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Polypyrrole-Ru(2,2′-bipyridine)$_3$$^{2+}$/MoS$_x$ Structured Composite Film As a Photocathode for the Hydrogen Evolution Reaction

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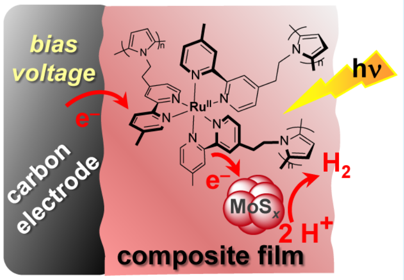
Supporting Information

ABSTRACT: The development of photoelectrochemical devices for solar light-driven water splitting and H_2 production requires new strategies for the fabrication of materials that combine the necessary photoredox and catalytic properties, to allow the hydrogen evolution reaction (HER) to take place at a low overvoltage under visible light irradiation. We report the first example of a structured composite, synthesized by electrodeposition of MoS$_x$ cocatalyst into a photosensitive Ru complex film deposited onto carbon electrodes by electropolymerization of a pyrrole-functionalized Ru^{II}(2,2′-bipyridine)$_3$$^{2+}$. Composite films show efficient photocatalytic activity for HER. Our study highlights the great simplicity of this versatile electrochemical procedure to synthesize photocathodes.



KEYWORDS: *MoS$_x$, Ru(2,2′-bipyridine)$_3$$^{2+}$, nanocomposite, photocathode, solar fuels, hydrogen evolution reaction*

Changing our modes of energy production is becoming a crucial scientific challenge. To achieve it, we must substitute fossil fuels with those issuing from the utilization of renewable and sustainable energy sources, such as solar energy. From this perspective, hydrogen gas has emerged as an attractive candidate for a storable clean fuel. An important step toward meeting this goal is to develop systems able to produce hydrogen from water by electrochemical, or better yet photoelectrochemical (PEC) water splitting. The construction of photoelectrochemical devices requires the development of efficient photocathodic materials which combine the necessary photoredox and catalytic properties, in order to allow the hydrogen evolution reaction (HER) to take place at a low overvoltage under visible-light irradiation. The first photocathodes of this type were made using deposited platinum on a photoactive layer,[1] this metal being well-known as the best catalyst for the HER. However, because Pt is a relatively rare and expensive noble metal, it is necessary to replace it by an earth-abundant element for large-scale applications. Among these molydenum derivatives and especially molybdenum sulfides (denoted MoS$_x$) appear to be promising HER materials.[2−4] Several examples of efficient photoelectrodes for the HER based on hetero (junction) structures combining MoS$_x$ with an inorganic or organic semiconductor as the light collector have been recently reported.[5−12] Surprisingly, although photocatalytic H_2 evolution has been achieved using a combination of a molecular redox photosensitizer and MoS_2 in solution,[13−16] no equivalent system fully immobilized on a conductive surface has been tested as photocathode for the HER. In this regard, we propose herein a novel concept for the straightforward fabrication of this type of photocathode, and we describe its performance toward photoinducing protons reduction and the HER in aqueous electrolytes.

Recently, we performed the electrosynthesis of composite electrode materials by encapsulation of noble metal oxide nanoparticles into functionalized cationic poly(pyrrole-alkylammonium) films.[17−19] These showed efficient electrocatalytic activity and an improved operational stability exceeding that of regular metal oxide-based electrode materials,[17−19] especially toward water oxidation and the oxygen evolution reaction.[19] The excellent catalytic performances of these composite electrode materials were attributed to their nanostructure. Inspired by this, we have designed a photocathode material by using thin films of polypyrrole bounded to a tris(bipyridyl)ruthenium(II) complex, coated on a conducting surface;[20] such films are known to be able to photoinduce redox reactions with electron acceptors.[21] We also took advantage of the good anion-exchange capacity of these cationic films[20] to efficiently incorporate tetrathiomolybdate anions (MoS$_4$$^{2-}$) species, and thereafter to electroreduce them in order to precipitate MoS$_x$ as a cocatalyst into the polymer matrix to form a photosensitive, catalytically active composite cathode material for the HER.

