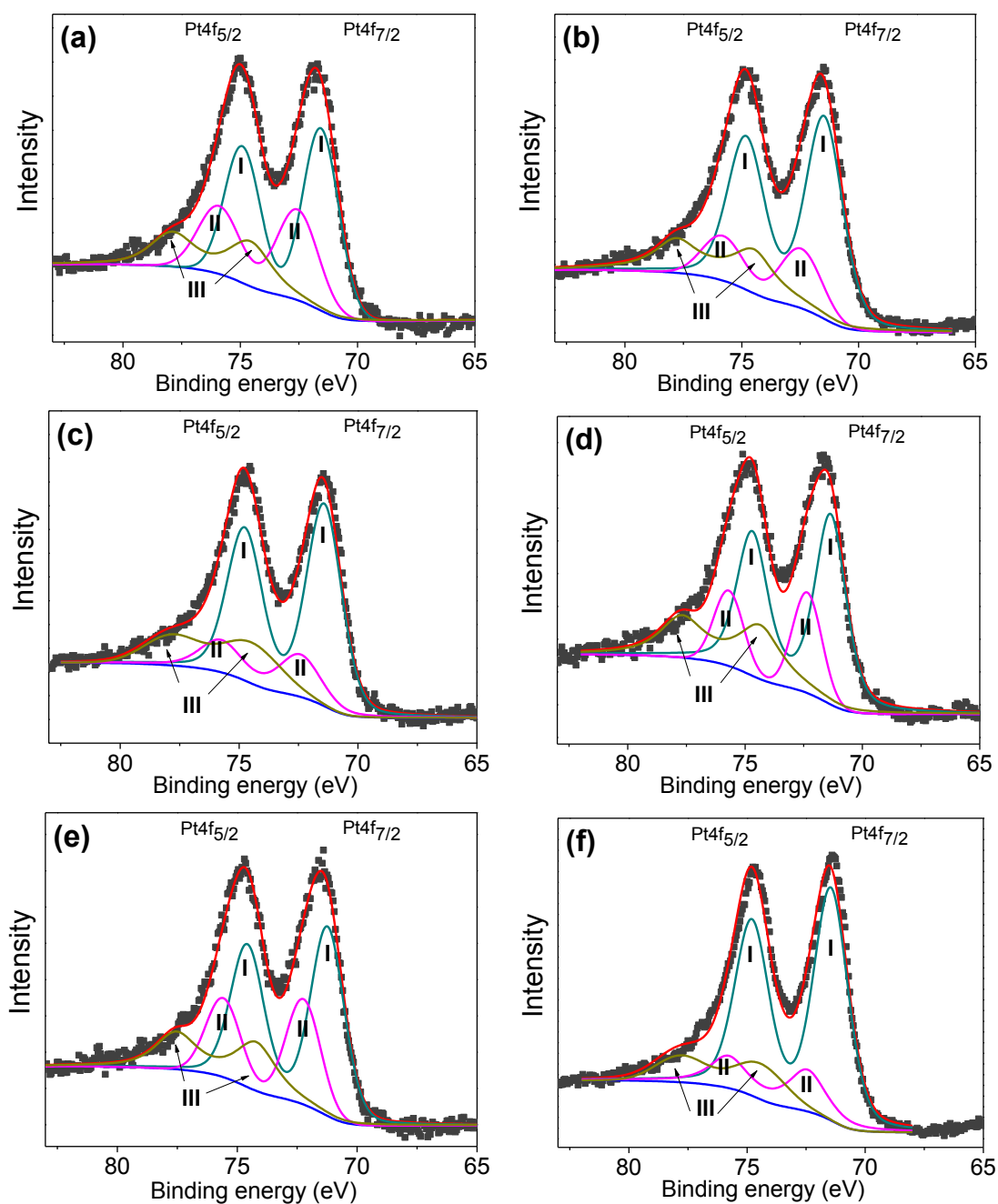


Figure S5. XPS survey spectra of the Pt4f: (a) Pt/FeRuC, (b) Pt/CoRuC, (c) PtNiRuC, (d) PtRuC, (e) Pt/OMC, and (f) JM.

