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Photoinduced Electron Transfer Processes of Ruthenium Tris(bipyridyl) and Methylviologen Doped in TiO_2 System by the Sol–Gel Method

Jinlong Zhang,[a]* Bin He,[a] Qin Zhang[a] & Deyin Huang[b]

[a]Institute of Fine Chemicals, East China University of Science and Technology, People's Republic of China
[b]Department of Applied Chemistry, Jiaotong University, People's Republic of China

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ABSTRACT

The efficiencies of charge separation by electron transfer from electron donor to acceptor via semiconductor TiO_2 xerogel particles are compared with respect to different electron donor and acceptors. At room temperature the product (MV^+) is metastable, and its lifetime is very short. At 77 K, MV^+ was checked by ESR; the intensity of the ESR signal increased as the electron donor and acceptor moieties increased. It can therefore be assumed that the molecules photosensitize the electron injection into the conduction band of TiO_2, and the conduction band electron can subsequently reduce methylviologen (MV^{2+}) which is also incorporated into the support. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Photoionization and photoelectron transfer in heterogeneous systems [1] has been studied with respect to light energy storage systems, as well as with respect to the photodecomposition of toxic wastes and pollutants [2]. The photoinduced charge transfer reaction between ruthenium *tris*(bipyridyl) cation ($RUBIPY^{2+}$) and dimethylviologen cation (MV^{2+}) has been studied in a variety of media, including ion-exchange resins [3], silicates [4], micelles [5], cellulose [6], porous Vycor glass [7], oxides [8], and other materials [9].

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*Corresponding author. Fax: 00 86 4777138.

The interest of researchers has often stimulated potential energy storage applications [8], and efforts have therefore focused on the role of the media in stabilizing the products of the photoinduced reaction against back electron transfer. The present work has examined this process in a TiO_2 system by the sol–gel method.

In recent years, the sol–gel method for producing solid materials has attracted attention as one of the most promising techniques for the design and development of well-characterized new photo-functionalized materials [10]. By this method, it is possible to encapsulate or stably dope various photo-functional molecules or compounds into thermally stable inorganic glass-like matrices such as SiO_2 and TiO_2 through the hydrolysis of various metal alkoxides at room temperature. Thus, the sol–gel method is a useful method for the synthesize of organic and inorganic photo-sensitive materials for techniques such as dye lasers [11], photo-hole burning [12], and photo-energy-conversion devices [13], and optical sensors [14].

The function of a solid support for photoactive electron donors and acceptors can be classified into three kinds, viz.

1. the support does not participate in photoreaction;
2. the support acts as a medium for electron transport;
3. the support generates electron-hole pairs.

A variety of techniques have been previously employed to probe the charge injection from an excited sensitizer into a large band gap semiconductor. These include emission [15], transient absorption [16], diffuse reflectance [17], internal reflection [18], microwave absorption [19], and resonance Raman spectroscopy [20]. The purpose of the present work is to study the photo-induced electron transfer processes by electron spin resonance (ESR) using the metal-ligand complex of $Ru(bpy)_3^{2+}$ and methylviologen (MV^{2+}) as the electron donor and acceptor respectively.

EXPERIMENTAL

Reagent: Tris(2,2′-bipyridyl)ruthenium(II)chloride hexahydrate ($Ru(bpy)_3Cl_2{\cdot}6H_2O$), methylviologen dichloride hydrate ($MVCl_2$) (Aldrich Chemical Co.); Tetra-i-propoxy titanium (TPOT) (Kishida Chemical Co); Ethanol (Amakasu Chemical Co. spectroscopic grade).

Preparation: TPOT(20 ml); 1×10^{-3} M $MVCl_2$ and $Ru(bpy)_3Cl_2$ solution in ethanol (5 ml) were mixed. The mixture was thoroughly stirred, before being poured into plastic cells covered with a plastic wrap film punctured with several pinholes. In this study, the gelation point of the sample was defined as the time at which the sample loses flow capacity in the cell. Drying the wet gel by evaporation of the solvents from the system at room temperature led to capillary pressure, resulting in shrinkage of the gel.

