

Photovoltaic Effect on Vanadium Pentoxide Gels Prepared by the Sol-Gel Method

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Transparent indium oxide electrodes were modified by a vanadium pentoxide gel layer prepared by a sol-gel route. An anodic photovoltaic effect induced by visible light was investigated on these modified electrodes, and a possible reaction mechanism was suggested. The ESR method was used to evaluate the effect of the V^V/V^{IV} ratio on photocurrent density.

Introduction

Vanadium pentoxide is known to exhibit an anodic photoeffect. Thus, single V_2O_5 crystal,^{2,3} V_2O_5 -modified electrodes,⁴ and V_2O_5 glasses in a mixture with PbO , BaO , TeO_2 , or GeO_2 under illumination with UV light⁵ have been studied. Vanadium pentoxide is also utilized as an industrial catalyst for oxidation of organic substances,⁶ and its photocatalytic properties have been investigated.⁷⁻⁹

The sol-gel route^{10,11} offers many advantages in low-temperature preparation of different types of glass. The vanadium pentoxide gel is a widely studied material¹² with potential application in lithium cells as cathodic material¹³ and in electrochromic devices¹⁴ and as a composite material for optical gratings.¹⁵ It also appears to be a promising material for microionics.¹⁶

The grain boundaries in polycrystalline electrode materials decrease the efficiency of photoelectrochemical solar cells. Monocrystalline electrodes can be deployed, which substantially increases the price. The amorphous gel preparation may represent a technique to solve these problems. In our study the indium oxide transparent electrodes were modified with a thin film of vanadium pentoxide gel prepared by the sol-gel route, and a photovoltaic effect was induced by visible light. The photochemical experiments with V^v and propylene carbonate in solution were performed to elucidate reaction mechanism.

Experimental Section

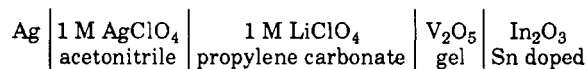
Vanadium pentoxide gels were prepared by hydrolysis and condensation of vanadium oxoethoxide, $VO(OCH_2CH_3)_3$.¹² Vanadium oxoethoxide was prepared by 8 h of heating, under reflux, of ammonium metavanadate with a large excess of dry ethanol. The resulting yellow solution was filtered from the remaining ammonium metavanadate. Water and ethanol were removed by distillation under reduced pressure.¹⁷ The liquid vanadium oxoethoxide was then sealed in ampules.

The vanadium pentoxide sol was prepared by standard procedure^{12,14} by adding three drops of vanadium oxoethoxide into 1 mL of water (hydrolysis ratio, $h > 100$). A red precipitate appeared instantly, and this mixture was sonicated for at least 5 min. The resultant green colloidal solution was deposited on an indium oxide electrode (CG-80IN-CUV from Delta Technologies) and on a quartz plate by spin coating, or on quartz tubing by the dipping method, or cast in a plastic weighing bowl. Drying under reduced pressure at ambient temperature for at least 24 h produces a green-yellowish xerogel transparent layer of average composition $V_2O_5 \cdot 1.8H_2O$.^{12,14}

The indium oxide electrodes were cleaned by sonication in a water-ethanol mixture for 10 min followed by 10 min of sonication in phosphate buffer at $pH = 8^{18}$ to maximize hydroxyl group surface concentration. After a quick wash with deionized water, the electrodes were immediately covered with vanadium pentoxide sol by spin coating. The gel can be removed completely from the indium oxide electrodes by soaking in water for several days.

The photoelectrochemical cell is depicted in Figure 1. The light from a 450-W mercury lamp was filtered through a water-cooled Corning glass filter 3389 and a Pyrex glass plate. After focusing with a lens, the beam was filtered through a 1-cm cuvette filled with saturated solution of $CuSO_4$ and Kodak Wratten gelatin filters No. 2C and No. 47 prior to irradiation of the electrode. This arrangement permitted transmission of a narrow band centered at 435 nm. The light intensity was monitored by a radiometer (YSI Kettering, Model 65).

The experiments were performed with an electrochemical cell of the following composition:



The acetonitrile and propylene carbonate solutions were separated by an asbestos diaphragm. For electrode polarization and current acquisition, a BAS 100A electrochemical analyzer was used for cyclic voltammetry, hold-and-ramp, and time base modes. Steady-state conditions were obtained by performing about 20 cycles in the cyclic voltammetry mode or by a 1-min hold on the starting potential.

