LETTERS

Novel Preparation and Photoelectrochemical Properties of a Tungsten Oxide/Tris(2,2′-bipyrizine)ruthenium(II) Complex Composite Film

Masayuki Yagi* and Saori Umemiya

Faculty of Education and Human Sciences, Niigata University, 8050 Ikarashi-2, Niigata 950-2181, Japan

Received: March 13, 2002; In Final Form: May 7, 2002

A first and unique preparation is reported of a WO_3/tris(2,2′-bipyrizine)ruthenium (II) ($Ru(bpy)_3^{2+}$) composite film by electrodeposition from a colloidal solution containing peroxotungstic acid and $Ru(bpy)_3^{2+}$ that is remarkably stabilized by poly(sodium 4-styrensulfonate). The composite film clearly demonstrated multiple electrochromism. The photoexcited $Ru(bpy)_3^{2+}$ was found to be quenched completely by WO_3 in the composite film, which is responsible for an electronic interaction of $Ru(bpy)_3^{2+}$ with WO_3. The complete quenching led to a photocharging−discharging character and a steady-state photoanodic current induced by visible light.

Tungsten oxide (WO_3) is attracting much attention as an electrochromic material and an n-type semiconductor[1,2] available to a large variety of devices such as displays,[3] smart windows,[4] photoelectrochemical conversions,[5] and photocatalyses.[6] WO_3 films have been prepared by using numerous techniques such as vacuum evaporation,[7] chemical vapor deposition,[8] sol−gel precipitation,[2] spin coating,[9] and electrodeposition.[10] Compositions of WO_3 films with functional molecules could lead to its promising expansion in photoelectronics based on WO_3 films. However, there is no example of WO_3/functional molecule composite films so far, despite many reports of composite films based on TiO_2.[11−13] Tris(2,2′-bipyrizine)ruthenium (II) complex ($Ru(bpy)_3^{2+}$) is an interesting functional molecule, which is thermodynamically capable of splitting water by visible light as well as being useful as a photoluminescent probe and electrochromic compound.[14,15] We now report a first and unique preparation of a WO_3/$Ru(bpy)_3^{2+}$ composite film by simple electrodeposition from a colloidal solution containing peroxotungstic acid (PTA) and $Ru(bpy)_3^{2+}$ that is remarkably stabilized by poly(sodium 4-styrensulfonate) (PSS).

An aqueous ethanol solution (30 vol %) containing 1 mM $Ru(bpy)_3^{2+}$ and 25 mM PTA solution was prepared.[16] However,

this solution gave a gradual orange precipitation, which could be formed by electrostatic interaction between the cationic $Ru(bpy)_3^{2+}$ and anionic PTA. An addition of poly(sodium 4-styrensulfonate) (PSS) to the PTA/$Ru(bpy)_3^{2+}$ solution remarkably suppressed the precipitation and provided a very stable colloidal solution after standing for ca. 5 h at room temperature. This colloidal solution is stable over 3 months. $Ru(bpy)_3^{2+}$ in the colloidal solution gave phosphorescence at $\lambda_{max} = 592$ nm from its photoexcited state. To see a microscopic environment around $Ru(bpy)_3^{2+}$ in the colloidal solution, a lifetime of photoexcited $Ru(bpy)_3^{2+}$ was measured to give the major and long lifetime component, 804 ns (fraction = 87.9%) and short lifetime component, 450 ns (fraction = 12.1%) (compare with 600 ns in water). The long lifetime component would result from decrease of the nonradiative decay process by the $\pi−\pi$ interaction between the bpy ligands of $Ru(bpy)_3^{2+}$ and 4-styrensulfonate units,[17] suggesting that the majority of $Ru(bpy)_3^{2+}$ is interacting with an anionic PSS polymer chain to refrain from the electrostatic interaction with anionic PTA for the precipitation.

