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Electrical conductivity of doped porous glasses as possible sensors for oxygen

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We are proposing Rubpy complex incorporated in a number of porous sol–gel thin films as a sensor for oxygen. The principle is based on the following fact: triplet oxygen reacts with the excited states of Rubpy resulting in decay of luminescence of the complex due to triplet quenching. The decrease of fluorescence is proportional to the amount of absorbed oxygen. We discuss here several sol–gel matrices with doped by $Ru(bpy)_3^{+2}$ deposited as thin films on ITO conducting glass. The absorption and emission spectra of the complex, and electrical conductivity of the doped films show how the fluorescence can be excited either by optical or electronic means. The decrease of fluorescence indicates the concentration of oxygen.

Keywords: Rubpy complex, porous glasses, sensors for oxygen, fluorescence, electrical conductivity.

1. Introduction

A sensor for oxygen is of major importance in environmental, industrial and medical applications. The amount of oxygen dissolved in water is an indication of the quality of the water, and careful control of oxygen levels is important in fermentation processes and in food preparation. A knowledge of oxygen levels in blood is necessary for physiological and other medical studies. Optical oxygen sensing is usually based on collisional quenching of a fluorophore embedded in a support matrix [1–6]. The quenching process is described by the Stern–Volmer equation [4]:

$$\frac{F_o}{F} = 1 + K_{SV}[Q]$$

where: F_o is the unquenched fluorescence intensity, F is the fluorescence intensity at $[Q]$, $[Q]$ is the quencher (oxygen) concentration, K_{SV} is the Stern–Volmer constant,

$K_{SV} = \kappa_q \tau_o$ (κ_q – the bimolecular quenching constant, τ_o – the fluorescence lifetime in the absence of quencher).

Ruthenium tris bipyridyl $Ru(bpy)_3^{+2}$, the well known oxygen-sensitive complex, can be used as a chemical sensor because of its attractive properties, such as luminescence with a long excited state lifetime, redox properties, excited state reactivity and relatively high thermal and chemical photostability. Such remarkable features allow to use ruthenium complexes as doped material for optical sensors, photocatalysts, photoelectrodes for solar cells, nonlinear optical materials [7–13]. The structural formula of ruthenium tris bipyridyl ion is presented in Figure 1. The complex is six coordinated with the calculated size of the molecule of about 1.2 nm. To assign bands in the spectra, we restrict ourselves to the system with a d^6 electron configuration (which means that the central Ru^{2+} ion has six d electrons) in the octahedral environment. The simplified energy level diagram of the $[Ru(LL)_3]^{2+}$

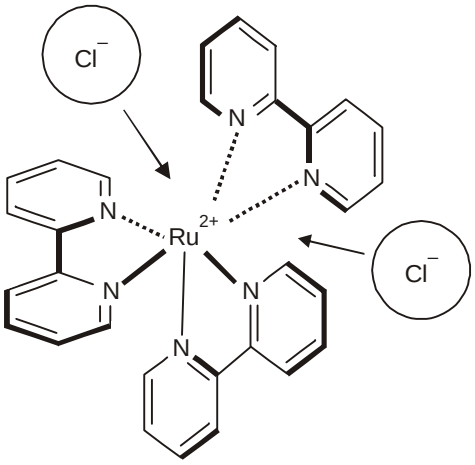

Fig. 1. The schematic structure of ruthenium tris bipyridyl ion.

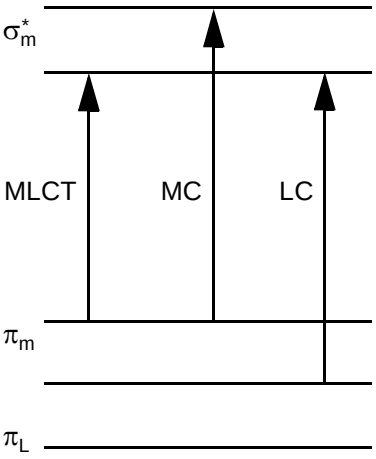

Fig. 2. Simplified energy level diagram of molecular orbitals for $Ru(LL)_3^{+2}$ complexes with octahedral symmetry. Tree types of transitions with the lowest energy are shown.

in the one electron approximation for the octahedral symmetry is presented in Fig. 2 [14]. Promotion of an electron from the π_M orbital of a metal to the π_L^* orbital of a ligand results in the metal-to-ligand charge transfer (MLCT), while promotion of an electron from the π_M orbital to the σ_M^* orbitals produces the metal centred (MC) excited state. The ligand-centred (LC) excited states result from the electron transfer from π_L orbitals to the π_L^* orbital. All these excited states can have singlet or triplet nature, although the spin-orbital coupling causes singlet- triplet mixing of the MC and MLCT excited states. The ground state of the complex is a singlet one.