Polypyrrole films bonded to a Ru(II) complex (denoted polyRu) were coated onto carbon electrodes by anodic polymerization of the pyrrole-substituted complex Ru(L)$_3$$^{2+}$, in which L is the 4-(4-pyrrol-1-ylbutyl)4′-methyl-2,2′-bipyridine ligand (Scheme S1 and Figure S1 in Supporting Information).[20] MoS$_x$ was then precipitated into polyRu films by incorporation of MoS$_4$$^{2-}$ by ion exchange performed in organic solution, followed by electroreduction of the trapped MoS$_4$$^{2-}$ species by repeated cyclic voltammetry (CV) cycles in near-neutral (pH 6) aqueous electrolyte. The CV features for the electroinduced transformation

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of MoS_4^{2-} to MoS_x (Figure S2, Supporting Information) are similar to those observed in the course of the electrodeposition of amorphous MoS_x films[22,23] from aqueous solutions of $[(NH_4)_2MoS_4]$ on a carbon electrode (see Figure S5A, Supporting Information). The amount of incorporated MoS_4^{2-}, and thus the quantity of MoS_x deposited in the polyRu films, was estimated to be one MoS_x per two $Ru(L)_3^{2+}$ units, on the basis of CV experiments carried out in CH_3CN electrolyte (see Figure S4 in the Supporting Information).

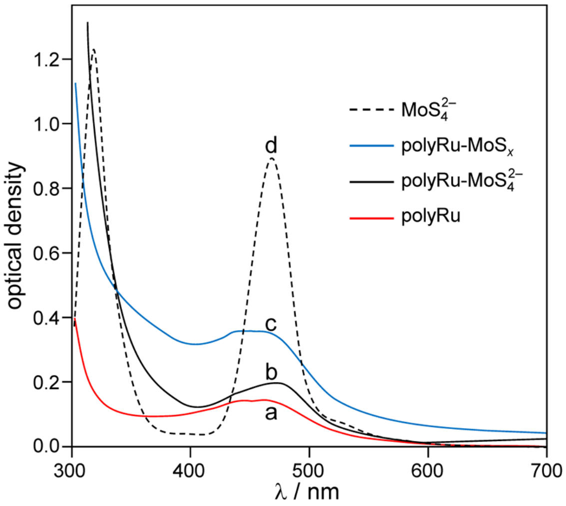

Figure 1. Absorption spectra of (a) a dry polyRu film (Γ_{Ru} = 1.2 × 10^{-8} mol cm^{-2}) coated onto an ITO electrode; (b) the same film soaked for 10 min in a 10 mM solution of $(Et_4N)_2MoS_4$ in CH_3CN and thoroughly rinsed, then (c) repeatedly cycled in 0.1 M aqueous $NaClO_4$ electrolyte (pH 6) over the 0.2 to −1.0 V potential range. (d) Absorption spectrum of 1 mM $(NH_4)_2MoS_4$ in H_2O.

Furthermore, the incorporation of MoS_4^{2-} into polyRu by ion exchange, and its electroreductive transformation in the film to MoS_x was clearly evidenced from UV−vis characterizations (Figure 1). The visible spectrum of a polyRu film coated onto an ITO electrode displayed the regular absorption band for a $Ru(2,2'\text{-bipyridine})_3^{2+}$ complex (λ_{max} = 454 nm; Figure 1, curve a).[21] The incorporation by ion-exchange of MoS_4^{2-} anions is evidenced by the rise of a new absorption band around 470 nm (Figure 1, curve b). This is consistent with the visible spectrum of MoS_4^{2-} in water, which is characterized by a strong absorption band (λ_{max} = 467 nm, ε = 12050; Figure 1, curve d).[23] Precipitation of MoS_x in the polyRu film following electroreduction of the entrapped MoS_4^{2-} anions is evidenced by a significant increase of the absorption in the near UV and visible regions, with no clear characteristic absorption onset (Figure 1, curve c), as has been previously shown for electrodeposited amorphous MoS_x films (see Figure S5C in the Supporting Information).[22]

Polarization curves recorded with the C|polyRu-MoS_x modified electrode in acidic aqueous electrolytes at almost constant ionic strength (0.1 M aqueous Na_2SO_4; Figure 2) are very similar to that obtained with an amorphous MoS_x film coated on naked glassy carbon (see Figure S5B in the Supporting Information), which demonstrates the good catalytic activity of the composite film toward proton reduction and hydrogen evolution.

