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Research paper

Comparative study of the anchorage and the catalytic properties of nanoporous TiO_2 films modified with ruthenium (II) and rhenium (I) carbonyl complexes

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ABSTRACT

In this article we study the anchoring of cis-[Ru(bpyC$_4$pyr)(CO)$_2$(CH$_3$CN)$_2$]$^{2+}$, cis-[Ru(bpy)$_2$(CO)$_2$]$^{2+}$ and cis-[Ru(bpyac)(CO)$_2$Cl$_2$], onto nanoporous TiO_2 employing electropolymerization, electrostatic interaction and chemical bonding. Also, the [Re(bpyac)(CO)$_3$Cl] rhenium(I) complex for chemical anchorage was analyzed. The characterization of TiO_2/Ru(II) and TiO_2/Re(I) nanocomposite films was performed by field emission scanning electron microscopy (FESEM), electron dispersive X-ray spectroscopy (EDS) and Raman spectroscopy. In addition, for the more stable nanocomposites obtained, the catalytic properties (solar energy conversion and CO_2 reduction) were evaluated. The efficiency improvement in redox process derived from the (photo)electrochemical evidence indicates that modified nanoporous TiO_2 structures enhance the rate of charge transfer reactions.

1. Introduction

The photovoltaic cells based on titanium dioxide are well-known for its high-efficiency in dye-sensitized solar cells since Grätzel and co-workers incorporated dinitrogenated ruthenium (II) complexes onto the TiO_2 surface [1–3]. TiO_2 surfaces as rutile or anatase-like forms have a skeleton of titanium and oxygen atoms spatially distributed [4,5] providing a high number of Ti–OH groups on the solid surface [6,7], which allows linking of organometallic compounds and organic chains for the preparation of hybrid materials [8–10]. On the other hand, the controlled manufacture of dye-sensitized TiO_2 structures at the nanometric scale allows either promote or suppress the recombination of electron and hole pairs upon UV–visible light excitation, conferring to TiO_2-based materials an increasing interest within renewable energy and environment fields as well as in nanotechnology [1–5,8,9].

In the last decades, numerous studies have been conducted involving auto-organized nanostructures of different metal oxides and semiconductors, which have received considerable attention due to the potential technological uses of these materials [11,12]. In this way, in order to increase the versatility of the physicochemical properties for different applications, novel modification strategies of nanostructured TiO_2 films have been investigated [13–15].

On the other hand, several reports on the general, flexible and modular ruthenium(II) complexes synthesis of type cis-Ru(N,N)$_2$X$_2$ (where N,N is a dinitrogenated ligand and X is an halide such as chloride) conclude that the electronic effects produced by the ligands nature and coordination position are fundamental to control their electrochemical properties [16–19]. In addition, numerous studies on electron transfer and transport processes in solar cells based on TiO_2 with ruthenium (II) complexes have demonstrated successful results in energy conversion [16,20]. These findings encourage the development of new methods to immobilize ruthenium-based catalysts onto semiconducting or conducting supports with the purpose of obtaining heterogeneous catalysts. Furthermore, other transition metal complexes such as rhenium compounds have been studied for their photo-

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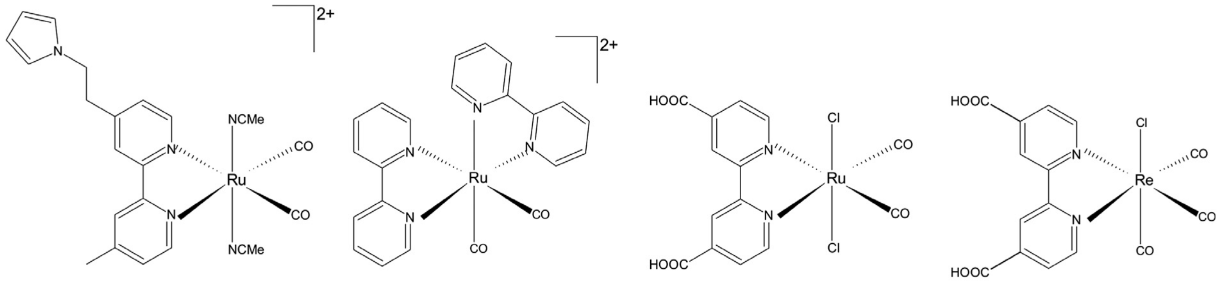

1 **2** **3** **4**

Scheme 1. Schematic representation of $[Ru(bpyC_4pyr)(CO)_2(CH_3CN)_2]^{2+}$ (1), $[Ru(bpy)_2(CO)_2]^{2+}$ (2), $[Ru(bpyac)(CO)_2Cl_2]$ (3) and $Re(bpyac)(CO)_3Cl]$ (4) complexes, respectively.

and electrocatalytic properties for the reduction of CO_2 [21–23]. Among several reported compounds, the ruthenium (II) and rhenium (I) complexes harboring carbonyl ligands have promising catalytic properties with the choice of suitable bidentate ligands [24–27]. This type of catalysts could have important applications in new devices for the conversion of CO_2 to value added molecules such as CO, which represent an important technological and environmental challenge [16,21,26,27].

