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Characterization of an innovative method for RuO_2 deposition using Electron Microscopy

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Abstract

Many photocatalysts work better or exclusively when a suitable cocatalyst, such as RuO_2, is deposited on their surface. An innovative method of RuO_2 deposition has been found to improve the performance of photocatalysts such as $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$, WO_3, $SrTiO_3$ and TiO_2. Here we use high angle annular dark field (HAADF) imaging, energy-dispersive X-ray (EDX) spectroscopy, and electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) to study the deposition of RuO_2 on TiO_2. The deposition process occurs in two steps, for each of which we are able to characterize the RuO_2 distribution, morphology and crystallinity.

Deposition method

- Deposition was carried out onto metal oxide powders, silicon wafers and glass substrates.
- Each substrate was coated with an organic linker molecule.
- The functionalized sample was then exposed to RuO_2, which binds to the linker.
- Calcination at 350°C was used to burn off the linker, leaving only RuO_2 on the substrate.
- Photolithography was used to pattern the substrate to define regions where deposition should occur.

Results

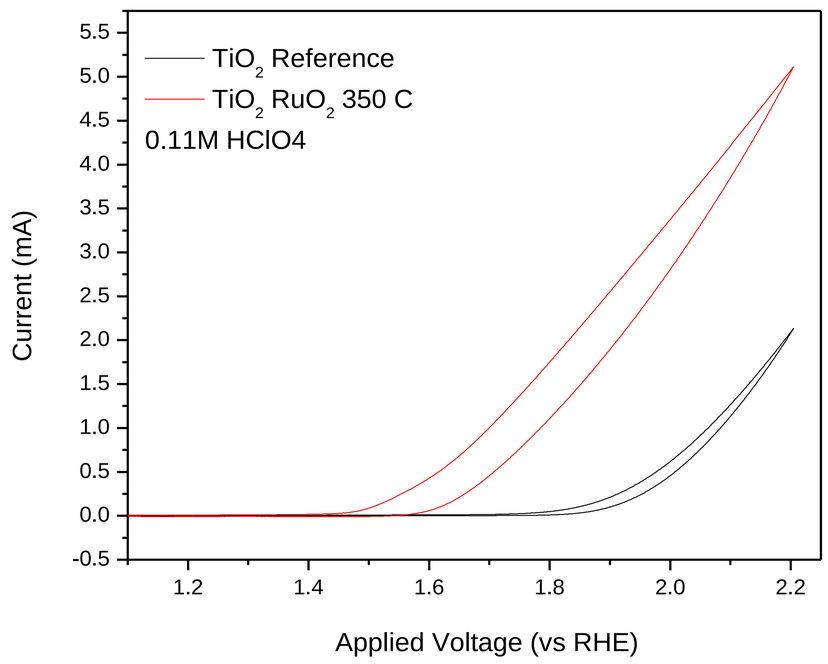

Figure 1. Oxygen Evolution Reaction (OER) performance plotted as a function of applied voltage with respect to the reversible hydrogen electrode (RHE). The red curve shows the improved activity of the coated and calcined sample as compared to bare TiO_2.