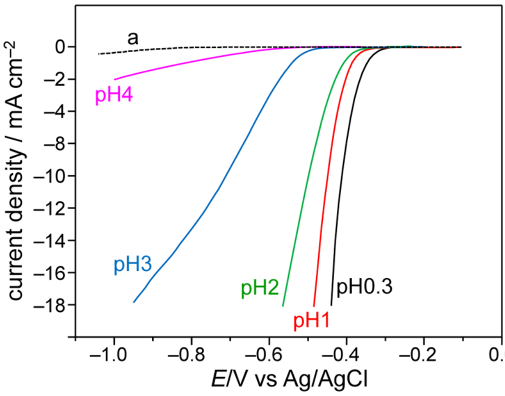

Figure 2. Polarization curves recorded at a C|polyRu-MoS_x modified electrode (Γ_{Ru} = 2.3 × 10^{-8} mol cm^{-2}, Γ_{MoSx} = 1.2 × 10^{-8} mol cm^{-2}) recorded in 0.1 M Na_2SO_4 at various pHs; curve a (---) is recorded at pH 0.3 before incorporation of MoS_x into the polyRu film; scan rate 20 mV s^{-1}.

Tafel plots recorded at C|polyRu-MoS_x and C|MoS_x (Figure S6 in the Supporting Information) show that the polymer-MoS_x composite film presented a slightly lower activity than the pure MoS_x film. However, the Tafel slope for the C|polyRu-MoS_x (60 mV dec^{-1}) is close to that obtained under the same conditions with the MoS_x film (50 mV dec^{-1}), and does match earlier reports for various MoS_x catalysts.[24,25]

AFM imaging in tapping mode of a polyRu film coated on an ITO surface showed the film to have a homogeneous granular topology (Figure 3A), with grains of average diameter of 17 nm and a root-mean square roughness (r.m.s.) of 4.3 nm (Figure 3D). After deposition of MoS_x, the composite polyRu-MoS_x film displayed a similar topography (Figure 3B), with a small increase in the diameter of the grains (20 nm) and in the r.m.s.(10 nm) (Figure 3E). In contrast, the direct electrodeposition of MoS_x onto ITO revealed the formation of rather large aggregates of MoS_x (Figure 3C), with an average diameter of 60 nm and a r.m.s. value of 23 nm (Figure 3F). These observations show that electrodeposition of MoS_x into a polyRu film results in the formation of a structured composite, characterized by a homogeneous distribution of smaller aggregates.

Figure 4 shows typical responses of a C|polyRu-MoS_x electrode in acidic aqueous electrolytes under visible photolysis (see general procedures in the Supporting Information), at various applied potentials and under different pH conditions. Stable steady state currents were observed provided that a bias voltage lower than 0.4 V was applied to the electrode (Figure 4A). The photocurrent significantly increased when the applied potential was decreased. Conversely the current dropped significantly when the pH of the electrolyte was increased from 0.3 to 3 (Figure 4B). Evolution of the photocurrent, i.e. the difference between the currents under visible light irradiation and in the dark, as a function of the applied bias voltage is summarized in Figure 4C. At pH 0.3 and with an applied potential of −0.3 V, the photocurrent density reached 40 μA cm^{-2}. In separate experiments, we have verified that photolysis of C|polyRu or C|MoS_x modified electrodes under the same pH and bias conditions did not cause any photocurrent.