Electrodeposition produced an WO_3/$Ru(bpy)_3^{2+}$/PSS composite film on an ITO electrode under the potentiostat conditions (−0.45 V vs Ag/AgCl) up to 1.0 C cm^{-2} from the colloidal solution containing 1 mM $Ru(bpy)_3^{2+}$, 25 mM PTA, and 30

* Corresponding author. Phone/FAX: +81-25-262-7151. E-mail: yagi@ed.niigata-u.ac.jp.

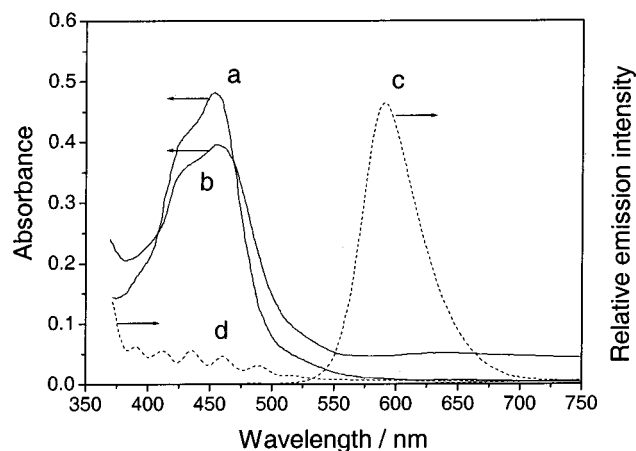**Figure 1.** Visible absorption spectra (solid lines) and photoluminescent spectra (dashed line) of Ru(bpy)$_3^{2+}$ in water (a and c) and WO$_3$/Ru-(bpy)$_3^{2+}$/PSS composite film (b and d).

Figure 2. Cyclic voltammograms of WO$_3$ film (A) and WO$_3$/Ru-(bpy)$_3^{2+}$/PSS composite film (B) dipped in 0.1 M KNO$_3$ aqueous solution (pH = 1.2) measured at 100 mV s^{-1} of scan rate. Inset illustrates electrochromism of the WO$_3$/Ru(bpy)$_3^{2+}$/PSS composite film, and the applied potentials are shown on the inset.

mM PSS. In contrast, the same electrodeposition from the solution only containing 1 mM Ru(bpy)$_3^{2+}$ and 25 mM PTA in place of the colloidal solution could not provide a WO$_3$ film containing Ru(bpy)$_3^{2+}$ even before forming precipitation (vide supra). When the electrodeposition was initiated before the colloidal formation in the solution containing Ru(bpy)$_3^{2+}$, PTA ,and PSS, a homogeneous film with a sufficient thickness could not be obtained. The colloidal formation is important for the preparation of the homogeneous and stable composite film.

The formation of the WO$_3$/Ru(bpy)$_3^{2+}$/PSS composite film on an ITO electrode was corroborated by a visible absorption spectrum and cyclic voltammogram (CV). The visible absorption spectrum of the composite film exhibited a maximum at λ_{max} = 456 nm based on metal to ligand charge-transfer transition of Ru(bpy)$_3^{2+}$ (Figure 1b), which is very similar to that (λ_{max} = 453 nm) observed in water (Figure 1a). The plots of the absorbance at 456 nm (no applied potential) vs the charge amount passed in the electrodeposition gave a linear relationship (slope = 0.50 C^{-1} (electrodeposition)) showing a homogeneous confinement of Ru(bpy)$_3^{2+}$ in the film.

The film thickness of the WO$_3$/Ru(bpy)$_3^{2+}$/PSS composite film was estimated to be 1.5 μm from the weight increase (1.07 mg cm^{-2}, 4.6 × 10^{-6} mol cm^{-2}) of the electrode by the electrodeposition and density (7.157 g cm^{-3}) of WO$_3$.[18] The coverage Γ/mol cm^{-2} of Ru(bpy)$_3^{2+}$ on the electrode was calculated from the absorbance data using the equation, Abs = $\epsilon\Gamma$ × 10^3, where Abs and ϵ/M^{-1} cm^{-1} are absorbance and molecular absorption coefficient of the composite film at 456 nm. The typical Γ at Abs = 0.40 was found to be 2.7 × 10^{-8} mol cm^{-2} using ϵ (14600 M^{-1} cm^{-1}) at maximum absorption (λ_{max} = 453 nm) in water.

