Characterization of an innovative method for RuO$_2$ deposition using Electron Microscopy

F. Cavalca$^{1,*}$, A. Kleiman-Shwarzstein$^{2}$, T. W. Hansen$^{1}$, J. B. Wagner$^{1}$, S. Dahl$^{2}$, and R. E. Dunin-Borkowski$^{1}$

$^{1}$ Center for Electron Nanoscopy, Technical University of Denmark, Fysikvej, Building 307, DK-2800 Lyngby, Denmark
$^{2}$ Center for Individual Nanoparticle Functionality, Technical University of Denmark, Fysikvej, Building 312, DK-2800 Lyngby, Denmark

*fica@cen.dtu.dk

Abstract

Many photocatalysts work better or exclusively when a suitable cocatalyst, such as RuO$_2$$_2$, is deposited on their surface. An innovative method of RuO$_2$ deposition has been found to improve the performance of photocatalysts such as ($\text{Ga}_x\text{Zn}_y\text{Ni}_z\text{O}_3$), 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

![STEM HAADF images of (a) uncalcined and (b) calcined samples. RuO$_2$ particles appear brighter, while the darker large gray 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.](image)

![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.](image)

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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