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High-performance water oxidation catalysts based on the spontaneous deposition of ruthenium on electrochemically exfoliated graphene oxide

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Experimental

Chemicals

Sulfuric acid, oxalic acid, phosphoric acid, ruthenium (III) chloride monohydrate, isopropyl alcohol, and potassium hydroxide were purchased from Sigma Aldrich. Potassium perruthenate(VII) and graphite rods (6.3mm diameter and 61 cm long) were purchased from Alfa Aesar. Nafion® was purchased from Ion Power Inc. TPG-H-090 Toray Paper 30% Wet Proofing Carbon fibre paper was purchased from Fuel Cell Earth LLC.

Catalyst Synthesis

Electrochemical graphene oxide was synthesized via a previously published procedure[1]. The synthesis of the modified EGO with ruthenium was adapted from literature procedures[2, 3]. Briefly, electrochemically synthesized graphene oxide (EGO), and the desired ruthenium salt (Ru^{3+} or Ru^{7+}) were added to a reaction vessel in the presence of 1M KOH. The amounts of material added afforded a targeted 5% metal loading on the EGO. The reaction was stirred under ambient conditions for 4 days. When the reaction was complete the Ru@EGO materials were centrifuged and washed with water, then aged in N_2 purged water for 1 week. After the aging procedure the samples were placed in an oven at ~70°C to dry.

Physical Characterization

Catalysts were characterized by a HITACHI FlexSEM 1000 scanning electron microscope equipped with Energy dispersive spectroscopy (EDS) analysis probe. EDS showed about 3% Ru deposited on EGO, which gives about 60% efficiency for the spontaneous reaction. TEM measurements were performed on a Zeiss Libra 200MC transmission electron microscope system operating at 200 keV using a slit width of 10 eV and a spot size of 1 nm. ImageJ software was used to calculate the particle size distribution. XPS measurements were performed on a Thermo Scientific K-Alpha Angle-Resolved X-ray photoelectron spectrometer with a monochromated Al Kα (1486.7eV) X-ray source and 180° double focusing hemispherical analyzer with 128 channel detector with charge compensation. A Shirley fit algorithm was used for the background subtraction and a Powell peak-fitting algorithm was utilized for the data analysis. Pore size analysis was performed on a Quantachrome NOVAe 1200 analyzer. Thermogravimetric analysis was performed on a TA insurements Q600 SDT thermal analyzer. The samples were ran in an air atmosphere at 10 mL min^{-1} with a ramp rate of 5°C min^{-1}. Raman Spectra were obtained using a Renishaw in Via onfocal Raman Microscope with a Renishaw Centrus OMCN39 CCD detector. Excitation wavelength of the Nd:YAG laser (Renishaw) was 532nm with a power output of 50 mW. Spectra were acquired by performing a scan from 100-4000 cm^{-1} with an exposure time of 30 seconds per scan, a laser power of 1% and at 50x objective. X-Ray diffraction was measured using a Rigaku Ultima IV with Cu Kα radiation. Patterns were recorded over the 20-90° 2θ range with a step size of 0.02°. HRTEM Electron microscopy was performed at the Canadian Centre for Electron Microscopy (also supported by NSERC and other government agencies).

Electrochemical Characterization

The water oxidation reaction was studied using a carbon fibre paper electrode in 0.5 M H_2SO_4. Catalyst inks were made by sonicating 10 mg of catalyst, 200 μL deionized water, 200 μL isopropyl alcohol, and 100 μL Nafion®. 10 μL of the catalyst was dropped onto a piece of carbon fiber paper and dried with heat (200 μg cm^{-2} catalyst loading). A mercury/mercury sulfate reference electrode was used and a graphite rod was used as a counter electrode. The electrochemical measurements were performed using a Solartron Analytical 1470E potentiostat connected to a Solartron SI 1260 impedance/gain-phase analyzer with corresponding Multistat and Zplot software.

