



IVS

Science, Technology & Applications

IVS2017

35th Annual Meeting

Corrections

Sunday, September 10th, 2017

Weizmann Institute of Science, Rehovot

Poster # 18

Visible-light driven water oxidation by polyoxometalates complexes of α -Fe₂O₃ cores in water

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An unprecedented role for metal-oxide cluster-anions (polyoxometalates, or POMs) as *covalently coordinated inorganic ligands* for individual hematite nanocrystals, gives isolable anionic clusters uniquely positioned between molecular macroanions and traditional colloidal nanoparticles.^[1] POM anions, α -XW₁₁O₃₉ⁿ⁻ (X= P^V, Si^{IV} and A^{III}; n = 7-9) and α -P₂W₁₇O₆₁¹⁰⁻ serve as pentadentate “capping” ligands for complexed Fe(III) ions linked via their sixth coordination site to 3-6 nm α -Fe₂O₃ cores. Raman, FTIR, EDS and XPS data show that numerous POMs are associated with each 3-6 nm hematite nanocrystal, and high-resolution TEM, cryogenic-TEM, and HAADF-STEM images clearly reveal the covalently bound POM ligands at the hematite surfaces. All these spectroscopic methods and analytical measurements confirm the presence of POM-capping ligands, $[\alpha$ -XW₁₁O₃₉Fe-O]ⁿ⁻, $[\alpha$ -P₂W₁₇O₆₁Fe-O]ⁿ⁻, *covalently* bound to the surfaces of the hematite cores. Moreover, covalent attachment of the POM anions allows for repeated precipitation (by added salt), and re-dissolution in water without any aggregation, and the clear orange solutions of these unique complexes are stable in water over a wide range of pH values (2.5-8), which spans the isoelectric point of hematite (pH 5.3). Differential-pulse voltammetry (DPV) was used to reveal the reversible redox chemistry of the covalently attached POM ligands. On illumination with a visible light ($\lambda_{\text{max}} \geq 420$ nm) for 8 h, the hybrid NCs oxidized water in presence of IO₄⁻ as sacrificial oxidant and produced ca. 3000 $\mu\text{mol g}^{-1}$ of O₂ (Figure 1). The photochemical water oxidation production rate depends on the pH values of the solution and O₂ production rate is highest, 781 $\mu\text{mol g}^{-1} \text{h}^{-1}$ at pH value 8. However, the photochemical O₂ production rate is almost similar for all the hybrids NCs with different POMs. Kinetic study with hybrid NCs suggested the rate of photochemical O₂ production depends on the concentration of [NCs] and [IO₄⁻] with ½ order dependence on both.

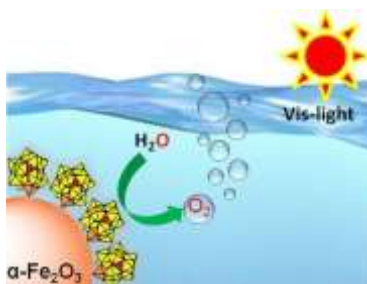


Figure 1. Visible-light driven water oxidation by the α -Fe₂O₃-POM hybrid.

References:

- [1] M. Raula, G. Gan Or, M. Saganovich, O. Zeiri, Y. Wang, M. R. Chierotti, R. Gobetto, I. A. Weinstock, *Angew. Chem. Int. Ed.* **2015**, *54*, 12416-12421.
- [2] B. Chakraborty, M. Raula, G. Gan Or, E. Gadot, T. Tabul, I. A. Weinstock, (manuscript in preparation)

Poster # 19

Visible Light Photochemistry on Top of CsPbBr₃ and CH₃NH₃PbBr₃ Perovskite Substrates

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Abstract

Inorganic and organic lead halide perovskite materials have attracted great interest in the scientific community because of their vast potential for low-cost and high efficiency solar cells. Herein we demonstrate the photocatalytic properties of inorganic (CsPbBr₃) and organic (CH₃NH₃PbBr₃) perovskites for the photodissociation of Ethyl Chloride (EC) employing 532nm LASER Irradiation under Ultra High Vacuum (UHV) condition with sample at 40 K. From the post irradiation Temperature Programmed Desorption (TPD), the photoproducts : Ethane (Mass 30), Allyl radical (Mass 41) and Propyl radicals (Mass 43) are found to increase with number of photons eventually reaching saturation. It was found that photoreactivity on top of the CsPbBr₃ surface is slightly faster than on the CH₃NH₃PbBr₃, with cross sections (for ethane formation): $\sigma_{\text{inorg}} = 3.8 \pm 0.3 \times 10^{-19} \text{ cm}^2$ and $\sigma_{\text{org}} = 3.1 \pm 0.6 \times 10^{-19} \text{ cm}^2$; allyl radical: $\sigma_{\text{inorg}} = 7.6 \pm 1.5 \times 10^{-19} \text{ cm}^2$ and $\sigma_{\text{org}} = 1.8 \pm 0.1 \times 10^{-19} \text{ cm}^2$; and Propyl radicals: $\sigma_{\text{inorg}} = 1.25 \pm 0.02 \times 10^{-18} \text{ cm}^2$ and $\sigma_{\text{org}} = 2.65 \pm 0.5 \times 10^{-19} \text{ cm}^2$. Luminescence properties were studied by exciting the sample with photon (355 nm) as well as electron (cathodoluminescence) excitation. The inorganic (CsPbBr₃) and organic (CH₃NH₃PbBr₃) substrates exhibit a sharp excitonic luminescence emission at 535 nm and 557 nm respectively, at 40K temperature for both photon and electron excitation. It was found that luminescence property is highly temperature sensitive. A blue shift and decrease in the intensity were observed during temperature increase. We conclude that the relatively long charge separation lifetime which leads to both luminescence and photovoltaic activity, explains also the photoreactivity in the visible.