A WO$_3$ film coated on an ITO electrode[19] gave a typical CV for n-type semiconductor shown in Figure 2A. Any redox wave was not observed above 0.3 V of its flat band potential. The redox below 0.3 V is based on the H$_x$WO$_3$/WO$_3$ accompanying electrochromic performance of dark blue/colorless. A CV of the WO$_3$/Ru(bpy)$_3^{2+}$/PSS film coated on the ITO electrode exhibited a reversible redox wave at 1.03 V, based on Ru-(bpy)$_3^{2+}$/Ru(bpy)$_3^{3+}$, which is nearly equal to its redox potential (1.06 V) measured in an aqueous solution, in addition to a redox due to H$_x$WO$_3$/WO$_3$ (Figure 2b). The linearity of the peak current at 1.15 V vs the charge amount passed in the electrodeposition (1.7 mA cm^{-2} C^{-1} (electrodeposition)) also supports the homogeneous confinement of Ru(bpy)$_3^{2+}$ in the film. The amount of the electroactive complex (2.5 × 10^{-8} mol

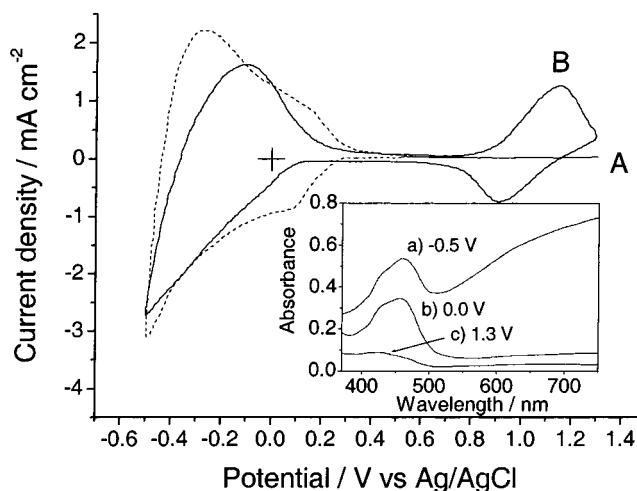cm^{-2}) calculated from integration of the anodic current (2.4 mC cm^{-2}), based on the oxidation of Ru(bpy)$_3^{2+}$, is consistent with the Γ (2.7 × 10^{-8} mol cm^{-2}) estimated from absorbance data. The flat band potential (0.13V) of the WO$_3$/Ru(bpy)$_3^{2+}$/PSS film-coated electrode is low by 0.17 V relative to that (0.30 V) of the WO$_3$ film-coated electrode.[20] This reveals that Ru(bpy)$_3^{2+}$ electronically interacts with the WO$_3$ film.

Electrochromic performances can be seen very clearly in the WO$_3$/Ru(bpy)$_3^{2+}$/PSS composite film, as shown in the inset of Figure 2. The absorption of the film covered all the visible region (due to H$_x$WO$_3$ and Ru(bpy)$_3^{2+}$) at −0.5 V of an applied potential. The absorption above 500 nm disappeared at 0.0 V, and an absorption band at 456 nm due to Ru(bpy)$_3^{2+}$ disappeared by applying 1.3V for the film which became colorless. It should be noted that all the Ru(bpy)$_3^{2+}$ in the film is oxidized, meaning even the complex at an interface between the WO$_3$ film and the bulk electrolyte solution is electroactive. Since Ru(bpy)$_3^{2+}$ is strongly interacting with the WO$_3$ matrix, it could not diffuse physically within the film. Presumably charge transport occurs by a hopping mechanism. We are currently undertaking advanced electrochemical experiment using potential step and impedance techniques to elucidate the detailed mechanism of this process.

