Ruthenium Polyoxometalate Water Splitting Catalyst: Very Fast Hole Scavenging from Photogenerated Oxidants.

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Supplementary Information

Materials

$Ru(bpy)_2(dpb)^{2+}$, hexafluorophosphate salt, was prepared according to: Gillaizeau-Gauthier I., Odobel F., Alebbi M., Argazzi R., Costa E., Bignozzi C.A., Qu P., Meyer G.J. *Inorg. Chem.* **2001**, *40*, 6073-6079.
1, lithium salt, was prepared as described in ref. 4.

Preparation of sensitized TiO_2 films.

A Dyesol DSL 18NR-T TiO_2 paste was used for the preparation of mesoporous films for photophysical measurements. A small amount of paste was deposited on top of a microscope slide partially covered with two strips of scotch tape as to create a channel of the desired length and width. A microscope slide with a smooth edge, or a glass rod, was used as tool to uniformly distribute the paste dragging it at constant velocity. The films were dried under a stream of warm air and heated in an oven at 450°C for 30'. Dye adsorption was accomplished by putting the films in a crystallizer and covering them with a solution 10^{-3}M of the complex in ethanol. Adsorption is completed within about 24hrs at room temperature or 2 hrs heating the solution near the boiling point. After rinsing with ethanol and drying, the films were stored in a desiccator over silica gel. The catalyst uptake was performed by contact of the sensitized TiO_2 film (30 min dipping) with 1.0 x 10^{-3} or 1.0 x 10^{-2} M aqueous solution of the catalyst, followed by rinsing and drying. The loading of the adsorbed species was estimated spectrophotometrically using the following molar extinction coefficients: $Ru(bpy)_3^{2+}$, $\varepsilon_{452} = 14710\ M^{-1}cm^{-1}$; **1**, $\varepsilon_{452} = 11560\ M^{-1}cm^{-1}$, $\varepsilon_{600} = 4290\ M^{-1}cm^{-1}$.

Apparatus and procedures

Transient absorption measurements were performed by means of a nanosecond laser spectrometer comprised of: a Continuum Surelite II Nd:YAG laser equipped with harmonic generators at 532nm and 355nm (FWHM: 8 ns) as excitation source, a continuous probing light source consisting of an Osram XBO150W/1 OFR xenon lamp housed in an Applied Photophysics mod. 720 lamp housing and powered by an Applied Photophysics mod. 620 power controlled supply in conjunction with a mod. 03-102 arc lamp pulser, an Acton SpectraPro 2300i imaging triple grating monochromator/spectrograph equipped with gratings having 50 grooves/mm, 150 grooves/mm and 600 grooves/mm, a Hamamatsu R3896 photomultiplier powered by a Hamamatsu mod. C9525 high voltage power supply, a LeCroy mod. 9360 600MHz digital storage oscilloscope. Laser excitation was provided at right angle with respect to the optical axis of the spectrometer. The entire apparatus was controlled by means of a PC running a custom LabVIEW software.

For flash photolysis in solution, the sample was contained in a 1-cm spectrofluorimeter cell, in a standard 90° excitation/analysis beam configuration.

For flash photolysis of films, the samples were obtained by clamping together a 4cm x 1cm glass slide, coated with a 1,5cm x 1 cm TiO_2 film, with a naked slide of the same size. Peak absorbance values of sensitized films were about 1.5, while at the excitation wavelength they were in the range 0.1-0.2. The solution chosen for the measure was drawn by capillary forces in the thin space between the slides and the assembly was placed diagonally in a 1 cm path length quartz cell at 45 degrees with respect to the optical axis of the spectrometer. Laser excitation pulses at 532nm were defocused by a concave lens in order to reach an energy density of about 18mJ/pulse/cm^2 on the film. The scattered laser light was eliminated by using an interference filter.