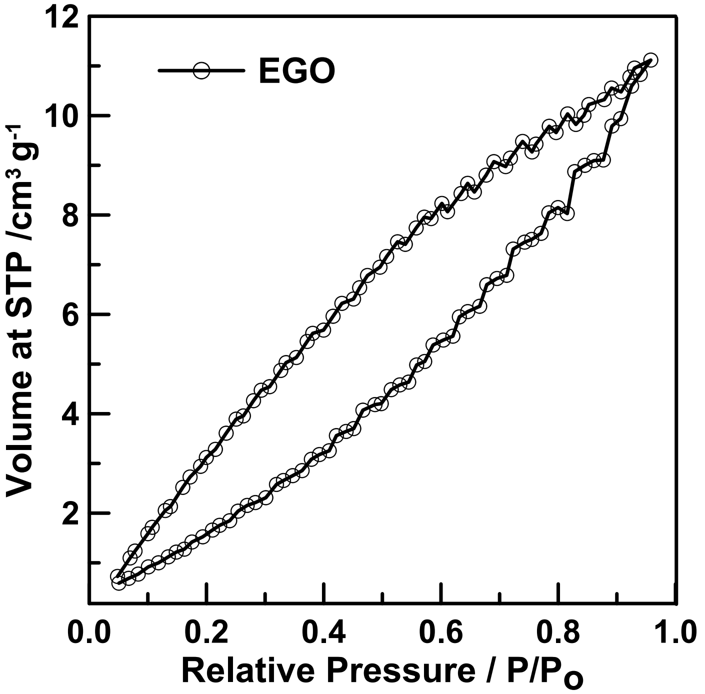

Figure S1. BET analysis of EGO with N_2 as the adsorbate.

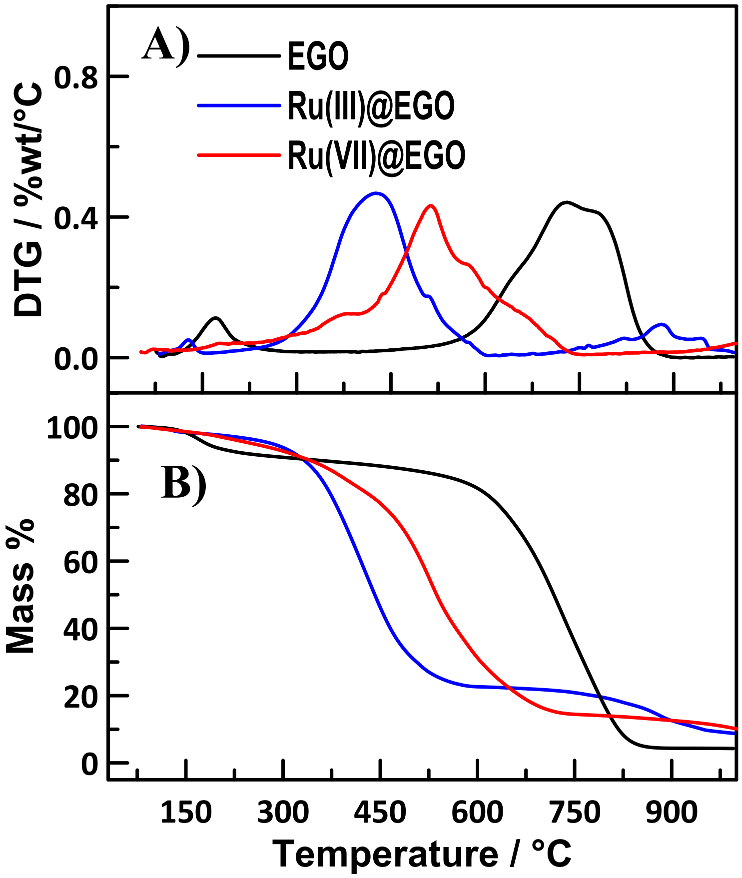

Figure S2. A) Differential thermogram of the synthesized materials in an air atmosphere at 10^{o}C min^{-1}. **B)** Thermogravimetry of the materials in an air atmosphere at 10^{o}C min^{-1}.

TGA results show for the EGO sample a mass loss at 150°C due to the removal of oxygen functional groups on the carbon. The combustion temperatures lower upon addition of the Ru metal. Metals in the presence of carbon can be combustion catalysts thus why the combustion temperature is lowered in the presence of Ru.