The experiments with vanadium species in solution were performed as described in ref 19, i.e., 10 mL of propylene carbonate was added to 40 mL of 0.1 M V^V solution in 50% sulfuric acid.¹⁷

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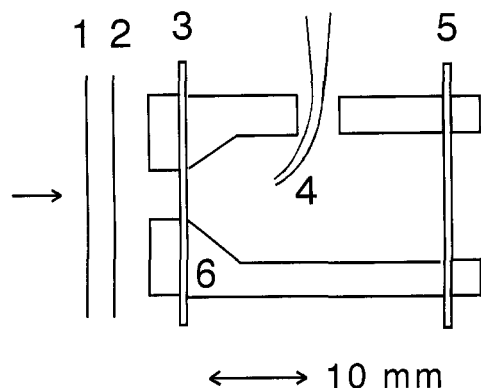


Figure 1. Experimental apparatus: (1) Kodak Wratten gelatin filter No. 2C, (2) Kodak Wratten gelatin filter No. 47, (3) vanadium pentoxide gel modified indium oxide transparent electrode (working electrode), (4) Luggin capillary tip for reference electrode connection, (5) transparent indium oxide electrode used as current electrode, (6) cell Teflon body held together by screws. The arrow indicates the light beam direction.

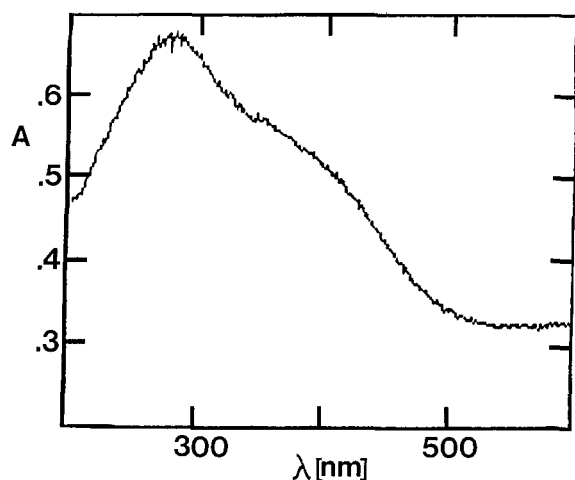


Figure 2. Absorption spectrum of vanadium pentoxide gel on quartz slide after background subtraction. *A* denotes absorbance, λ is wavelength.

The mixture was illuminated with the optical system described above.

Electron spin resonance spectra were acquired at room temperature using a Bruker Model ESP 300 ESR spectrometer (X-band). The klystron was tuned to a microwave frequency between 9.44 and 9.49 GHz. Spectra for gels were obtained using a 1-cm-diameter quartz ESR tube as a sample holder. These quartz tubes were checked, and no signal was apparent. The gel was peeled off the plastic substrate and put into the quartz tube which was then inserted into the sample holder. The position of the gel in the cavity was optimized for maximum signal intensity. The maximum signal was achieved at a $\sim 45^\circ$ angle between the magnetic field and gel plane. The modulation amplitude was chosen to afford maximum signal intensity without compromising resolution of lines. Multiple scans were added in instances in which signal strength was weak at optimal microwave power.

Anhydrous (\pm)-propylene carbonate (Aldrich), anhydrous 1,2-dichloroethane (Aldrich), 99% *N,N*-dimethylformamide (Aldrich), and spectra grade 2-propanol (Fisher Scientific) were used as solvents. Propylene carbonate and 1,2-dichloroethane were stored in a water and oxygen free environment. Lithium perchlorate (Fisher Scientific), tetrabutylammonium perchlorate (Kodak), and tetrabutylammonium hexafluorophosphate (Aldrich) were used as supporting electrolytes. The silver wire reference electrode was immersed into 1 M solution of silver perchlorate hydrate (Aldrich) in acetonitrile (EM Science). The vanadium oxoethoxide was prepared from ammonium metavanadate 99% (Aldrich) and dehydrated 100% ethyl alcohol (Quantum Chemical). Sulfuric acid for bulk experiments was purchased from J. T. Baker. Deionized water was used for all experiments.