The performance of the nanocomposite material for hydrogen production under visible light was evaluated using carbon modified cathodes with a larger area (1 cm^2), the amount of evolved hydrogen being evaluated by gas chromatography (see the Supporting Information). Table 1 summarized a few typical experimental results obtained with this setup. Control experiments

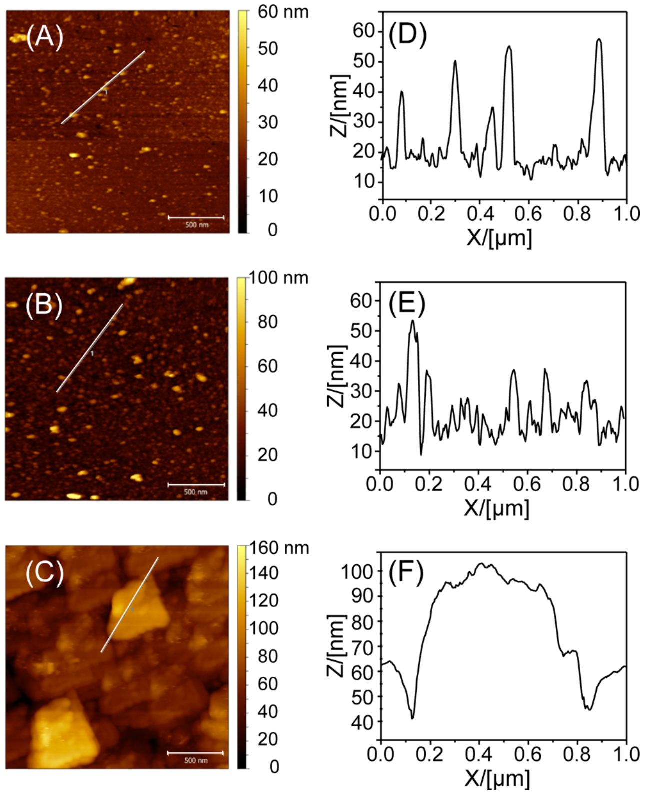

Figure 3. AFM images in tapping mode of (A) an ITO surface coated with a polyRu film (Γ_{Ru} = 1.2 × 10^{-8} mol cm^{-2}); (B) the surface shown in A, after incorporation of MoS_x into the polyRu using the ion exchange-electroreduction process (Γ_{Ru} = 1.2 × 10^{-8} mol cm^{-2}; Γ_{MoSx} = 7 × 10^{-9} mol cm^{-2}); (C) ITO covered with a MoS_x film upon repeated CV scans (25 cycles) in a 10 mM solution aqueous solution of $(NH_4)_2MoS_4$; (D–F) section analysis of the films shown in A, B, and C, respectively.

revealed that no H_2 was detected without light irradiation, or in the absence of MoS_x catalyst in the polyRu films. This last observation confirms that the MoS_x particles are the active H_2 evolution catalyst in the polyRu-MoS_x + H^+ system. Stable steady state currents were observed for hours when a bias voltage of 0.1 V was applied to the electrode. As expected from the photocurrent responses observed under different pH conditions at modified microelectrodes, the photocurrent and the amount of H_2 evolved increased significantly when the pH of the electrolyte was decreased from 1 (Table 1, Entry 1) to 0.3 (Table 1, Entry 2). At this last pH, a quantitative production of H_2 is obtained with a significant TOF of 16 per hour.