The long-wavelength absorption band of polypyridine complexes of ruthenium(II) in a porous glass with a maximum at 450 nm corresponds to the MLCT transitions. This band virtually does not shift when the complex is transferred from solution to the absorbed state. However, the short-wavelength absorption bands (270–340 nm), which are assigned to the LC transitions, show appreciable changes in their shape, intensity, and position upon adsorption of complexes. This can be qualitatively explained by the heterogeneous environment of adsorbed complexes on the surface of a porous glass.

The absorption at 450 nm arises from electron transfer of the ground state of the complex to the relatively long-lived MLCT excited states. The fluorescence is the opposite process. The quenching of the excited states of ruthenium polypyridyl complexes by molecular oxygen can, in principle, occur mostly *via* two mechanisms. One is energy transfer triplet quenching (Eq. (1)) generating the ground state sensitizer and singlet oxygen; the other is electron transfer quenching (Eq. (2)) generating the oxidized Ru complex and the superoxide radical anion:

$$RuL_3^{2+*} + O_2 \rightarrow RuL_3^{2+} + O_2(^1\Delta_g) \tag{1}$$

$$RuL_3^{2+*} + O_2 \rightarrow RuL_3^{3+} + O_2^{*-} \tag{2}$$

Sol–gel porous glass films as attractive material for oxygen sensors can be produced at low temperatures by the sol–gel technique. Sol–gel process is very well adapted for thin-film fabrication either by spin-coating or dip-coating techniques. Sol–gel porous films has been increasingly used as a solid matrix for entrapment of chemical and biochemical agents in sensor development, such as pH, gases or glucose sensors, for entrapment of organic dyes, proteins, enzymes and microbiological cells. The advantage of using doped sol–gel glasses for sensing material preparation is that they are thermally, chemically and photochemically stable. Sol–gel based ormosil optical sensors for both gas phase and dissolved oxygen were investigated [3]. The principle of the sol–gel sensor is based on fluorescence quenching of ruthenium tris bipyridyl $Ru(bpy)_3^{+2}$ which is entrapped in a porous sol–gel film.

Here we are considering the sol–gel porous films with strong luminescence of the $Ru(bpy)_3^{+2}$ around 600 nm as a potential material for oxygen sensor. Several matrices were prepared by sol–gel methods: zirconia, silica, zirconia-glymo, silica-

-polyurethane, stannic oxide and tungsten oxide doped by various concentrations of $Ru(bpy)_3^{+2}$. The electrical conductivity was measured for tungsten oxide and tin oxide doped films. In addition, optical absorption and luminescence spectra were obtained. Here we discuss the several sol–gel matrices with doped $Ru(bpy)_3^{+2}$ deposited as a thin film on ITO conducting glass. Based on previous results [15], which show that electrically excited complex of Rubpy exhibits electroluminescence identical with the luminescence excited optically, we conclude that Ru complexes incorporated in sol–gel porous glasses can be used as oxygen sensors excited optically or electrically.

2. Experimental section

Thin films doped by Rubpy were prepared by sol–gel method. ZrO_2, SiO_2, SiGl (silica combined with glycidoxypropyltrimethoxysilane (glymo)) WO_3 and SnO_2 sol–gel matrices were used as host material.

The preparation of the sol–gel solutions:

1. ZrO_2 matrix was obtained using a procedure similar to that reported in [16]. The 10 ml of zirconia(IV) *n*-propoxide diluted in 20 ml of *n*-propanol with addition of 3.5 ml of glacial acetic acid has been hydrolyzed with 4 ml of acetic acid-water solution (1:1) under stirring for 30 min, filtered and stored in refrigerator for some days.

2. SiO_2 sol–gel matrix was prepared as described in [17]. The 1.5 ml of tetramethoxysilane (TMOS) diluted in 10 ml ethanol has been hydrolyzed with 1.1 ml water at the presence of 0.5 ml of hydrochloric acid. After filtration, silica sol–gel solution was stored in refrigerator.

3. SiGl matrix was obtained by intermixing the precursor of SiO_2 matrix and glymo at molar ratio 1:1 and stirred about 1 hour.

4. Diurethane olygomer and zirconia-silica-polyurethane films were obtained as described in [18].

5. SnO_2 sol–gel matrix was obtained using slightly modified procedure presented in [19]: 4.17 g of tin(II) chloride 2-hydrate has been dissolved in 50 ml of ethanol to get 0.37 molar solution and hydrolyzed for 6 hours at 80 °C and 17 hours at room temperature, filtered, diluted by glycerol and stored in refrigerator.