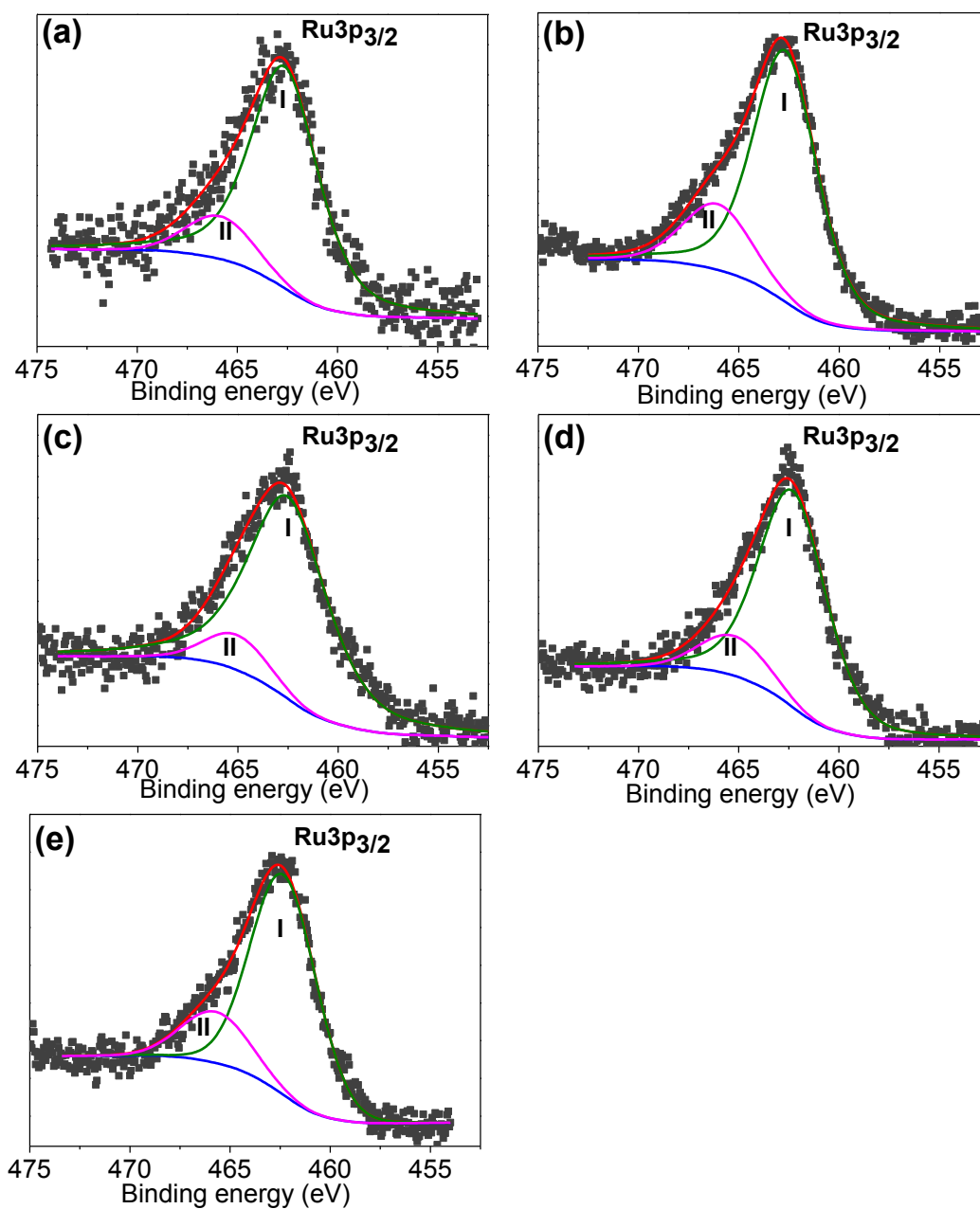


Figure S6. XPS survey spectra of the Ru3p: (a) Pt/FeRuC, (b) Pt/CoRuC, (c) PtNiRuC, (d) PtRuC, and (e) JM.