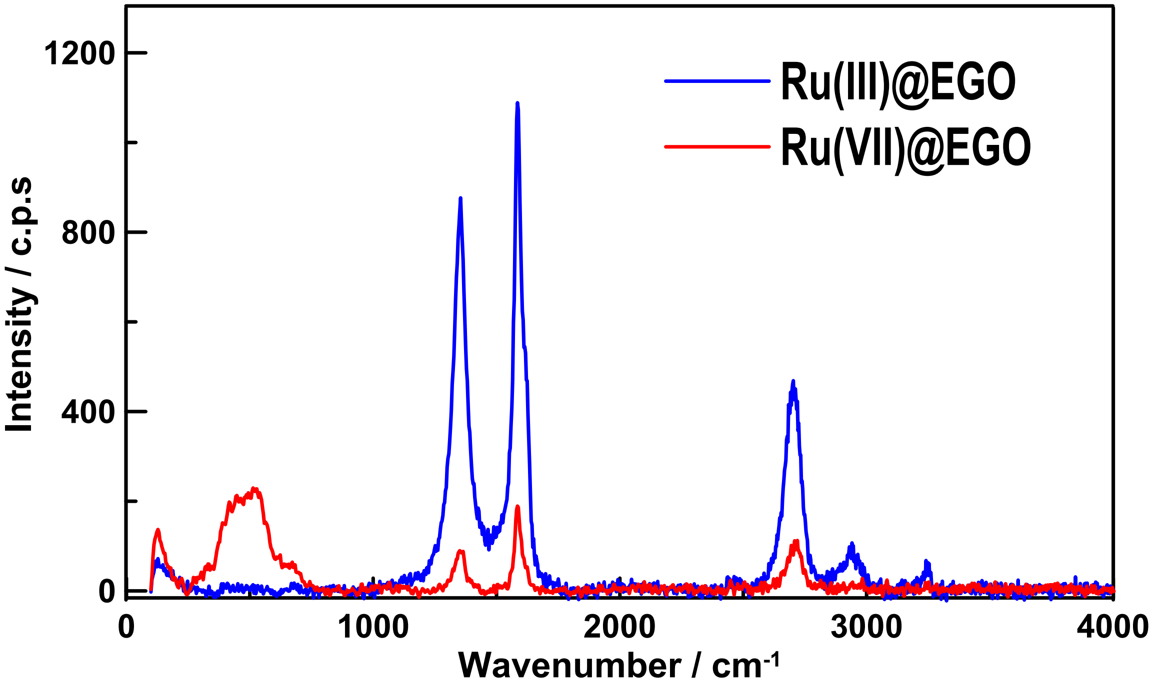

Figure S3. Raman spectra of the synthesized materials.

Raman peaks from the EGO are present in all cases (1500 cm^{-1}, 1300 cm^{-1}, and 2700 cm^{-1}). The broad peak present at 520 cm^{-1} is due to RuOx on the surface[4].

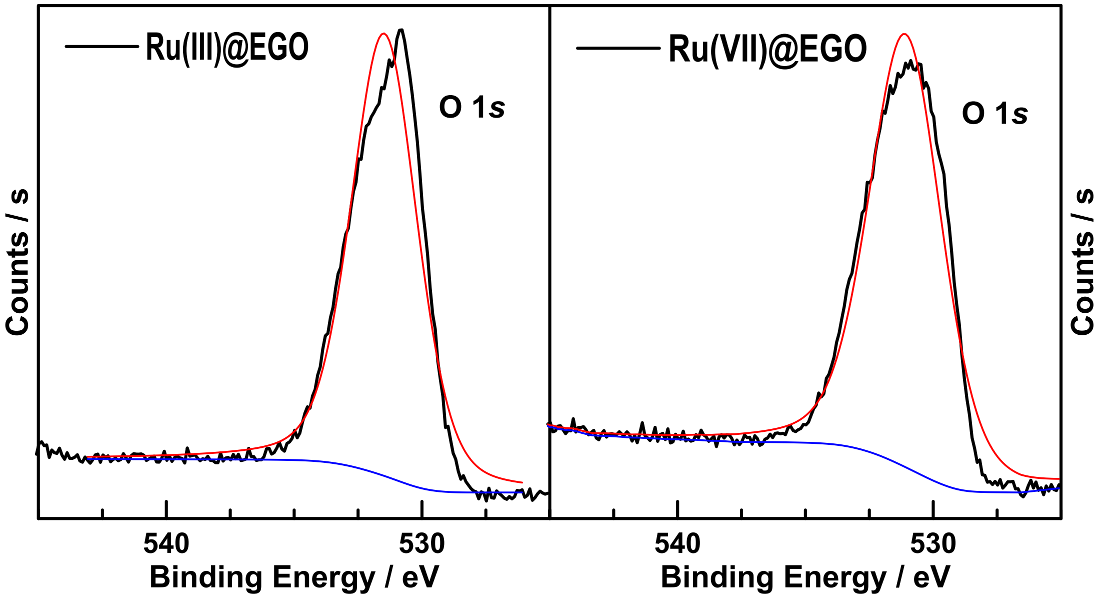

Figure S4. XPS O 1*s* spectra of the Ru(III)@EGO and Ru(VII)@EGO before testing. Red line corresponds to the O 1*s*.