Ru(bpy)$_3^{2+}$ emits an intense photoluminescence from its excited state in water and organic solvents as well as solid phases such as polymer films, intercalation compounds and ion exchange regions.[21] This is illustrated by the photoluminescent spectrum of Ru(bpy)$_3^{2+}$ in water shown in Figure 1c, whereas Ru(bpy)$_3^{2+}$ in the WO$_3$/Ru(bpy)$_3^{2+}$/PSS composite film does not emit any photoluminescence at all (Figure 1d). To evaluate the quenching of the excited Ru(bpy)$_3^{2+}$ by WO$_3$, photoluminescence was measured for a WO$_3$ particle film adsorbing Ru-(bpy)$_3^{2+}$ under the comparable coverage conditions (4.6 × 10^{-6} mol cm^{-2} for WO$_3$ and 2.7 × 10^{-8} mol cm^{-2} for Ru(bpy)$_3^{2+}$).[22] A distinguishable photoluminescence allowed us to measure a lifetime of the photoexcited state, giving the major lifetime component of 572 ns (93.5%). This result indicates that simple physical adsorption of Ru(bpy)$_3^{2+}$ onto WO$_3$ does not result in the complete quenching as observed for in the WO$_3$/Ru(bpy)$_3^{2+}$/PSS composite film. The electronic interaction between WO$_3$ and Ru(bpy)$_3^{2+}$ is considered to be a crucial factor for the effective quenching in the composite film.
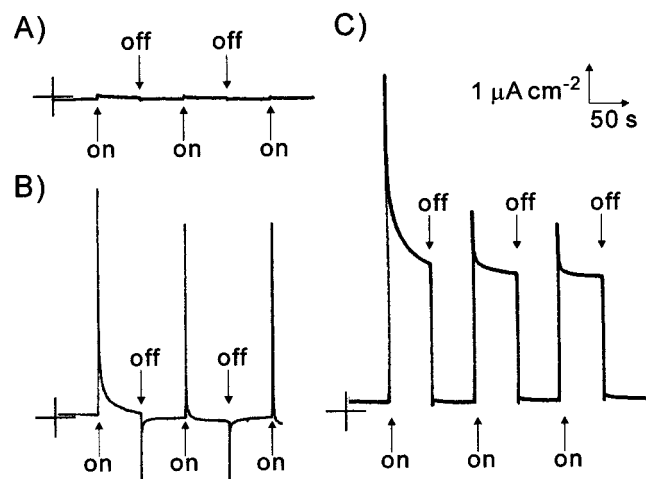
Letters

J. Phys. Chem. B, Vol. 106, No. 25, 2002 **6357**

Figure 3. Photocurrent responses induced by visible light at WO_3 film (A) and $WO_3/Ru(bpy)_3{}^{2+}/PSS$ composite film (B and C) coated on ITO electrodes dipped in 0.1 M KNO_3 aqueous solution (pH = 1.2) at 0.4 V of a rest potential. 0.1 M *p*-Cresol is present in the electrolyte of C).

Visible light irradiation on the $WO_3/Ru(bpy)_3{}^{2+}/PSS$ film-coated electrode induced an anodic spike current (4.7 μA cm^{-2}) that is remarkably high relative to only a trace of the photoresponse on the WO_3 film-coated electrode at the rest potential of 0.4V. (compare Figure 3A,B). In switching light off, a cathodic spike current was generated. This film-coated electrode demonstrates such a photocharging-discharging character in the range of 0.2 ∼ 0.7 V of bias potentials. The same photocurrent response experiment was conducted in an electrolyte solution including 0.1 M *p*-cresol as an electron donor for $Ru(bpy)_3{}^{3+}$ that is reported to work efficiently in an acidic aqueous solution.[23] The visible light irradiation provided significantly a steady-state photoanodic current (2.7 μA cm^{-2}) after the spike response shown in Figure 3C. The photocurrent induced by photoexcitation of $Ru(bpy)_3{}^{2+}$ was corroborated by an action spectrum of the photocurrent consistent with the absorption spectra of $Ru(bpy)_3{}^{2+}$ in the WO_3 film. The photocharging process is explained by an electron injection from excited $Ru(bpy)_3{}^{2+}$ presumably to the conduction band of WO_3. Back-electron transfer from the conduction band to photogenerated $Ru(bpy)_3{}^{3+}$ could be responsible for the discharging process under the dark. In the presence of *p*-cresol in the electrolyte solution it should scavenge $Ru(bpy)_3{}^{3+}$ efficiently, producing the steady-state anodic current.

