SYNTHESIS AND CHARACTERIZATION OF SENSITIZERS FOR SURFACE DERIVATIZATION OF NANOCRYSTALLINE PHOTOCATALYST FILM DEVICES

Final Report

by

Michael Grätzel, Ph.D.
Professor of Chemistry

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Michael Grätzel, Ph.D.
Professor of Chemistry
Laboratoire de Photonique et Interfaces
Ecole Polytechnique Fédérale
CH-1015 Lausanne, Switzerland

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ABSTRACT

The work performed over the period from Sept. 1996-Oct. 1997 under the original grant no. DAJA 45-90-C-0007 from the European Research Office of the US. Army was in line with the principal objectives of the proposed investigations, i.e. the synthesis of ligands, the complexation of the ligands to appropriate metal ions, the application of the metal complexes to nanocrystalline semiconductor surfaces, the examination of the properties of such films and the use of nanocrystalline semiconductor films to accomplish the catalytic and photocatalytic decomposition of toxic chemicals, in particular warfare agents or simulants. The first line of interest was to develop efficient charge transfer sensitizers for nanocrystalline anatase films in order to render the photo-catalytic action efficient in daylight. To this end, compounds containing transition metal ions complexed by ligands containing anchoring groups as well as bystander molecules were synthesized. Specifically, the synthesis of the dithiol-derivative of pyrazine and the tetrathiooxalate anion were undertaken, as well as of a new ruthenium charger transfer sensitizer having a high oxidation potential (Eo=1.7V vs. NHE). Sensitization of nanocrystalline TiO₂ films employing this complex was investigated and exhibited interesting wavelength dependent quantum yields for electron injection; a phenomena attributed to electron injection from vibrationally unrelaxed («hot») sensitizer states. The work over the past year also focused on the use of nanocrystalline WO₃ as photocatalyst for the decomposition of organic contaminants and CW agent simulants. To this end mineralisation of the contaminants methanol, 4-chlorophenol and the CW simulant, paraoxon, were tested. Both colloidal dispersions and mesoscopic particle films were investigated. The majority of experiments were, however, performed on nanocrystalline films and, thus, several different methods of film preparation were investigated. Despite the low thermodynamic driving force due to the unfavorable Fermi level position in WO₃ it is possible to achieve efficient oxygen reduction by conduction band electrons if catalysts such as Pt are deposited on the surface of the oxide.
Synthesis and Characterization of Sensitizers for Surface Derivatization of Nanocrystalline Photocatalyst Film Devices.

Research over the last year on grant no. DAJA 45-90-C-0007 R & D continued along the two major directions of the program outlined in the original proposal submitted to the European research office of the US Army. The first line of interest is to develop efficient charge transfer sensitizers for nanocrystalline anatase films. The goal is to increase the light harvesting capacity of the film in the visible region in order to render the photo-catalytic action efficient in daylight. The second line of research over the last several months has been dedicated to nanocrystalline oxide films which bear great promise for applications in the field of photocatalytic destruction of simulants. The goal here is to obtain films that exhibit high photocatalytic activity under visible light. To this end, nanocrystalline WO₃ films in the micron thickness range and with a roughness factor exceeding 1000 have been produced via a colloidal precursor solution.

Complexes of interest along the first line of research contain a transition metal ion, e.g. ruthenium, iron and platinum, in their center. One of the ligands is a polypyridyl type compound, such as 2,2'-bipyridyl or 2,2',2''-terpyridyl, substituted by carboxylate or phosphonate groups. The latter serve as anchoring groups to attach the complex to the nanocrystalline oxide surface. Apart from the anchoring group, the complex contains at least one more ligand, called bystander, whose role is to tune the opto-electronic properties of the complex in the desired fashion. Preliminary studies carried out during the last year in our group have shown the great potential of sulfur containing bystander ligands which exert a profound effect on the absorption spectra of the charge transfer complex. The studies focused, therefore, on the synthesis of sulfur containing compounds, such as dithiacarbamates and dithiolates that form very stable bidentate complexes with all three of the metals cited above. The synthesis of the two ligands A and B depicted below was thus undertaken.