6. WO_3 sol–gel matrix solution was obtained according to the method of KUDO *et al.* [20, 21]. The 22 ml of H_2O_2 (30%) were reacted with small pieces of tungsten metallic powder (5 g, Fluka, 99%). The mixture was stirred for 12 hours at room temperature until all the tungsten had dissolved. A platinum net was then added to the mixture to remove any unreacted H_2O_2. After the addition of ethanol (20 g), the solution was heated at 80 °C for 4 hours until the color of the sol turned from milky to a clear orange.

The concentration (0.6 mol%) of Rubpy was dissolved in 1.7 ml ethanol and added to 8 ml of each matrix. Films were deposited on quartz slides (for optical measurements) or on ITO film (for electrical measurements) by dip-coating technique. Films were dried at room temperature and annealed at 150 °C during 30 min.

3. Results and discussion

3.1. Optical measurements

Figure 3 shows absorption spectra (**a**) and excitation and fluorescence spectra (**b**) of Rubpy complex incorporated in various sol–gel thin films. Quenching of Rubpy by oxygen in silica sol–gel glasses was shown by many authors, for example [3]. This effect is used for fluorescence oxygen sensor.

3.2. Electrical measurements

Figure 4 presents the device for electrical measurements [22]. Experimental setup consists of Au/sol–gel-doped film/ITO device, where: 1 – glass substrate, 2 – ITO film 3 – Au contacts, 4 – sol–gel-doped film. Figure 5 shows electrical measurements

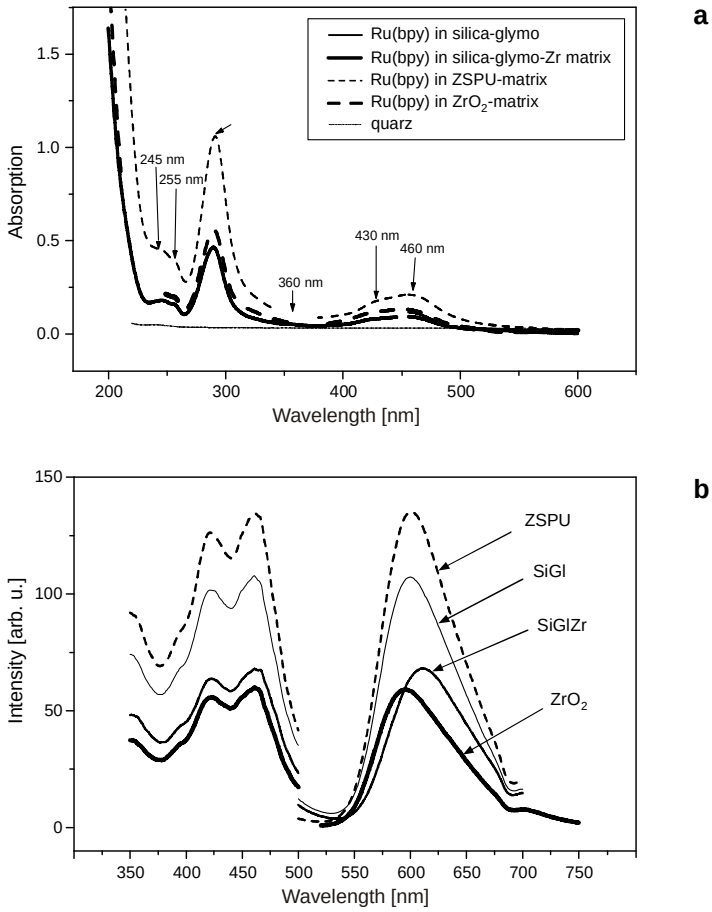

Fig. 3. Absorption spectra (**a**) and excitation and fluorescence spectra (**b**) of Rubpy complex (c = 0.25 mol%) in silica-glymo, silica-glymo-zirconia, zirconia-silica-polyurethane and zirconia, thin films.

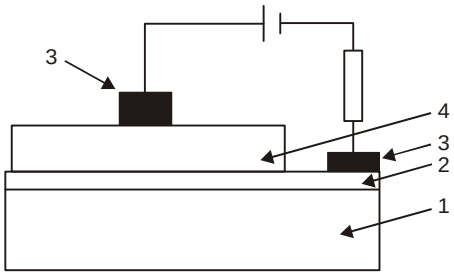

Fig. 4. Experimental setup of Au/sol–gel-doped film/ITO device (1 – glass substrate, 2 – ITO film, 3 – Au contacts, 4 – sol–gel-doped film).

results obtained on the films of WO_3 and SnO_2 (as a reference) and doped films with Rubpy.

