

DRIVING WATER OXIDATION CATALYST BY VISIBLE LIGHT CHROMOPHORE ACROSS PRODUCT SEPERATING, PROTON PERMEABLE MEMBRANE

Anil Agiral, Han Sen Soo, Heinz M. Frei

Physical Biosciences Division, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, California 94720 USA

Introduction

Design of a solar-to-fuel system will require integration of photocatalytic processes into functional nano-assemblies which include light absorbing chromophores, molecular linkers and reaction centers for charge separation, catalytic units for multi-electron redox processes and separation membranes [Fig. 1]. One of the most important challenges towards the realization of an integrated artificial photosynthetic system is the development of an efficient, molecularly-defined charge transport link between a visible light absorbing chromophore and a multi-electron transfer catalyst for water oxidation. Here, oligo-para-phenylene vinylene (OPV) molecular wires enabling hole transport from chromophore to the Co_3O_4 water oxidation catalyst is reported. Molecular wires have the HOMO energetically matched between the potentials of visible light sensitizer $[\text{Ru}(\text{bpy})_3]^{2+}$ and Co_3O_4 nanoparticles as the water oxidation catalyst, while the LUMO remains inaccessible to the excited sensitizer and thus will block back electron transfer. The issue of oxidative damage of OPV molecular wires during water oxidation conditions can be solved by embedding them into a silica shell around Co_3O_4 nanoparticles. In this system, protons generated during water oxidation can diffuse through the silica layer, while water and oxygen molecules are transported through the pores in the shell.

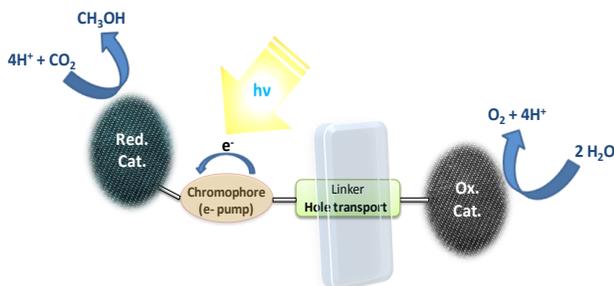


Figure 1. A schematic diagram showing the essential elements of an artificial photosynthetic system.

Experimental

Co_3O_4 nanoparticles with size (3 – 100 nm) and shape control were prepared using modified solvothermal routes, and silica shell (1 – 4 nm) coating was done by Stober synthesis. Nanoparticles can be stabilized with surfactants in either aqueous or organic media. Functionalization of the surface of Co_3O_4 nanoparticles with molecular wires (amine or carboxylate end groups) was performed in-situ, during surfactant – assisted solvothermal synthesis. Conformational structure and orientation of the nanoparticle-bound molecular wire was examined by FTIR and FT-Raman spectroscopic methods. Hole injection from sensitizer into molecular wire and kinetics of the competing processes is monitored by transient

absorption spectroscopy and the ability of hole conducting molecular wire – nanoparticle system to drive water oxidation was analyzed. Photochemical oxygen evolution measurement was done by Clark electrode (oxygen dissolved in water) and by mass spectrometer (gas phase oxygen).

Results and Discussion

Fig. 2(a) shows the resulting 10 nm Co_3O_4 nanocrystal. XRD patterns (not shown) showed that nanoparticles are pure spinel oxide Co_3O_4 (JCPDS card no. 43-1003, space group: $\text{Fd}\bar{3}\text{m}$, $a = 8.084\text{\AA}$). No obvious peaks corresponding to other cobalt oxides were detected in the XRD pattern, which indicated the high purity of the final products synthesized under the present experimental conditions. By changing solvent type, pH or the concentration of starting material (cobalt acetate), it was possible to synthesize nanoparticles with sizes ranging from 3 nm to 100 nm. Fig. 2(b) shows the TEM image of a Co_3O_4 - SiO_2 core-shell system. Amorphous silica coating around the nanocrystals was done by controlled hydrolysis of TEOS at pH 10. Initial concentration of TEOS can determine the thickness of the final coating. Elemental composition of the core-shell structures measured by EDX, indicated the high purity of core-shell system and Co_3O_4 spinel phase was maintained during silica coating. Attachment of distyryl benzene type molecular wires with carboxylate functional groups to Co_3O_4 nanocrystals was successfully done through a condensation reaction. Initial water oxidation experiments with Co_3O_4 nanocrystals revealed a very efficient water oxidation process. At pH 7 and irradiation with 476 nm light, TOF values could reach $0.03 \text{ O}_2 \cdot \text{s}^{-1}$ per surface cobalt and initial quantum efficiency could be up to 48 %. Water oxidation rates increased with decreasing particle size. Initial transient absorption spectroscopy experiments showed that holes could be injected from sensitizer to the nanocrystal through molecular wires.

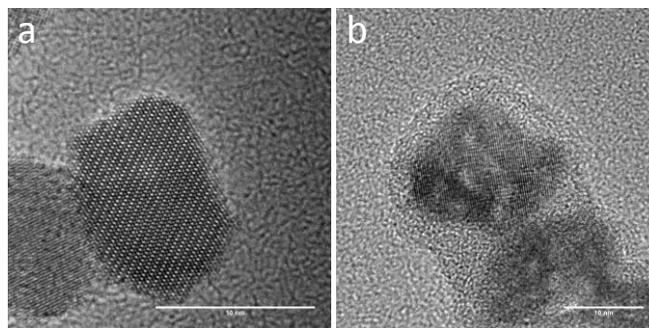


Figure 2. (a) HR-TEM image of a 10 nm Co_3O_4 nanocrystal and (b) Co_3O_4 - SiO_2 core-shell system.

Conclusions

Driving water oxidation catalyst (Co_3O_4 nanocrystals) by visible light chromophore through OPV molecular wires embedded into proton permeable silica membrane was demonstrated.

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