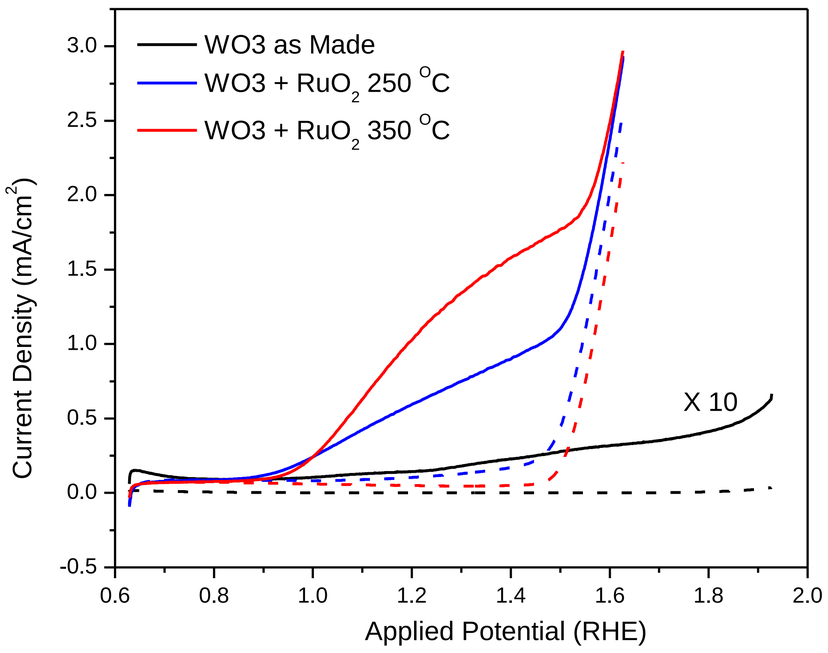

Figure 2. Cyclic Voltamogram acquired from electrodeposited WO_3 on FTO with RuO_2 calcined at 250°C (blue) and 350°C (red) and without RuO_2 (black) in 1M $HClO_4$. Dashed lines show the response in the dark, while continuous lines show the photoresponse. The photocurrent from the as made WO_3 (black) is scaled to 10 times its original value.

Characterization

- STEM HAADF imaging is sensitive to variations in atomic number (Z-contrast). Therefore, it allows direct visualization of the RuO_2 deposits.
- STEM EDX and EELS maps and spectra can be used to acquire compositional information from lines or two dimensional regions of the sample.

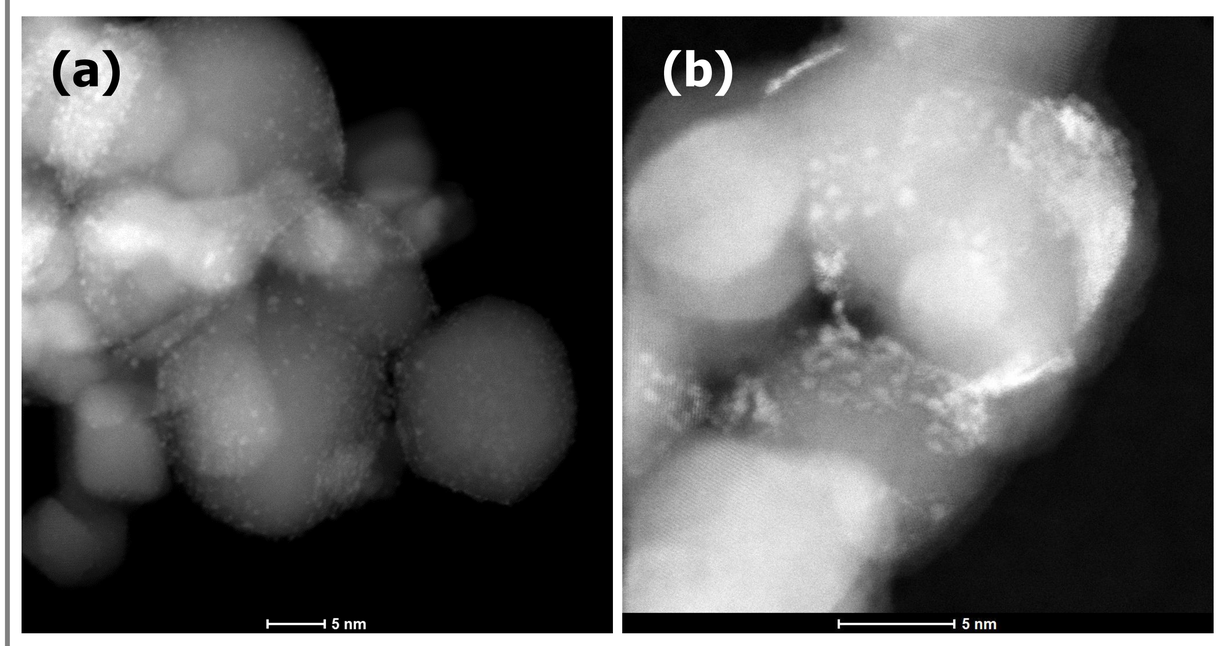

Figure 3. STEM HAADF images of (a) uncalcined and (b) calcined samples. RuO_2 particles appear brighter, while the darker large grey areas are TiO_2. In (a) the particles cover the substrate homogeneously, whereas in (b) some segregation is noticeable. The images suggest that migration across the surface may occur during the thermal treatment.