A is the dithiol-derivative of pyrazine while B is the tetrathiooxalate anion. The preparation and characterization of these
compounds was carried out in collaboration with Dr. Harold Banks who assisted in their synthesis.

The ground state redox potential of the sensitizer should be as high as possible to allow for oxidation of the simulant by the sensitizer cation following light induced electron injection into the solid. The complex Ru(II)L'L''(NCS), presented below, was synthesized keeping the above mentioned objectives in mind.

\[
\Delta E = 1.7 \text{ eV} \\
\phi^0 (S^+/S) = +1.80 \text{ V}
\]

\[
\text{Ru(II)N}^\text{L''(NCS)}}
\]

\[
\text{L'} = 4,4'\text{-dicarboxy-2,2'bisquinoline} \\
\text{L}_{2} = 2,6\text{-bis(1'-methyl-benzimidazol-2'-yl)pyridine}
\]

The redox potential of Ru(II)L'L''(NCS) is at 1.8 V against the standard hydrogen reference electrode and the energy difference between the lowest electronically excited state and the ground state is 1.7 eV. Laser experiments on nanocrystalline TiO₂ anatase films covered with a monomolecular film of this complex were performed, and the quantum yield for charge injection as a function of excitation wavelengths was plotted. A striking observation is that the quantum yield decreases at wavelengths above 580 nm reaching zero at 1.75 eV, i.e. well within the MLCT absorption of the dye. With conventional charge transfer sensitizers, such as RuL₂(NCS)₂ , \( L = 4,4'-\text{dicarboxy-2,2'-bipyridyl} \), the quantum yield of electron injection is independent of wavelength over their whole visible absorption band.

This unusual and important finding is interpreted in terms of hot electron injection from a vibrationally unrelaxed excited state of the complex into the conduction band of the titanium dioxide. The lowest excited state of Ru(II)L'L''(NCS) has a redox potential of 0.1 V (vs.NHE) which is about 0.2 eV below the energy of the conduction band of TiO₂ under our experimental conditions, rendering electron injection thermodynamically unfavorable. Increasing the excitation energy of the dye, i.e. from the absorption threshold situated at 1.7 eV to 2.1 eV leads
to a dramatic increase in the quantum yield which reaches practically 100 % at 2.1 eV, i.e. 0.4 eV above the absorption threshold of Ru(II)L'LL"(NCS). This clearly illustrates that the injection of electrons can occur very efficiently from vibrationally unrelaxed states, widening the scope of sensitizers for photocatalytic applications.

An important research effort during the last year has been dedicated to nanocrystalline oxide films which bear great promise for applications in the field of photocatalytic destruction of simulants. The goal here is to obtain films that exhibit high photocatalytic activity under visible light. To this end, nanocrystalline WO₃ films in the micron thickness range and with a roughness factor exceeding 1000 have been produced via a colloidal precursor solution. These films have been subjected to photo-electrochemical studies.

Several preparation techniques of these films were undertaken:

**First film preparation**

The colloidal WO₃ precursor solution was prepared by first dissolving 3.6 gm of H₂WO₃ (tungstic acid) in 50 ml of water to which were added 4 ml of concentrated NH₃. This solution was then diluted to 800 ml and boiled for 6 hours. The final solution, a transparent colloidal solution of white tungstic acid, attains pH = 3.7. The WO₃ particulate films are prepared by adding 0.1 ml of 4% PVA (polyvinyl alcohol) to 0.1 ml of the 2 M WO₃ precursor colloidal solution and diluted to 0.24 ml by adding 0.04 ml H₂O. We then applied 0.1 ml of this mixture to a conducting glass [Nippon Sheet Glass, 10 ohm/square, fluorine-doped SnO₂ glass (TCO)] surface of 3.7 cm². The film was initially dried in a stream of hot air for 5 to 10 minutes at approximately 90 °C and then sintered at 500 °C under a stream of O₂ for 1 hour.

