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Synthesis and Characterization of Hetero-Binuclear Oxo-Bridged Photocatalyst Systems

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Introduction

Hetero-binuclear oxo-bridged photocatalysts based on transition metals have been researched in the past few years for several different photochemical reactions including visible light-driven oxidation of water and reduction of CO_2. This projects' goal was to synthesize and characterize a catalyst of two transition metals (Zr and Co) bonded to silica nano-particles with a diameter of 15-20 nm. The main challenge of this synthesis was to receive a product consisting of the hetero-binuclear oxo-bridge, and not any other form of metal oxides.

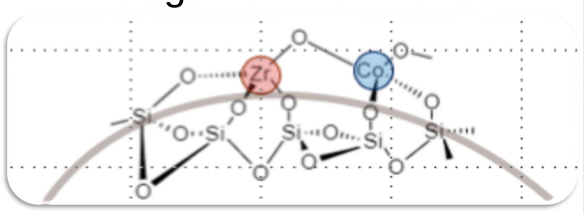
Methods

A. <u>SiO2-ZrO synthesis</u>

1. Vacuum on SiO_2 nanoparticles overnight
2. Dissolving SiO_2 and the **Zirconocene dichloride** (vacuumed or not) with DCM
3. Mixing Triethylamine overnight
4. Vacuum and Calcination

B. <u>SiO2-ZrOCo synthesis</u>

1. Vacuum on SiO_2-ZrO overnight
2. Dissolving SiO_2-ZrO and the **Cobalt dichloride** (vacuumed or not) with Acetonitrile
3. Mixing Triethylamine overnight
4. Filtration in ambient or nitrogen environment.



Schematic description of the required product

Sample holder for UV-Vis transmission measurement under vacuums

Results

(A) XPS calculated atomic

	SiO2-Zr-Co [2]	Avg. SiO2-Zr-Co	Stdv
Co 2p3	0.16	0.14	0.03
Zr 3d	0.4	0.58	0.01
Si 2p	40.86	34	1