Based on these findings, we carried out the study of nanocomposites based on nanoporous TiO_2 films modified with ruthenium (II) and rhenium (I) complexes (see Scheme 1) by electropolymerization, electrostatic interaction and chemical bonding. The morphologic and chemical characterization of the nanocomposite films obtained for the different anchorage methods is performed by field emission scanning microscopy (FESEM), electron dispersive X-ray spectroscopy (EDS) and Raman spectroscopy. In addition, for the more stable and homogeneous nanocomposite materials obtained, the potential applications in the electroreduction of CO_2 and its applicability as a solar to electrical energy converter by photoelectrochemical methods are evaluated.

2. Experimental

All the starting materials were purchased from Merck and Aldrich and used without further purification. The cis-$[Ru(bpyC_4pyr)(CO)_2(CH_3CN)_2]^{2+}$, cis-$[Ru(bpy)_2(CO)_2]^{2+}$, cis-$[Ru(bpyac)(CO)_2Cl_2]$ and $[Re(bpyac)(CO)_3Cl]$ complexes used in this study were prepared according to literature procedures [28–31]. The anodization of titanium was performed as previously reported [32]. $TiO_2/[Ru(bpyC_4pyr)(CO)_2(CH_3CN)_2]_n$ polymetallic (Ru-Ru) films were grown by continuously cycling the potential between −0.90 and −1.70 V on a TiO_2 nanoporous electrode in a 1 mM solution of $[Ru(bpyC_4Pyr)(CO)_2(CH_3CN)_2]^{2+}$. For the $TiO_2/[Ru(bpy)_2(CO)_2]^{2+}$ modified surface, a previous reduction of the TiO_2 nanoporous electrode by application of a potential pulse at −1.50 V in a solution of CH_3CN + 0.1 M TBAP for 5 min was performed. After that, the ruthenium complex was anchored to the TiO_2 nanoporous film by dipping in a 5 mM of $[Ru(bpy)_2(CO)_2]^{2+}$ in acetonitrile solution for 80 h. Otherwise, prior to the nanoporous TiO_2 surface modification with the $[Ru(bpyac)(CO)_2Cl_2]$ or $[Re(bpyac)(CO)_3Cl]$ complexes, the TiO_2 films was soaked for 1 h in a NaOH aqueous solution (pH 13), copiously washed with water, rinsed with 5 mL of acetonitrile and dried with argon. After that, the catalysts were anchored to the TiO_2 nanoporous films by dipping in a 5 mM of $[Ru(bpyac)(CO)_2Cl_2]$ or $[Re(bpyac)(CO)_3Cl]$ acetonitrile solution for 20, 40, and 80 h.

Electrochemical measurements were made using an EG&G Princeton Applied Research model 273 or 173 potentiostat/galvanostat equipped with a Sefram TGM 164 X–Y recorder. All cyclic voltammograms were obtained in a conventional three-electrode cell under argon or carbon dioxide atmosphere. All potentials reported in organic media are relative to $Ag/AgNO_3$ 10 mM in CH_3CN + 0.1 M TBAP. Supporting electrolyte was n-Bu_4NClO_4 (TBAP) from Fluka. Acetonitrile from Rathburn (HPLC grade) was used as received.

The surface morphology of the modified TiO_2 electrodes was characterized using a Carl Zeiss ∑igma model FESEM microscope. The chemical identification and mapping of the atomic elements in the modified nanoporous TiO_2 films were performed using an EDS spectrometer coupled to the FESEM microscope. Raman experiments were performed ex situ (in air) using a Horiba LabRAM HR spectrometer employing an Ar laser (514.5 nm wavelength). Photoelectrochemical measurements were carried out under solar simulation conditions, employing an UV enhanced Xe lamp of 150 W (Newport Oriel Instruments 6254) mounted in a lamp holder (Oriel 67,005), a water filter (Oriel 61,945) and connected to the cell with a 1 m length optical fiber (Oriel 77,578). A power supply of 40–200 W (Oriel 68,907) was used to generate the arc in the lamp. The illumination power was quantified inside the cell by means of an energy radiant meter (Oriel 70,260). The samples were illuminated at a constant light intensity of 4.0 mW cm^{-2}.

3. Results and discussion

3.1. Preparation and characterization of TiO_2/[M complex] nanocomposites

In order to obtain stable TiO_2/[M complex] nanocomposites for (photo)electrocatalytic investigations, three different ruthenium (**1**–**3**, Scheme 1) and one rhenium (**4**, Scheme 1) coordination complexes were employed. Additionally, according to the chemical nature of the ligands present in the complex molecules, the modification of the nanoporous TiO_2 film was performed by different methods. Furthermore, for the more stable and homogeneous nanocomposites obtained, the chemical characterization by electron dispersive X-ray spectroscopy (EDS) and Raman spectroscopy as well as the photoelectrochemical and electrocatalytic performance are studied.

3.1.1. Electropolymerization

Anodic electropolymerization of the N-functionalized pyrrole (pyr) side of $[Ru(bpyC_4pyr)(CO)_2(CH_3CN)_2]^{2+}$ complex (**1**), is one of the possible ways to modify conductive surfaces [33]. However, for semiconductor materials like TiO_2 nanoporous electrodes, is not possible to carry out the anodic pyr electropolymerization of the complex because of the nanoporous TiO_2 surface does not present enough electronic conductivity in the anodic potential region. For this reason, the anchorage on TiO_2 nanoporous electrodes was