The sample was put into a quartz tube and the ESR signals were measured using an Electron Spin Resonance ER200D, with X-band and magnetic field modulation of 100 KHz and a 250 W xenon lamp as light source. The measurement was done in a rotating liquid nitrogen dewar; the light passed through a 10 cm water filter and a corning 5-61 blue filter. The filter was selected to cover the absorption band of $Ru(bpy)_3{}^{2+}$ at $\lambda_{max} = 452\,nm$ with $\varepsilon = 14300\,cm^{-1}$ and to avoid excitation of MV^{2+} at $\lambda_{max} = 260\,nm$.

RESULT AND DISCUSSION

Experimental ESR spectra of photolyzed xerogel of TiO_2 containing an electron donor $\{Ru(bpy)_3{}^{2+}\}$ or acceptor (MV^{2+}) in 77 K are shown in Fig. 1. Each spectrum consists of a singlet, with $g = 2.003$, and a line width of 17 G, which has been previously assigned to the MV^+ cation radical [21]. At room temperature, in the above system, the ESR signal of MV^+ was not detected. No ESR spectrum of $Ru(bpy)_3{}^{3+}$ was detected in the xerogel of TiO_2 either at room temperature or at 77 K. The intensity of the singlet in all samples initially increased linearly with the photolysis time and reached a 'plateau' after a few minutes. A typical dependence of the ESR line intensity on the MV^+ cation radical is shown in Fig. 2. Since their line width is constant, the intensity of the ESR signals were demonstrated with the height of peak to peak [22]. The analysis of the photoyield is based on a comparison of the MV^+ ESR intensities after they reached the 'plateau' level.

Figure 3 shows the ESR signal intensities of MV^+ after photolysis of every mol TiO_2 xerogel containing 1×10^{-5} mol $Ru(bpy)_3{}^{2+}$ and different amounts

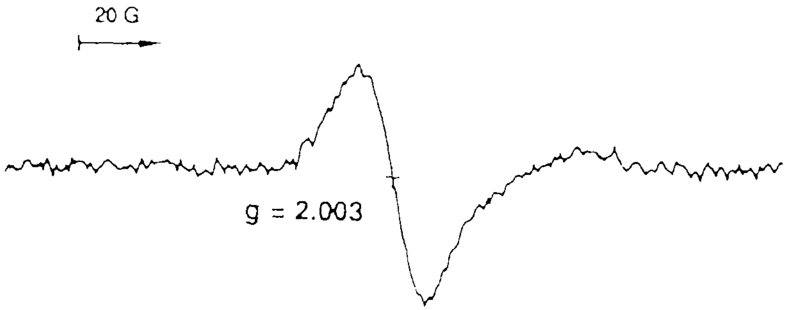

Fig. 1. ESR spectra at 77K after 20min of photolysis of every mol TiO_2 xerogel containing 1.45 mol $Ru(bpy)_3{}^{2+}$ and MV^{2+}, respectively.