As a comparison, we conducted the same photocurrent experiments using a $Nafion/Ru(bpy)_3{}^{2+}$ film-coated ITO electrode,[24] but no photoresponse are detected at the electrode in the potential range of 0.0−0.8 V. $Ru(bpy)_3{}^{2+}$ in the Nafion film showed an intense photoluminescence, in contrast to complete quenching in the $WO_3/Ru(bpy)_3{}^{2+}/PSS$ composite film. The effective quenching by the WO_3 matrix could lead to significant visible light-induced current.

The $WO_3/Ru(bpy)_3{}^{2+}/PSS$ composite film could expand molecular photoelectronics including multiple electrochromic devices and photochemical solar energy cell. We are starting to design the multilayer electrochromic devises as well as efficient solid-state photochemical solar cells, based on the present composite film.

References and Notes

(1) Giraudeau, A.; Fan, F. R. F.; Bard, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 5137.

(2) Santato, C.; Odziemkowski, M.; Ulmann, M.; Augustynski, J. *J. Am. Chem. Soc.* **2001**, *123*, 10639.

(3) Bechinger, C.; Ferrer, S.; Zaban, A.; Sprague, J.; Gregg, B. A. *Nature* **1996**, *383*, 608.

(4) Nagasu, M.; Koshida, N. *J. Appl. Phys.* **1992**, *71*, 398.

(5) Santato, C.; Ulmann, M.; Augustynski, J. *J. Phys. Chem. B* **2001**, *105*, 936.

(6) Sayama, K.; Mukasa, K.; Abe, R.; Abe, Y.; Arakawa, H. *Chem. Commun.* **2001**, 2416.

(7) Colton, R. J.; Guzman, A. M.; Rabalais, J. W. *J. Appl. Phys.* **1978**, *49*, 409.

(8) Yous, B.; Robin, S.; Donnadieu, A.; Dufour, G.; Maillot, C.; Roulet, H.; Senemaud, C. *Mater. Res. Bull.* **1984**, *19*, 1349.

(9) Yamanaka, K.; Oakamoto, H.; Kidou, H.; Kudo, T. *Jpn. J. Appl. Phys. Part 1—Regul. Pap. Short Notes Rev. Pap.* **1986**, *25*, 1420.

(10) Shen, P. K.; Tseung, A. C. C. *J. Mater. Chem.* **1992**, *2*, 1141.

(11) Gallagher, L. A.; Meyer, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 5308.

(12) O'Regan, B.; Gratzel, M. *Nature* **1991**, *353*, 737.

(13) Trammell, S. A.; Meyer, T. J. *J. Phys. Chem. B* **1999**, *103*, 104.

(14) Yagi, M.; Kaneko, M. *Chem. Rev.* **2001**, *101*, 21.

(15) Yagi, M.; Takahashi, Y.; Ogino, I.; Kaneko, M. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3125.

(16) 0.92 g (5.0 mmol) of tungsten powder was slowly dissolved in a 30% hydrogen peroxide solution and then excess hydrogen peroxide was decomposed by Pt black. Ethanol was added to the solution for stabilizing PTA solution[10] to prepare finally an aqueous ethanol solution (30 vol %) containing 50 mM PTA (100 mM respect to W concentration; the structure of PTA in an aqueous solution is reported to be $[(O_2)(O)W \cdot O \cdot W(O)(O_2)]^{2-}$ (ref 9 and 10)). This solution was used as a stock PTA solution. $Ru(bpy)_3{}^{2+}$ solution was added to the PTA stock solution to obtain the aqueous ethanol solution (30 vol %) containing 1 mM $Ru(bpy)_3{}^{2+}$ and 25 mM PTA solution.