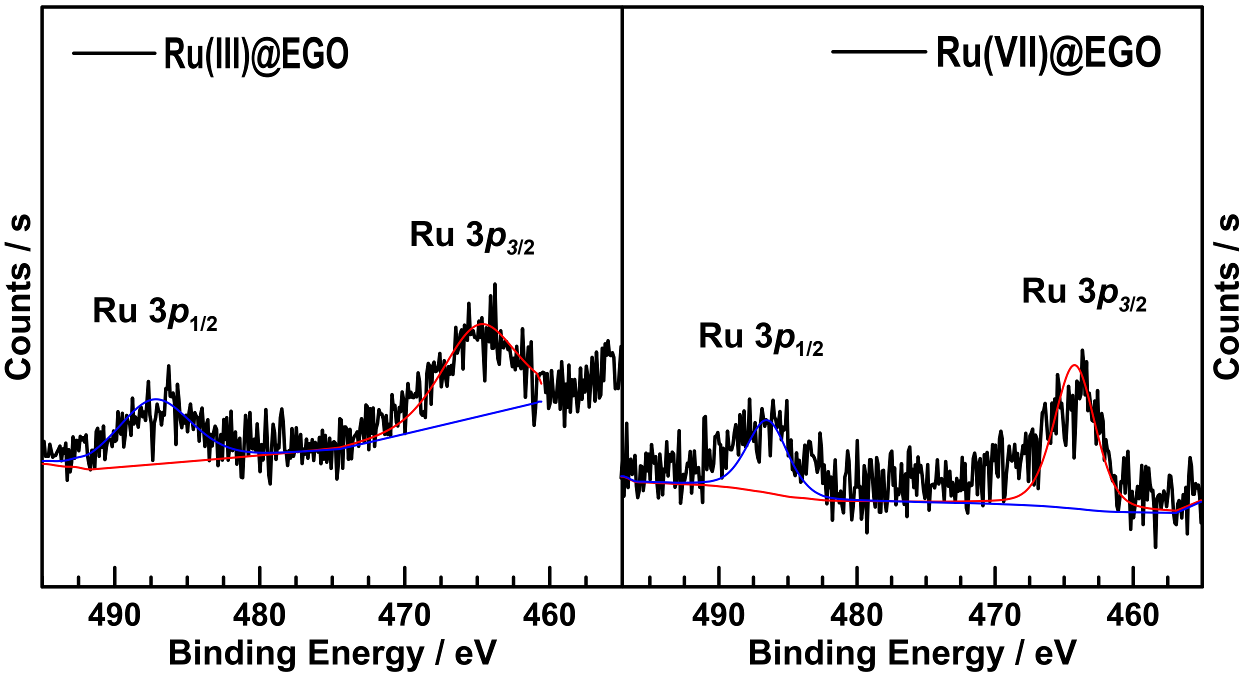

Figure S5. XPS spectra of the Ru 3*p* Ru(III)@EGO and Ru(VII)@EGO after WOR testing. Red line corresponds to the Ru $3p_{3/2}$, Blue line corresponds to Ru $3p_{1/2}$

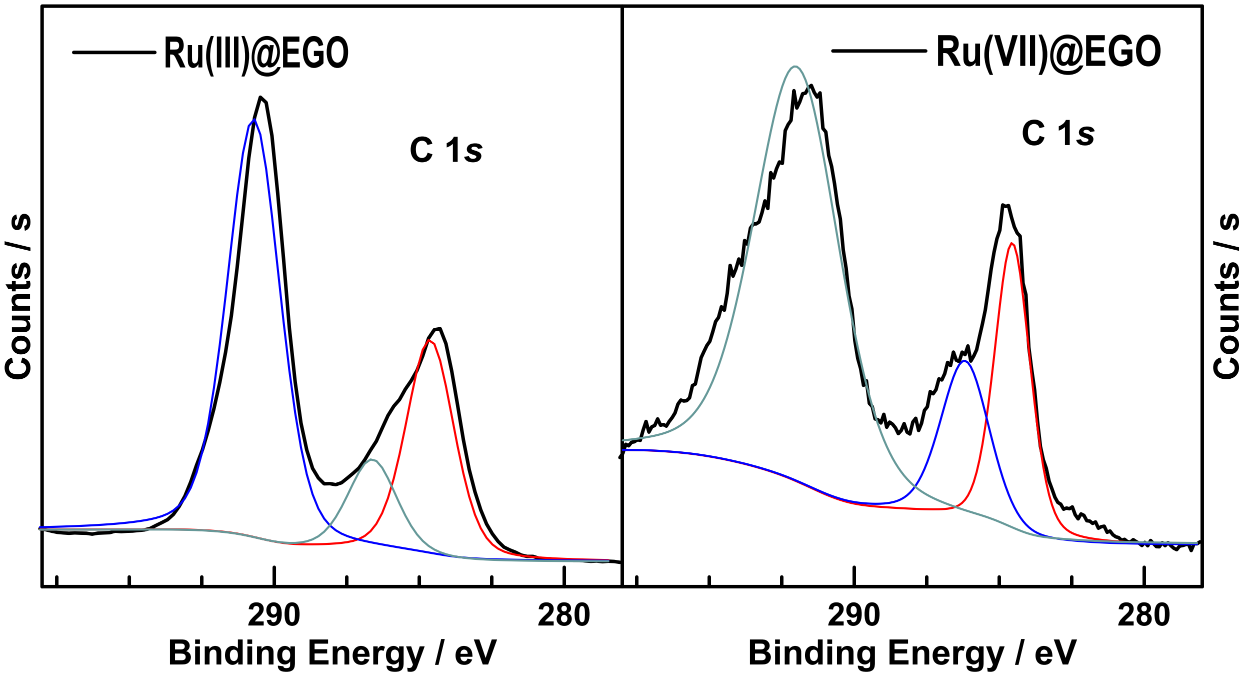

Figure S6. XPS spectra of the C 1*s* Ru(III)@EGO and Ru(VII)@EGO after WOR testing.