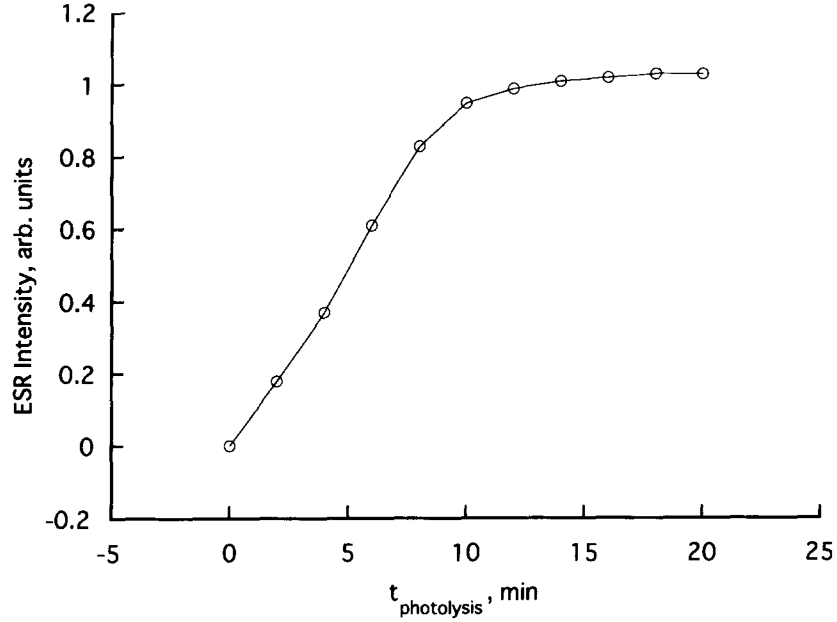

Fig. 2. Accumulation of MV^+ cation radical in TiO_2 xerogel during photolysis at 77 K measured by the peak-to-peak ESR line intensity. Every mol TiO_2 contained 1.45×10^{-5} mol $Ru(bpy)_3{}^{2+}$ and MV^{2+}, respectively.

of methylviologen chloride. In this system, photosensitization of TiO2 by $Ru(bpy)_3{}^{2+}$ occurs by injection of an electron from the metal-to-ligand charge transfer (MLCT) excited state (*) of the complex into the conduction band of TiO_2 [eqn (1)]:

$$Ru(bpy)_3^{2+} + h\nu(532\,\mathrm{nm}) \rightarrow^{*} Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e_{cb}(TiO_2) \qquad (1)$$

Because MV^{2+} are doped in TiO_2 with $Ru(bpy)_3{}^{2+}$ at the same time, it is likely that the process involves the photoinduced transfer of an electron from the conduction band to MV^{2+} acceptors, according to eqn (2):

$$e_{cb}(TiO_2) + MV^{2+} \Longleftrightarrow MV^{+} \qquad (2)$$

The products are metastable and exist transiently at room temperature, and at longer times at 77 K. From eqn (2), it can be seen that when the amount of MV^{2+} used is increased the intensity of the ESR signal is simultaneously increased. This implies that the photoelectrons of the photolysis are excessive in the conduction band of TiO_2. Therefore, recombination between the resultant Ru(III) complex, $Ru(bpy)_3{}^{3+}$, and conduction band electron, $e_{cb}(TiO_2)$, restores the system to its initial state [eqn (3)].

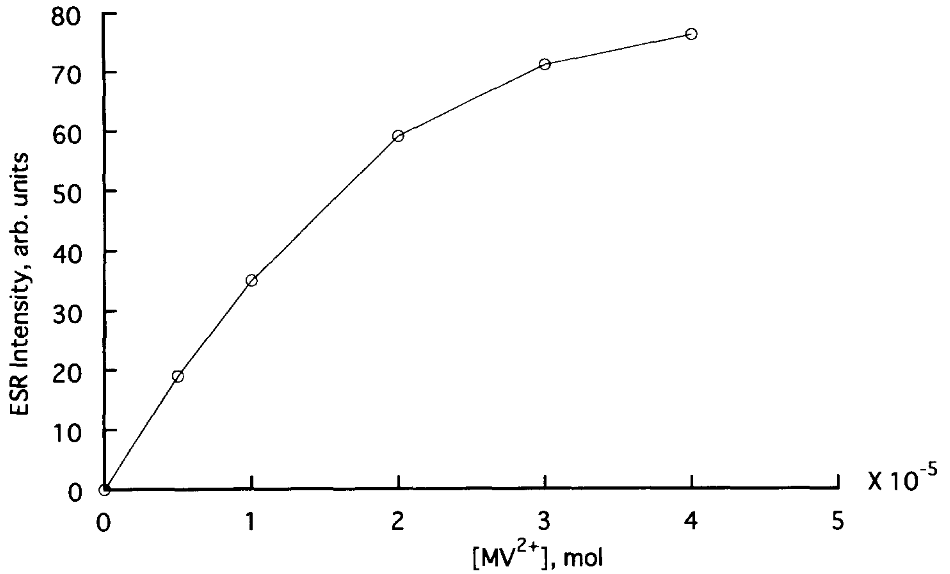

Fig. 3. Peak-to-peak ESR line intensities of MV^+ cation radical accumulated after 20 min of photolysis of TiO_2 xerogels at various cocentrations of MV^{2+}. Every mol TiO_2 xerogel contained 1×10^{-5} mol $Ru(bpy)_3{}^{2+}$. Measured at 77 K.