**Second film preparation**

The second preparation consisted of dissolving 5 gm of H₂WO₄ in 30 ml of 30% hydrogen peroxide by sonication at 40°C and diluted to 100 ml. Then 0.4g of the above solution was boiled with 0.08 g of ethylene glycol until the total weight reaches 0.3g after which 0.7g of 6% polyethylene glycol (MW= 8000) was added to the latter solution .0.1 ml of this solution was applied on 7 cm² of conducting glass plate and sintered at 500°C for 15 minutes.

The scanning electron microscope analyses for both preparations showed the particulate nature of the porous film electrode (thickness 7
nm). X-ray diffraction analysis was also performed and showed the films to consist of monoclinic WO₃.

In the initial phase of the work methanol was used as a model substrate for oxidation. Valence band hole transfer to this scavenger leading to complete mineralization was witnessed. For comparison, photoelectrochemical phenol oxidation on sensitizer-derivatized thin film TiO₂ optically transparent electrodes was also investigated. Meanwhile, this type of photo-oxidative degradation was extended to various organic CW simulants, such as the organic phosphate containing pesticides. The first simulant tested was paraoxon.

The white light photocurrent versus voltage curves of aqueous solutions containing 1M NaClO₄ (pH=1) in the absence and presence of 0.1 M (1st preparation) and 0.001 M (2nd preparation) paraoxon were plotted. These experiments employed the nanocrystalline WO₃ films described above (first and second preparations) as working electrodes, a saturated calomel reference electrode, and a Pt sheet counter electrode. The global output of the Xe-lamp used as a light source corresponded to standard sunlight, i.e. 1000 W/m². Only visible light was used to excite the nanocrystalline oxide, the UV part being filtered with a 395 nm cut-off filter. Applying a reverse bias to the nanocrystalline films (preparations 1 and 2) strongly enhances the photocurrent in both cases (i.e., in the absence and presence of paraoxon); however, the anodic photocurrents are higher and occur at less positive potentials for the solutions containing the simulant as compared to pure water. In particular, a hump in the anodic photocurrent appears at potentials between 0.5 and 0.6 V which is totally absent in the curve of the blank. Since this effect appears already at very low concentrations of the simulant, it can be inferred that efficient hole transfer from the valence band of the WO₃ film to the paraoxon is taking place. The enhancement of the photocurrent with increasing paraoxon concentration, witnessed in the photocurrent-voltage curves, is evident, particularly at low overvoltages where the oxidation of the simulant by valence band holes of the WO₃ film dominates largely over water oxidation.

Analysis of the TOC (total organic carbon content) value performed after photolysis showed that the hole reaction ultimately leads to the total mineralisation of the phosphate ester according to the equation:

\[
\text{EtO}_2\text{PO}_2\text{O} + 12.5\text{O}_2 \rightarrow 10\text{CO}_2 + \text{HNO}_3 + \text{H}_3\text{PO}_3 + 5\text{H}_2\text{O}
\]
The WO$_3$ particulate film action spectrum at pH=3 in the photo-electrochemical oxidation of paraoxon ($10^{-4}$ M) in aqueous solution (supporting electrolyte 0.1 M NaClO$_4$) with the WE potential adjusted to 500 mV vs SSCE was recorded. The incident monochromatic photon to current conversion yield (IPCE) was plotted as a function of excitation wavelength.

The IPCE values were derived from the photocurrents (mA/cm$^2$) by means of the equation

$$\text{IPCE} = 1240 \cdot \frac{i_{ph}}{I(nm)} \cdot P$$

where P is the incident monochromatic light intensity expressed in W/m$^2$. The IPCE values increase towards the blue steeply starting from a threshold wavelength at 480 nm. The conversion yield at 420 nm attains a value close to 40% in the presence of paraoxon indicating that efficient hole capture is taking place. From this finding one infers that light induced charge separation is greatly favored in the nanocrystalline oxide films. The decline in efficiency at wavelengths shorter than 400 nm is an artifact due to the glass absorption as can be seen from the absorption spectrum of the film coated WO$_3$ electrode.