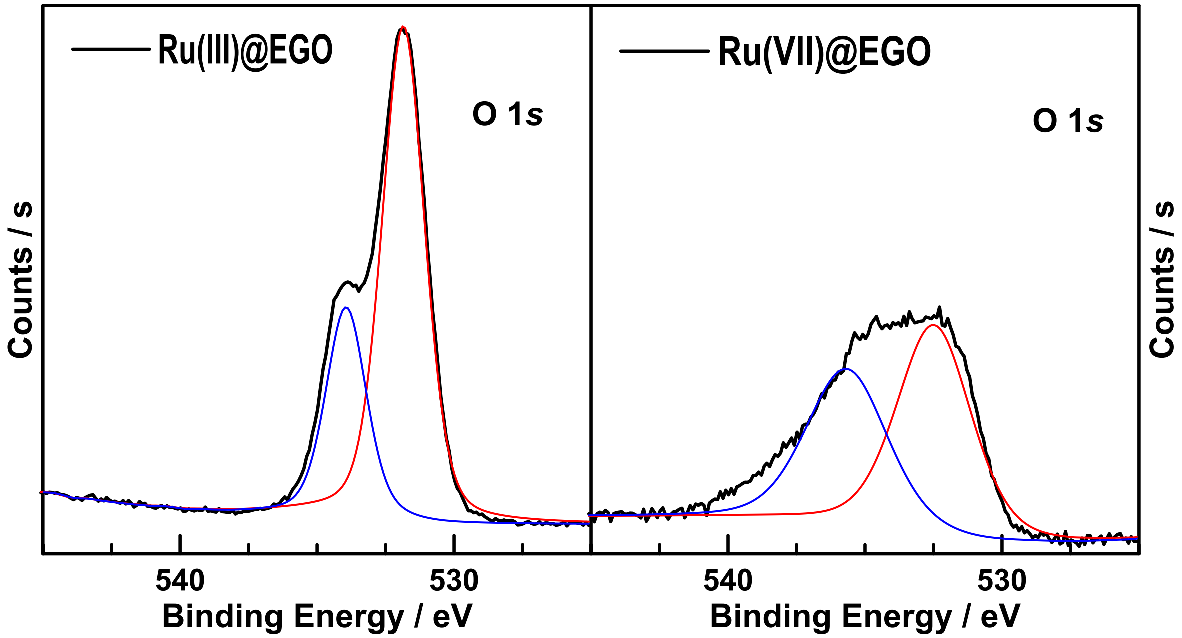

Figure S7. XPS O 1*s* spectra of the Ru(III)@EGO and Ru(VII)@EGO before testing. Red line corresponds to the O 1*s*.

Before WOR testing on the materials the Ru species present as indicated by XPS is RuO_2 at 529.3 eV, this is characteristic of RuO_2[5, 6]. In the Ru 3*p* spectra the peak at 463.68 eV is also indicative of RuO_2 species present on the surface. After testing for over 24 hours, the C 1*s* for both Ru(III)@EGO and Ru(VII)@EGO show signs of the substrate oxidizing over the course of the constant testing. It is also clear from the Ru 3*p* spectra after the 24 hours of testing that some Ru is leaching from both samples, however from both this spectra and the O 1*s* after the fact that the dominate species present is still RuO_2. The peak at 535 eV in the O 1*s* spectra is due to oxygen groups in the Nafion® ionomer used in the test.