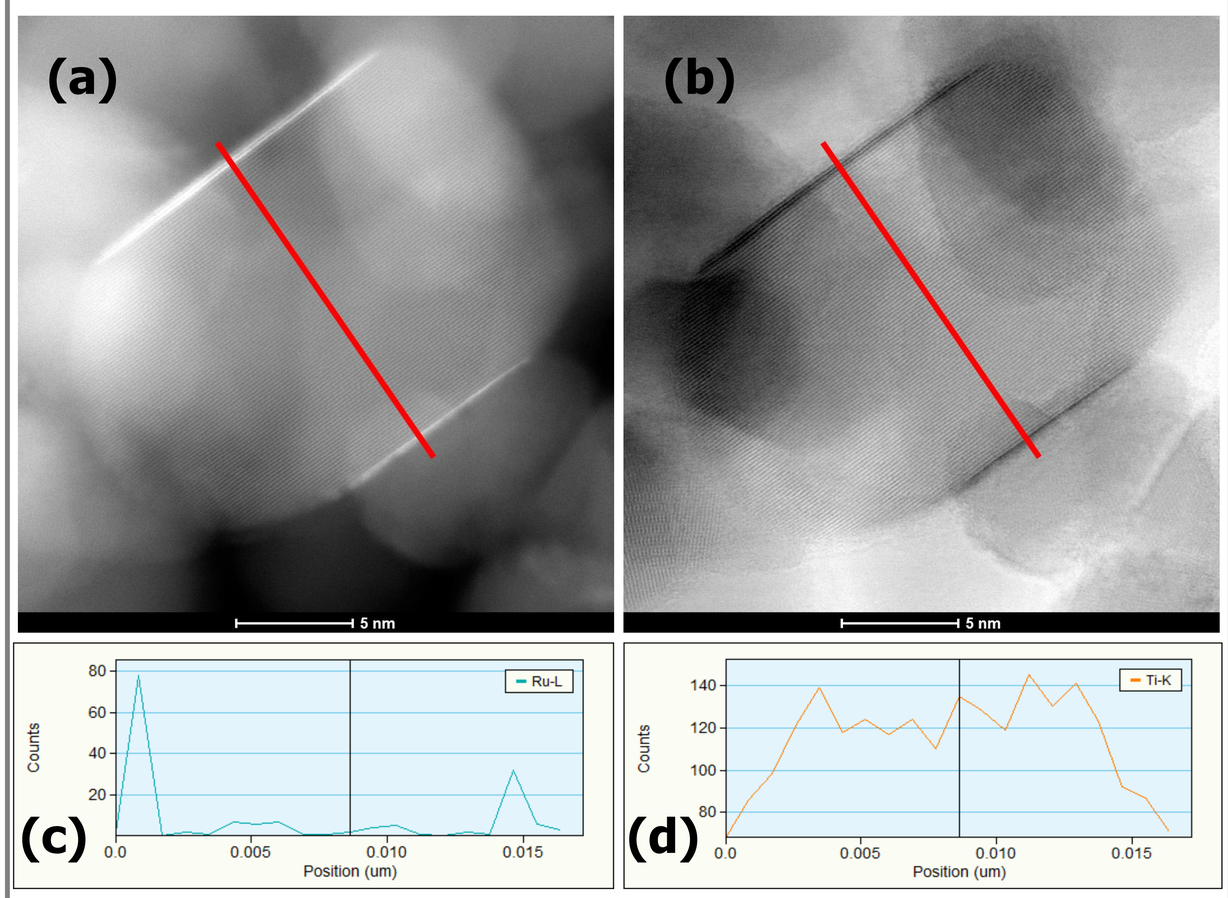

Figure 4. (a) STEM HAADF and (b) corresponding bright field image of a RuO_2 coated TiO_2 particle. (c-d) Ruthenium and Titanium EDX spectrum profiles acquired along the red line.

Conclusions

- The RuO_2 deposition method is effective and yields a uniform distribution of RuO_2 nanoparticles on the substrate before calcination. Their average size is 0.8 nm.
- After calcination the RuO_2 particles sinter into larger clusters (1-3 nm) and form uniform platelets that cover large areas of the substrate (10-200 nm^2 in area and 0.5 to 1 nm in thickness).
- The segregation process appears to be relevant for the catalytic properties.
- Future TEM investigation will include the *in situ* study of the calcination process during heating and exposure to a controlled gas atmosphere.

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