We also carried out a comparative study of the photo-catalytic activity of WO$_3$ colloids with the nanocrystalline films. Preliminary studies indicated that aqueous dispersions of WO$_3$ decompose organic contaminants such as methanol to CO$_2$ if an oxygen reduction catalyst such as Pt is deposited onto the oxide. The WO$_3$ was a commercial powder obtained from Johnson Matthey and the Pt loading was carried out by photo-platinization in the following manner: H$_2$PtCl$_6$ was added to water containing 1% WO$_3$ at a concentration corresponding to the required loading of the powder with Pt. Afterwards, 0.1 M methanol was added to the dispersion which was then illuminated for 6 hours with the full output of a Hanau Solar simulator. The powder was subsequently separated from the solution by centrifugation, washed several times, and then used as a photo catalyst.

Experiments performed clearly show that methanol is converted to CO$_2$ under simultaneous consumption of oxygen in the presence of platinized WO$_3$ powder. The visible light-induced mineralisation of the organic contaminant is achieved under these conditions. No photo-reaction at all was observed in blank experiments carried out in the absence of WO$_3$ or with naked WO$_3$ powders lacking the Pt. Thus the
presence of the oxygen reduction catalyst on the WO₃ appears to be imperative, in order to accomplish the destruction of the organic contaminant. We suspected that this effect is a consequence of the sluggish reaction of conduction band electrons with O₂ as the flat band potential of WO₃ is known to be only 200 to 300 mV more negative than the equilibrium potential of the O₂/water redox couple. In order to prove that this kinetic impediment is indeed responsible for the observations made with the colloidal WO₃ dispersion, we carried out a series of electrochemical investigations with nanocrystalline WO₃ films deposited onto conducting glass electrodes. The films used in these studies were prepared as in preparation 2 followed by the above described photo-platinization technique. The advantage of using nanocrystalline films is that the valence and conduction band processes can be investigated separately by carrying out electrochemical experiments in the dark and under light, respectively.

The feature observed in current-voltage curves obtained with platinized WO₃ films in Ar saturated water at pH 3 in anaerobic conditions reflects mainly the capacitive charging of the nanocrystalline oxide surface as the electrode potential is swept from the accumulation to the depletion regime. Similar polarization curves were also recorded at various oxygen concentrations in solution. Augmentation of the current as the solution O₂ increased demonstrated in a striking fashion the pronounced catalytic effect the Pt deposit has on the cathodic oxygen reduction. In the absence of Pt one observes practically the same small current under aerobic and anaerobic conditions indicating that the reduction of O₂ does not take place on WO₃ in the absence of the catalyst. This is in good agreement with the data obtained from the colloidal WO₃ dispersions.

We continued our photo-electrochemical studies on nanocrystalline WO₃ films by investigating the photo-decomposition of 4-chlorophenol. The white light photocurrent/voltage plots of aqueous solutions containing 1M NaClO₄ (pH01) in the absence and presence of 4 x 10⁻⁴ M 4-chlorophenol employing the nanocrystalline WO₃ films described above as the working electrode, a Ag/AgCl reference electrode, and a Pt-sheet counter electrode were examined. The global output of the Xe-lamp used as a light source corresponded to standard sunlight, i.e. 1000 W/m². Only visible light was used to excite the nanocrystalline oxide, as previously, the UV part being filtered with a 395 nm cut-off filter. Applying a reverse bias to the nanocrystalline films strongly enhances
the photocurrent both with and without simulant; however, the anodic photocurrents are higher and occur at less positive potentials for the solutions containing chlorophenol as compared to pure water. Since this effect appears already at very low concentrations of the simulant, it can be inferred that efficient hole transfer from the valence band of the WO₃ film to the chlorophenol and, thus, oxidative degradation of the simulant, is taking place.

These experiments confirm that the oxidative degradation of the simulant chlorophenol proceeds efficiently under visible light illumination of nanocrystalline WO₃ electrodes. This should be of great importance for the application of these films to the complete mineralisation of warfare agents by photocatalytic reactions.