(B) XRF

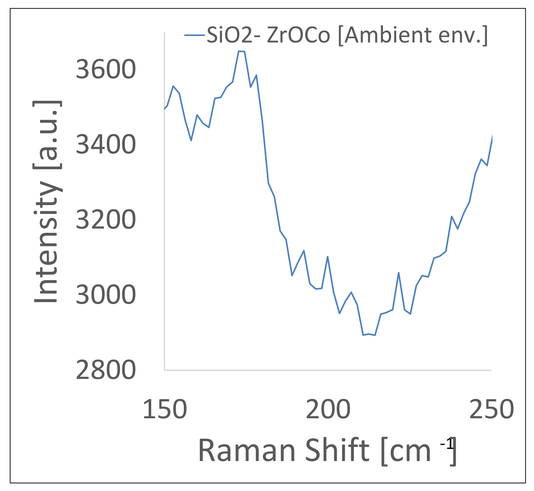
(1) Element concentration

Element	Conc.[%]
O	52.7
Si	45.4
Zr	0.969

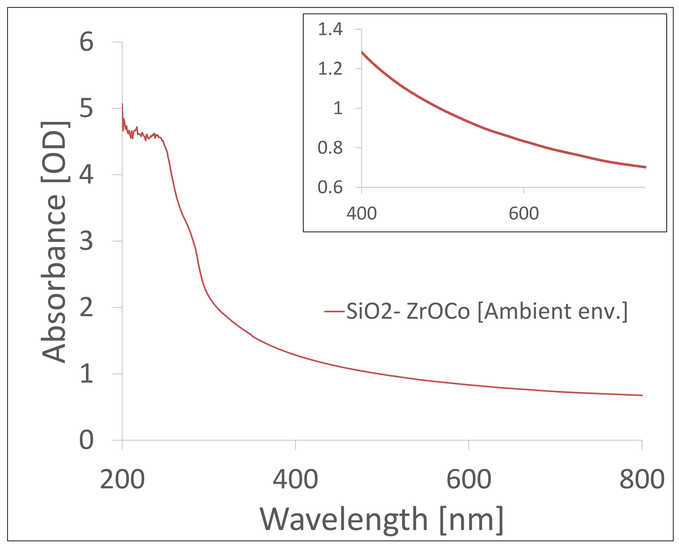
(2) Compound concentration

Compound Name	Conc.[%]	Absolute Error [%]
SiO2	97.0	0.2
ZrO2	1.31	0.03

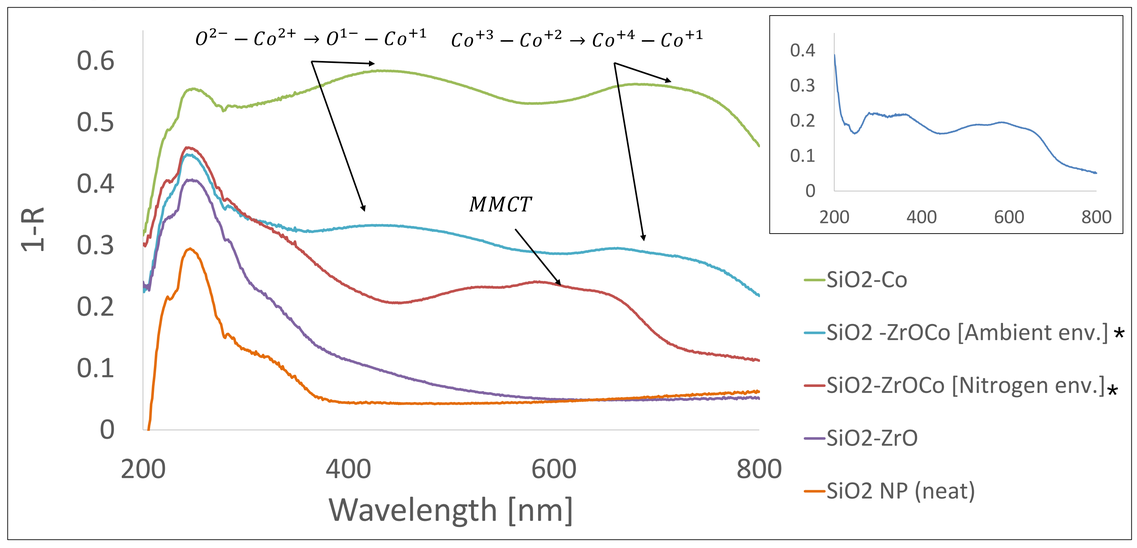
(C) FT-Raman Spectra



(D) UV-Vis Transmission (Vacuum env.)



(E) Diffuse Reflectance spectroscopy (Ambient env.)



(A) XPS elemental composite results - Comparison of at% of SiO_2 –ZrOCo [ambient env.] Synthesized in our lab to the results in other work[2]. **(B) XRF** measurement of synthesized SiO_2-ZrOCo [ambient env.] presenting non detectable amount of Co and existence of metal oxide ZrO_2 **(C) FT-Raman Spectra** results presenting peaks at 170-180 $[cm^{-1}]$ attributed to ZrO_2, and the increase in intensity, starting at 200 $[cm^{-1}]$, might be attributed to existence of the oxo-bridge or for bond of SiO_2-Zr **(D) UV-Vis Transmission** measurement results with no evidence of MMCT absorption in 400nm-700nm as known from literature [1][2]. **(E) Diffuse Reflectance Spectroscopy** – in all of the measurement there is a high absorption at 250nm, attributed to SiO_2 NP. This can be seen also in the measurement of SiO_2 NP (neat). In the measurement of SiO_2-ZrOCo [nitrogen env.] absorption is also seen in 436nm-715nm, which might include the MMCT absorption [1][2]. In the measurement of SiO_2-ZrOCo [ambient env.], there is no evidence of MMCT absorption at 400nm-700nm, and the absorbance at 450nm and 750nm can be attributed to absorption of Co_3O_4 [3], similar to absorption seen in measurement of SiO_2-Co. As predicted, there is no absorbance in SiO_2-Zr[4] at wavelength larger than 240nm. The Inset presents the subtraction of SiO_2 NP (neat) spectrum from SiO_2-ZrOCo [nitrogen env.] spectrum, which indicates absorption at 350nm attributed to SiO_2 NP, and absorption at 465nm-690nm, attributed to the d-d transition of Co and the MMCT absorption.

*the environment referred to is that of the filtration step.

Conclusions

We characterized the materials by XPS, XRF, Raman and UV-Vis and found that the product of our synthesis is consistent with a stoichiometric ratio suitable for creation of an oxo-bridge photocatalysts, Zr-O-Co. Based on spectroscopic UV-Vis analysis, we found **evidence for the formation of a hetro-binuclear oxo-bridged photocatalysts for the product of the synthesis that included filtration in nitrogen environment**. **For the product synthesized with filtration in ambient environment, we found evidence of formation of clusters of metal-oxides, ZrO_2 and Co_3O_4 upon SiO_2.**

We propose that the step conducted in nitrogen environment reduces the possibility of creation of metal-oxide clusters, due to minor concentration of oxygen and water.

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References

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