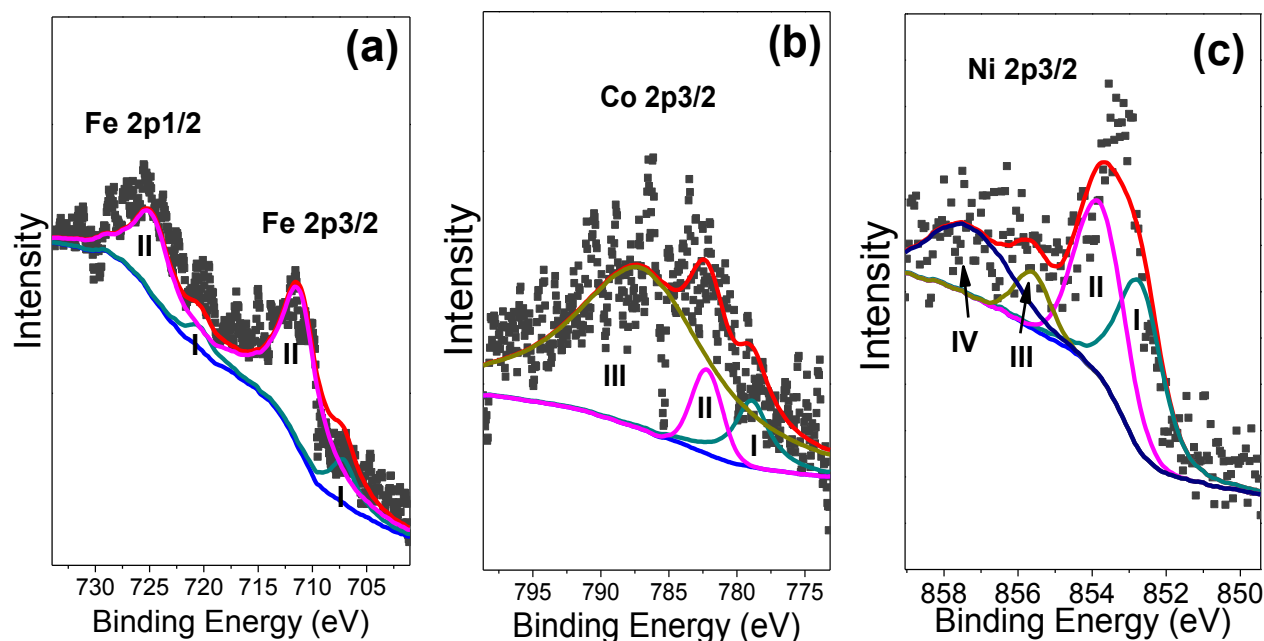


Figure S7. XPS survey spectra of the elements on the Pt catalysts: (a) Fe 2p of Pt/FeRuC, (b) Co 2p_{3/2} of Pt/CoRuC, (c) Ni 2p_{3/2} of Pt/NiRuC.

Figure S7a shows the XPS spectrum of Fe 2p_{3/2} and Fe 2p_{1/2} for Pt/FeRuC. The spectrum was deconvoluted into two pairs of doublets at 707.1 and 720.3 eV which is labeled as I and 711.2 and 724.8 eV which is labeled as II. The two doublets I and II corresponding well to metallic iron and iron oxides (Fe²⁺/Fe³⁺), respectively.⁵ The Co 2p_{3/2} spectrum (Figure S7b) of Pt/CoRuC catalyst shows the presence of Co species with metallic Co⁰, Co²⁺ and Co³⁺ oxides with the binding energies of 778.9, 782.2 and 787 eV, respectively.^{6,7} The deconvoluted peaks for Co⁰, Co²⁺ and Co³⁺ are labeled as I, II and III in Figure S7b. For Pt/NiRuC catalyst, the Ni 2p_{3/2} spectrum (Figure S7c) shows the presence of Ni species in the 850–860 eV range. Ni 2p_{3/2} was found to be consisted of four component peaks at 852.7, 853.8, 855.6 and 857.3 eV which correspond to metallic Ni (peak I), NiO (peak II), Ni(OH)₂ (peak III) and NiOOH (peak IV) respectively.^{8,9}

References

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