$$Ru(bpy)_3^{3+} + e_{cb}(TiO_2) \rightarrow Ru(bpy)_3^{2+} \quad (3)$$

Electron injection is rapid compared to recombination, and competes effectively with the intrinsic decay of $^*Ru(bpy)_3{}^{2+}$, so that the quantum efficiency of formation of $Ru(bpy)_3{}^{2+}$ and e_{cb} approaches unity. In this system, the reactions of eqns (2) and (3) exist simultaneously.

Figure 4 shows an MV^+ ESR signal in TiO_2 xerogel when the amount of $Ru(bpy)_3{}^{2+}$ is increased; the intensity of ESR is also increased simultaneously. It is interesting to note that there is a detectable ESR signal of MV^+ in TiO_2 xerogel, even if no $Ru(bpy)_3{}^{2+}$ is added. This means that the support itself (TiO_2 xerogel) can generate the electron hole pairs.

The $Ru(bpy)_3{}^{3+}$ cation radical, previously detected in dehydrated Y-zeolite[23] and silica[24] ($g \perp = 2.35$), could not be detected in our systems by ESR even at high microwave power and modulation amplitude. Further studies are in progress.

CONCLUSIONS

The efficiencies of charge separation by electron transfer from an electron donor to an acceptor *via* semiconductor TiO_2 xerogel particles are compared

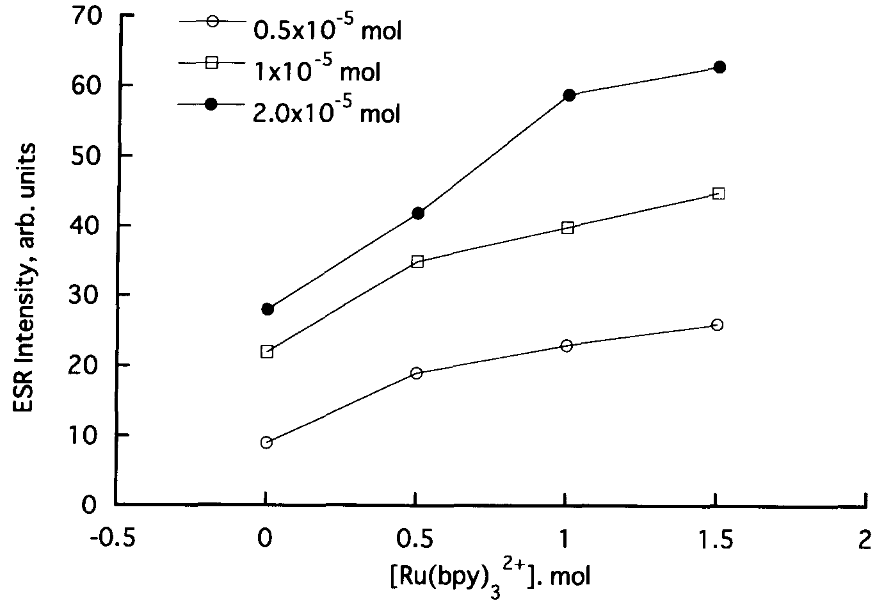

Fig. 4. ESR line intensities of MV^+ radical in TiO_2 xerogel containing different amounts of $Ru(bpy)_3{}^{2+}$ and MV^{2+}.

for different electron donors and acceptors. At room temperature, the product (MV^+) is metastable and its lifetime is very short. At 77 K, the product (MV^+) was checked by ESR. The intensity of the ESR signal increased as the concentration of electron donor and acceptor residues increased. It can be concluded that the molecules photosensitize electron injection into the conduction band of TiO_2, and the conduction band electron can subsequently reduce methylviologen (MV^{2+}), which is also incorporated into the support. The photochemical response of wide band gap semiconductors can be extended to long wavelength by adsorption of appropriate electron donor molecules on their surfaces.

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