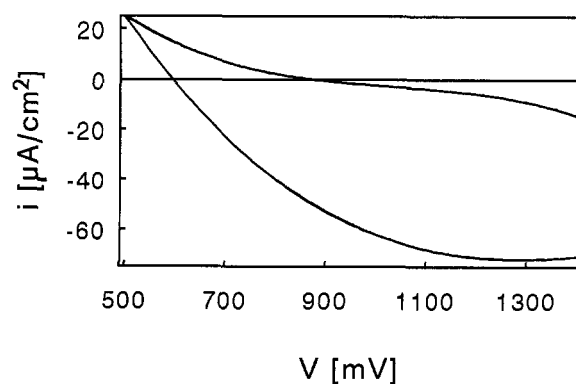


Figure 3. Potential dependence of photocurrent (lower line). Negative current corresponds to electron transfer to the electrode. The potential is vs Ag/Ag^+ electrode. Gel absorbance is 0.4, light intensity $20 \text{ mW}/\text{cm}^2$. Electrolyte: 1 M LiClO_4 in propylene carbonate. The upper line responds to the dark current.

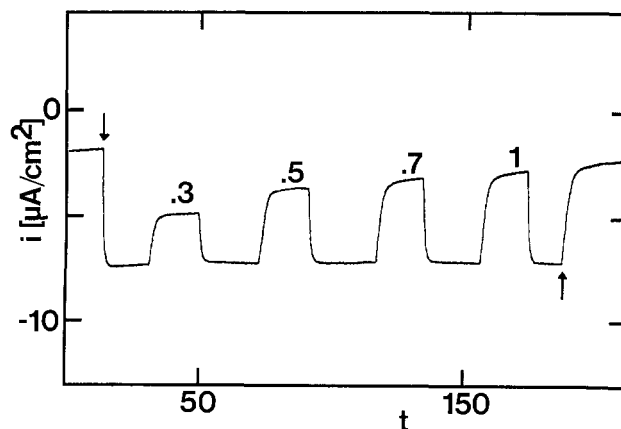


Figure 4. Photocurrent dependence on light intensity. Initial light intensity $10 \text{ mW}/\text{cm}^2$, gel absorbance 0.3, electrolyte 1 M LiClO_4 in propylene carbonate. The decrease corresponds to the decrease of light intensity due to Kodak grey Wratten gelatin filters in the optical pathway. The number denotes the neutral density of the filters; 0.3, 0.5, 0.7, and 1 neutral density filters transmit 50%, 32%, 20%, and 10% of light beam energy, respectively. Current convention is the same as in Figure 3, the *x* axis is time *t* (in seconds) from the beginning of experiment. The arrows indicate when the light was switched on and off.

Table I. Dependence of Relative Photocurrent Densities on Solvent

solvent	photocurrent relative to the highest value
<i>N,N</i> -dimethylformamide (DMF)	1.00
propylene carbonate (PC)	0.64
1,2-dichloroethane (DCE)	0.61
2-propanol	0.57

Results

The absorption spectrum of vanadium pentoxide gel is shown in Figure 2. The absorbance (*A*) of gel layers prepared by the method described varies between 0.3 and 0.6 for 435 nm for the different samples. For excitation with 435-nm light, a potential-dependent photocurrent is observable (Figure 3). Within these absorbance limits the photocurrent is proportional to the absorbance. The photocurrent density is proportional to the light intensity (Figure 4) and is also influenced by drying procedure and by the solvent used (Table I). Drying under reduced pressure increases the photocurrent about 20%, and drying under reduced pressure at 250°C decreases the photocurrent by 50%. The gel temperature treatment is accompanied by total oxidation of V^{IV} to V^{V} (see ESR section). The vanadium pentoxide gel modified electrodes

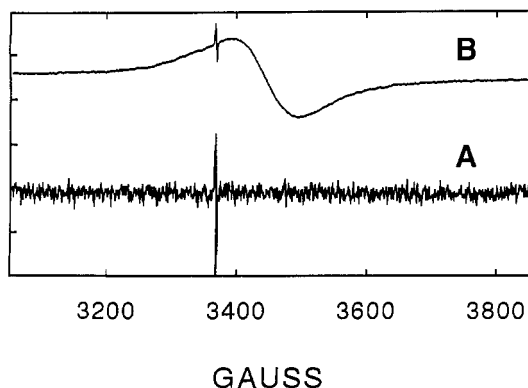


Figure 5. ESR spectra of vanadium gel (A) following heat treatment and (B) prior to heat treatment.