The specific conductivity of 0.7×10^{-3} $\Omega^{-1}cm^{-1}$ was obtained on SnO_2 layer of about 200 nm thickness, while the conductivity of 0.5×10^{-4} $\Omega^{-1}cm^{-1}$ was obtained on WO_3 layer with the same thickness. It has been found that the conductivity of SnO_2

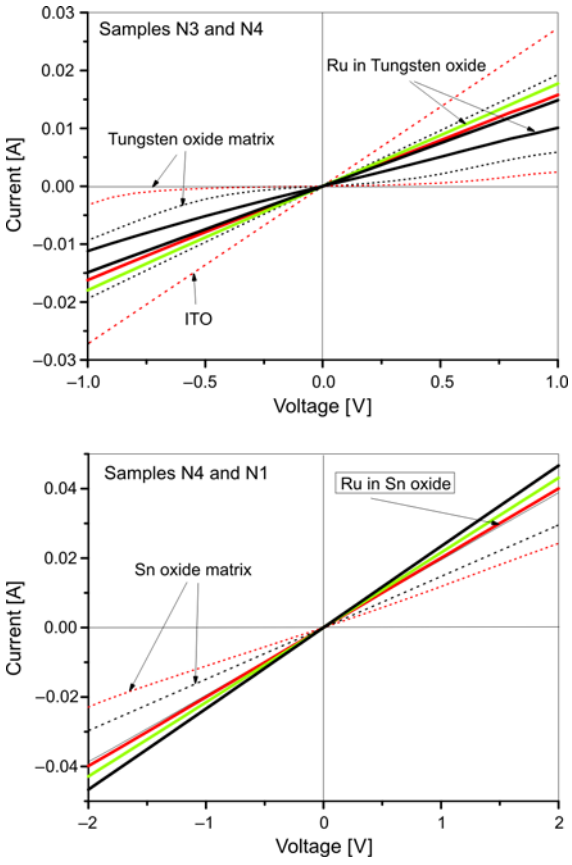

Fig. 5. Electrical measurements performed on the films of WO_3 and SnO_2 (as a reference) and doped films with Rubpy.

T a b l e. Resistance and specific conductivity of Tin and Tungsten films and Tin and Tungsten films doped by ruthenium complex (h = 200 nm), h_{Au} = 25 nm.

	SnO_2 film	SnO_2 film doped by ruthenium complex	WO_3 film	WO_3 film doped by ruthenium complex
R [Ω]	80	20	1000	40
Conductivity [$\Omega^{-1}cm^{-1}$]	0.7×10^{-3}	2.5×10^{-3}	0.5×10^{-4}	1.25×10^{-3}

doped by Rubpy was increased by 3.5 times and WO_3 films doped by Rubpy was improved by twenty-five times.

YANG *et al*. [15] have studied the thin film light emitting device using a ruthenium(II) (4, 7-diphenyl-1, 10-phenanthroline)$_3$ complex as an emitter in a structure of ITO// Ru(dphphen)//Ag, and shown that electroluminescence (EL) of thin films is identical with the luminescence excited optically. Therefore we can conclude that Rubpy complexes incorporated in sol–gel porous glasses can be used as oxygen sensors excited optically or electrically.

4. Conclusions

We have shown that Rubpy complex incorporated in porous thin films prepared by the sol–gel method can be used as an oxygen sensor. The principle is based on the following fact: triplet oxygen reacts with the excited states of Rubpy resulting in decay of luminescence of the complex due to triplet quenching; the decrease of fluorescence is proportional to the amount of absorbed oxygen.

In this paper we have shown experimental results of absorption and emission of Rubpy complex incorporated in a number of sol–gel films. We have shown that sol–gel films of WO_3 and SnO_2 doped by Rubpy exhibit electrical conductivity enhanced by the presence of Rubpy.

Based on many papers [15] showing electroluminescence (EL) of thin films doped by various Ru complexes, we come to the conclusions that by using a proper experimental arrangement it is possible to excite EL of Rubpy in sol–gel matrices. Since the origin of the emission of Rubpy is independent of the way by which it was excited, such emission, either optically or electrically excited, can be the origin of a sensor of oxygen.

Obtained absorption and emission spectra of the complex, and electrical conductivity of the doped films show how the fluorescence can be excited either by optical or electronic means.

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