(17) Kurimura, Y.; Yokota, H.; Shigehara, K.; Tsuchida, E. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 55.

(18) Shen et al. reported that their WO_3 film prepared by similar electrodeposition up to 600 mC cm^{-2} has the thickness of 0.5−1.0 μm. The estimated thickness (1.5 μm) of our film is reasonable when considering our WO_3 film was prepared by the electrodeposition up to 1.0 C cm^{-2}. The dark blue color due to H_xWO_3 generated in applying potential of −0.5 V (see inset of Figure 2) is a measure of the amount of WO_3 deposited. Nearly the same absorbances (0.719 and 0.733) at 750 nm were obtained for the WO_3 film and $WO_3/Ru(bpy)_3{}^{2+}/PSS$ composite film in applying −0.5 V, both of which were prepared under the same electrodeposition conditions. This result suggests the almost identical film thickness between the WO_3 film and $WO_3/Ru(bpy)_3{}^{2+}/PSS$ composite film.

(19) AWO_3 film was electrodeposited on an ITO electrode under the potentiostat conditions (−0.45 V vs Ag/AgCl) from an aqueous ethanol solution (30 vol %) containing 25 mM PTA and 30 mM PSS.

(20) To evaluate the shift (0.30 to 0.13 V) in the flat band potential by $Ru(bpy)_3{}^{2+}$, the redox response between Prussian Blue (PB; ferric ferrocyanide, $Fe^{II}-Fe^{III}$) and Prussian White (PW; $Fe^{II}-Fe^{II}$) (redox potential = 0.16 V) was investigated on the WO_3 film or $WO_3/Ru(bpy)_3{}^{2+}/PSS$ composite film. If the flat band potential shifts from 0.30V to 0.13V, the redox response between PB and PW could be observed on the WO_3 film, but could not on the $WO_3/Ru(bpy)_3{}^{2+}/PSS$ composite film. A clear reversible redox wave between PB and PW was actually seen at an $ITO/WO_3/PB$ bilayer electrode, whereas the redox response was not observed at all at an $ITO/(WO_3/Ru(bpy)_3{}^{2+}/PSS)/PB$ bilayer electrode. This result shows that the flat band potential (0.30 V) of WO_3 films shifts down by electronic interaction of $Ru(bpy)_3{}^{2+}$ with WO_3 to prevent electron transfer between the electrode and PB layered on the $WO_3/Ru(bpy)_3{}^{2+}/PSS$ film.

(21) Lin, R.-J.; Kaneko, M. Photoelectrochemical Devices Utilizing Molecular-based Excited-state Reaction at Coated Polymer Membrane. In *Molecular Electronics*; Sienicki, K., Ed.; CRC Press: London, 1993; Vol. 1; p 207.

(22) A WO_3 aqueous suspension (100 mM, 46 μL) was cast and vacuum-dried on a grass substrate to form the WO_3 particle film, and then $Ru(bpy)_3{}^{2+}$ aqueous solution (1mM, 27 μL) was dropped on the WO_3 particle film and air-dried to form the WO_3 particle film adsorbing $Ru(bpy)_3{}^{2+}$.

(23) Hirata, J.; Yagi, M.; Oriyama, T.; Kaneko, M.; Kurimura, Y. *J. Chem. Soc.-Faraday Trans.* **1996**, *92*, 969.

(24) A Nafion film was prepared by casting and air drying of a 2.5 wt % Nafion solution onto an ITO electrode. The film was immersed in an aqueous solution $Ru(bpy)_3{}^{2+}$ to incorporate it into the film to obtain a $Nafion/Ru(bpy)_3{}^{2+}$ film-coated ITO electrode. (The film thickness is 1.0 μm, and absorbance at 453 nm is 0.420.)