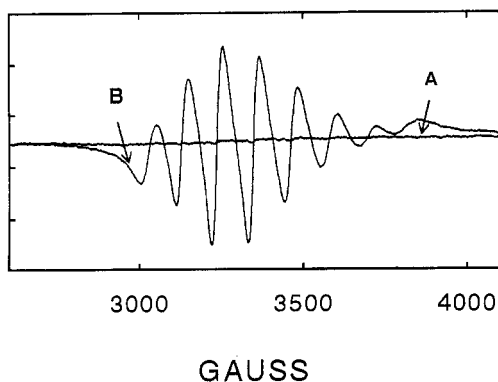


Figure 6. ESR spectra of V^{5+} , H_2SO_4 , propylene carbonate, and water solution (A) prior to illumination and (B) after illumination.

retain their activity at least several weeks, if stored in a vacuum desiccator.

The photocurrent density was influenced by the solvent used (Table I), but the experimental variation is limited, because vanadium pentoxide gel is soluble in common solvents (water, methanol, ethanol, THF, chloroform). The supporting electrolyte does not affect the magnitude of the photocurrent. Neither oxygen nor reducing agent (tris-(bipyridyl)iron(II) perchlorate) influences the current measured.

ESR spectra of vanadium pentoxide gels were obtained before and after heat treatment at 250 °C under vacuum (Figure 5). Prior to heat treatment the spectrum exhibits two superimposed lines. The first of these lines is broad with a ΔH_{p-p} width of 104 G and a g value of 1.959 and a narrow line with $\Delta H_{p-p} = 1.8$ G and $g = 2.002$. Following heat treatment the narrow line remains while the broad line is absent. The eight line fine structure characteristic of V^{IV} in solution (Figure 6) is absent in gel spectra both before and following heat treatment. ESR spectra of gels stored in vacuum desiccators are reproducible for weeks following preparation. Blanks run in all cases gave no ESR signal.

Solution Experiments. A color change was observed in experiments with V^V species in solution under illumination only when V^V , sulfuric acid, and propylene carbonate were all initially present. The color changes from pale yellow to blue-green characteristic of V^{IV} and the presence of V^{IV} species was confirmed by ESR observation (Figure 6). The propylene carbonate is also decomposed directly by sulfuric acid, but no color change was observable in the dark.

ESR spectra of this solution are given in Figure 6. Prior to illumination the solution does not contain a V^{IV} characteristic signal. Following illumination, the solution gives the eight line signal characteristic of V^{IV} in solution. This

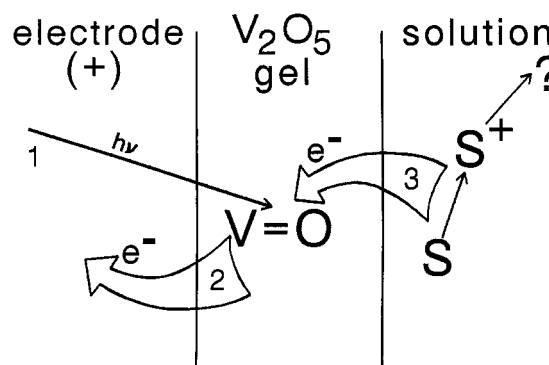
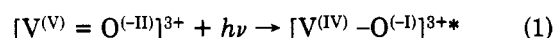


Figure 7. Proposed reaction scheme; S denotes the solvent molecule. The numbers denote the step sequence.

signal has $g = 1.985$ and $(a) = 110$ G. Thus, propylene carbonate can also be photooxidized by photoexcited V^V .

Discussion and Conclusions

The absorption of 435-nm light quanta causes electron transfer from coordinated oxygen to vanadium and vanadium ion is thus photoreduced:²⁰



As we can conclude from the direction of the photocurrent flow and its potential dependence (Figure 3), this electron is immediately transferred to the positively charged electrode and may be replaced in the vanadium-oxygen bond by an electron from an organic solvent molecule, as was demonstrated by the solution experiments (Figure 7).

The broad-line ESR is produced¹² by V^{IV} , and the narrow line is characteristic of a defect center in a solid. We speculate that this defect species is localized at an oxygen or H_2O site within the gel since the g factor (2.002) and the absence of hyperfine structure precludes localization of the unpaired electron adjacent to a V^{IV} site.

Questions remain about the exact mechanism leading to a photocurrent. We speculate that the reaction site on the gel surface may be a photoexcited triplet state of the vanadium-oxygen species^{7,21,22} which is reductively quenched by organic substances in solution. The photocurrent is in this case restricted only to the gel surface.

The second possibility is that the $V^{(V)}O^{(-I)}$ bond can serve as an active center for oxidation of organic substances.⁶ Excited states can be generated in the entire gel volume and quenched by electron transfer to the electrode and hole transfer to the gel surface. Reaction sites for oxidation of organic substances are thus created by hole diffusion from the bulk to the surface.