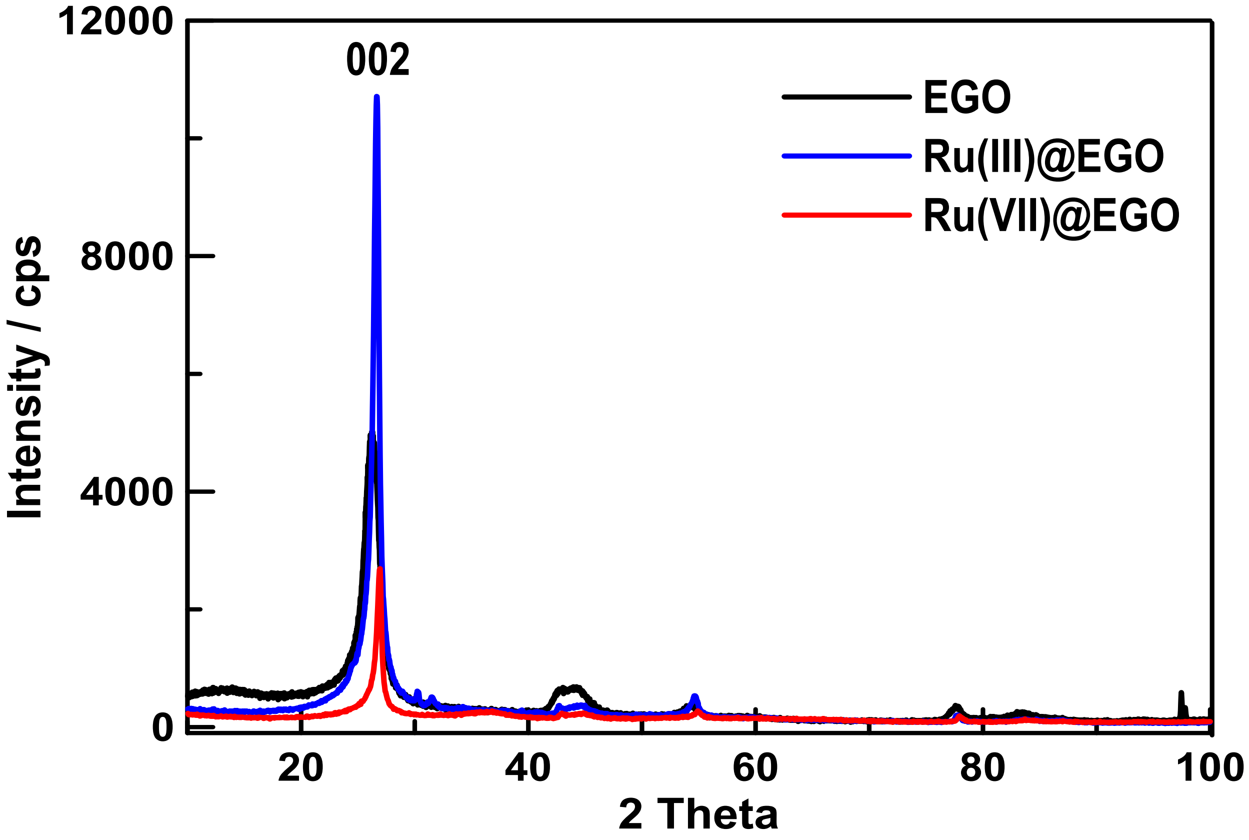

Figure S8. XRD spectra of the synthesized Ru(III)@EGO and Ru(VII)@EGO.

Based on the TEM analysis and particle size distributions of the Ru materials it is clear that the Ru is amorphous and thus makes characterization with XRD challenging. However, the peak at 26° for the Ru(VII)@EGO sample has greatly decreased which could be an indication that the Ru(VII)@EGO is more oxidized than the Ru(III)@EGO sample[7].