Although the hydrolysis ratio was larger than 100, the resulting gel was green and not red as reported.¹² The probable reason is reduction of V^V by organic groups.¹² There is no doubt that the concentration of V^{IV} in vanadium pentoxide gels is closely connected with water concentration,¹² but the precise relationship is still unclear.^{12,23,24} Both reduction with dehydration²³ and higher water content in reduced gels²⁴ were reported. As was

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shown the thermal treatment in condition of low air humidity under reduced pressure leads to the total diminishing to V^{IV} species.

The quantum yield of conversion of absorbed photons to electrical current was determined to be about 2%, assuming that all incident photons have the same 435 nm wavelength. This quantum yield is not large, but could be increased. For example, the excited state (eq 1) likely is quenched immediately after its creation, probably by water molecules present in the gel structure and thus photocurrent is diminished. The vanadium pentoxide conductivity influences the transport of an electron to the

electrode or holes to the solution and is affected by water concentration and $V^{(IV)}$ concentration in the gel. A better understanding of the role of H_2O and V^{IV} in gel structure, charge transfer and their relation may enable an increase in photocurrent by systematic variation of the water and V^{IV} concentration. Thus, the gel current can be optimized.

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Registry No. PC, 108-32-7; In_2O_3 , 1312-43-2; $VO(OCH_2CH_3)_3$, 1686-22-2; V_2O_5 , 1314-62-1; H_2SO_4 , 7664-93-9; ammonium metavanadate, 7803-55-6.

Discrete Layers of Ordered C_{60} Molecules in the Cocrystal $C_{60} \cdot CH_2I_2 \cdot C_6H_6$: Synthesis, Crystal Structure, and ^{13}C NMR Properties

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The first crystals containing crystallographically ordered (at room temperature) unmodified fullerene (C_{60}) molecules, with chemical composition $C_{60} \cdot CH_2I_2 \cdot C_6H_6$, have been prepared. The fullerene molecules are arranged in novel hexagonally close-packed layers, separated by the solvent components. A monoclinic (space group $C2/c$) crystal structure of $C_{60} \cdot CH_2I_2 \cdot C_6H_6$ was determined at room temperature [lattice parameters: $a = 21.239$ (7) Å, $b = 17.403$ (4) Å, $c = 10.106$ (2) Å, $\beta = 106.03$ (2)°, $V = 3590$ (2) Å³] and at 122 K [$a = 21.024$ (7) Å, $b = 17.298$ (4) Å, $c = 10.043$ (2) Å, $\beta = 105.93$ (2)°, $V = 3512$ (2) Å³]. The ordered nature (on the X-ray time scale) of the compound allows a detailed determination and discussion of the intermolecular interactions between neighboring fullerene molecules as well as between the C_{60} and the solvent molecules. Solid-state ^{13}C NMR under MAS shows three distinct resonances for C_{60} , benzene and CH_2I_2 ; static NMR measurements set a lower limit for the rate of molecular rotation of C_{60} on a time scale of tens of microseconds.

Introduction

When macroscopic quantities of buckminsterfullerene, C_{60} , became available,¹ attempts were immediately made to confirm the proposed truncated-icosahedral geometry of the molecule by use of diffraction techniques. Shortly thereafter it was demonstrated that crystals of pure C_{60} consisted of closely packed spherical carbon molecules in a face-centered cubic array (space group $Fm\bar{3}m$), but the molecules were completely disordered crystallographically, undergoing essentially free rotation at a rate of more than a billion times per second.^{2,3} Thus, neither atomic coordinates nor detailed investigation of the C_{60} - C_{60} interactions could be obtained from diffraction experiments at room temperature. The geometry of the molecule was subsequently demonstrated at atomic resolution in the crystal structures of the ordered derivatives $C_{60}[OsO_4(4\text{-tert-butylpyridine})_2]$ ⁴ and $[(C_6H_5)_3P]_2Pt(\eta^2-C_{60}) \cdot C_4H_8O$,⁵ where the bulky "tagging" substituents prevented the

otherwise free rotation of the fullerene molecule. Upon cooling, solid C_{60} undergoes a phase transition at 249 K to a primitive crystal lattice space group $Pa\bar{3}$. The symmetry-lowering nature of the phase transition normally results in twinned crystals when they are cooled through the phase transition. The structure of the low-temperature phase was investigated at 110 K on a twinned crystal⁶ and at 5 K by use of powder neutron diffraction.⁷ Both low-

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