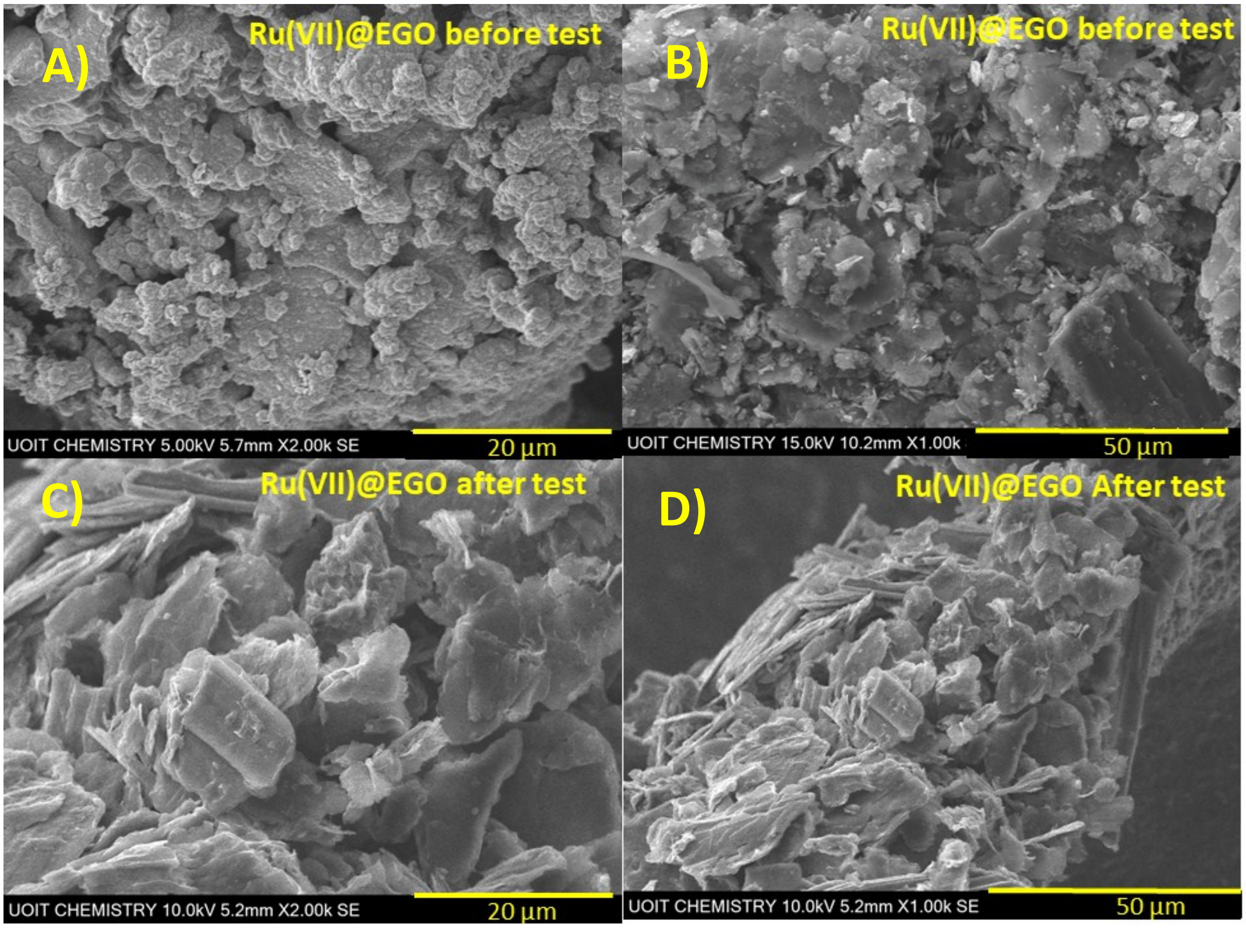

Figure S9. SEM images of **A-B)** Ru(VII)@EGO sample before WOR testing and **C-D)** after WOR testing.

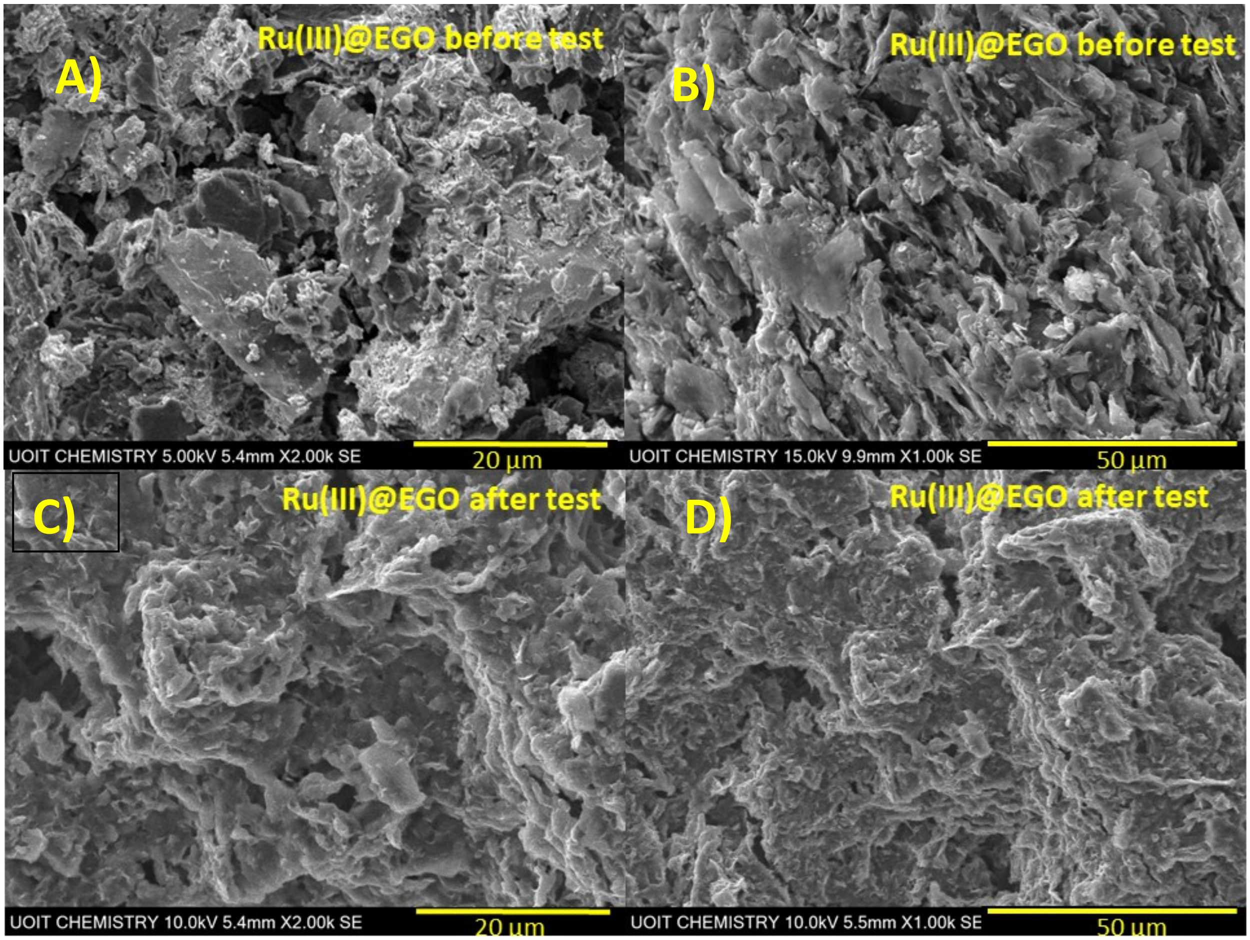

Figure S10. SEM images of **A-B)** Ru(III)@EGO sample before WOR testing and **C-D)** after WOR testing.

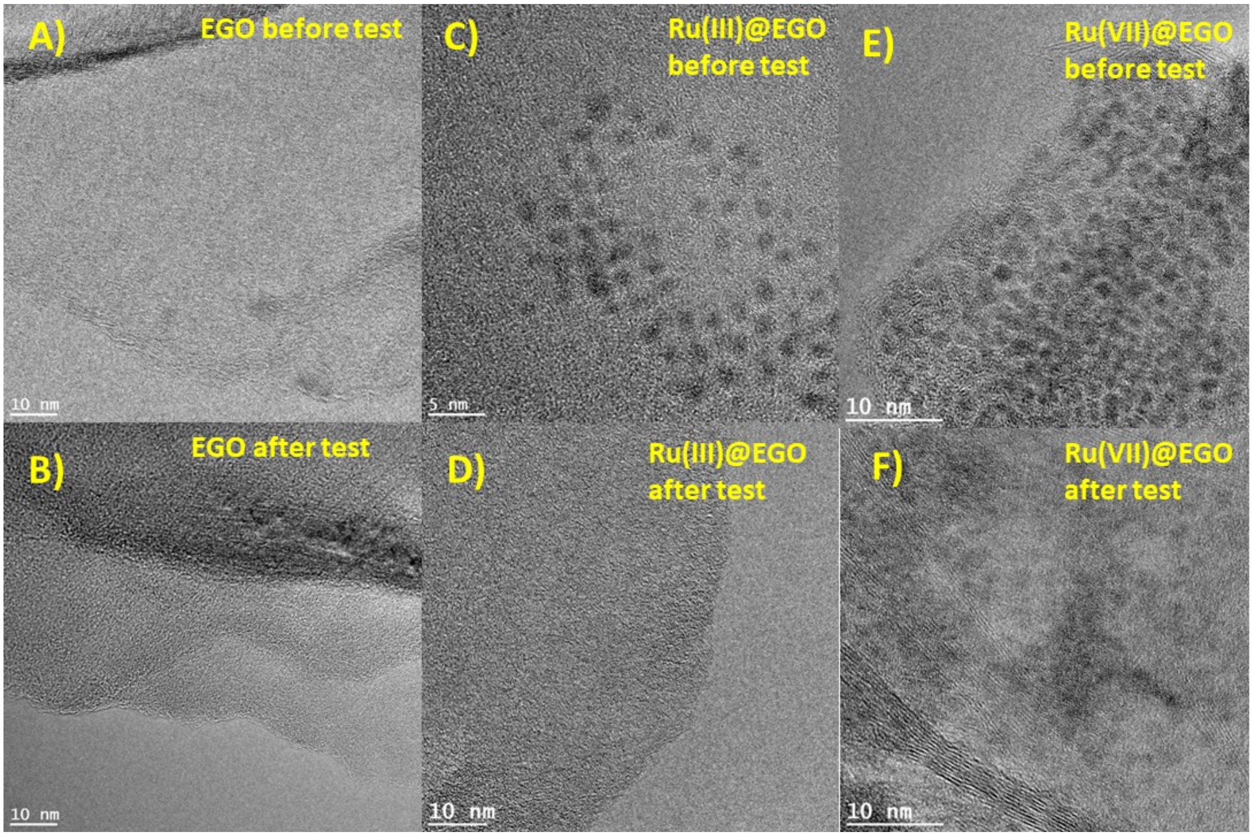

Figure S11. HRTEM images of **A)** EGO before WOR testing **B)** EGO after WOR testing **C)** Ru(III)@EGO before WOR testing **D)** Ru(III)@EGO after WOR testing **E)** Ru(VII)@EGO before WOR testing **F)** Ru(VII)@EGO after test.

References

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