The mechanism for the catalytic evolution of H_2 under visible-light irradiation involves a photoinduced electron transfer that can proceed either by oxidative or reductive quenching of the excited state of the photosensitizer ($Ru(L)_3^{2+*}$). In the previously reported photocatalytic system for the HER using Ru(2,2′-bipyridine)$_3^{2+}$ in solution together with colloidal MoS_2,[13] the process is initiated via a reductive quenching of $Ru(L)_3^{2+*}$ by ascorbate anions acting as a strong irreversible electron donor. Here, in the absence of an additional electron donor in solution, the initial step of the photoprocess is probably the oxidative quenching of $Ru(L)_3^{2+*}$ leading to the $Ru^{III}(L)_3^{3+}$ species and a not yet identified reduced form of MoS_x, here denoted $[MoS_x]^-$ (eq 1), as in the photocatalytic system utilizing Erythrosin B as photosensitizer.[16] Although the electrocatalytic activity of MoS_x is well-recognized, the mechanism of protons reduction is still unclear. Two competing theories have been proposed; one involves adsorbed hydrogen atoms, whereas the other involves the formation of a Mo-hydride intermediate.[26] In a strongly acidic medium $[MoS_x]^-$ reacts with protons leading to the formation of H_2 and to the regeneration of $[MoS_x]$ (eq 3), this reactivity preventing the back electron transfer between $[MoS_x]^-$ and $Ru^{III}(L)_3^{3+}$ species (eq 2). The latter is reduced at the biased electrode, leading to the rise of a photocurrent.

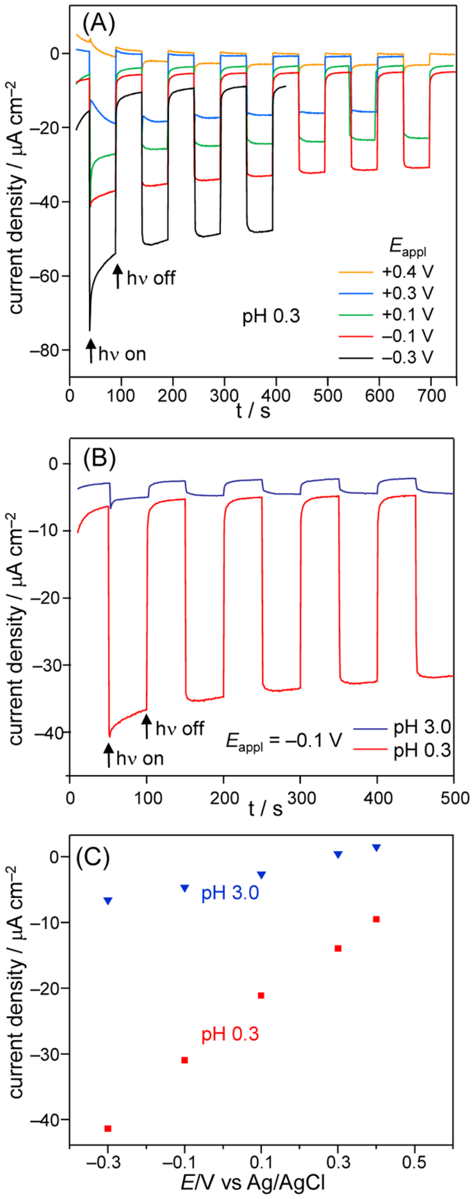

Figure 4. Photocurrent response of a polyRu-MoS_x composite film (Γ_{Ru} = 1.3 × 10^{-8} mol cm^{-2}; Γ_{MoSx} = 7 × 10^{-9} mol cm^{-2}) coated onto a 3 mm C disc electrode; (A) at pH 0.3 (0.5 M H_2SO_4) and different applied potentials; (B) at pH 0.3 (red curve) and pH 3 (phosphate buffer; blue curve), applied potential of −0.1 V; (C) photocurrents (i.e., the difference between the currents measured under visible irradiation and in the dark) recorded at different applied potentials at pH 0.3 (red squares) and pH 3 (blue triangles); irradiation was performed over the 400–700 nm visible region.

$$Ru^{II}(L)_3^{2+*} + MoS_x \rightarrow Ru^{III}(L)_3^{3+} + [MoS_x]^- \quad (1)$$

$$Ru^{III}(L)_3^{3+} + [MoS_x]^- \nrightarrow Ru^{II}(L)_3^{2+} + MoS_x \quad (2)$$

Table 1. Photocatalytic H_2 Production at ClpolyRu-MoS_x Film Modified Electrodes

cathode[a]	pH	photocurrent (μA)[e]	time (min)	charge consumed (mC)	H_2 evolved (μmol)[f]	yield (%)	TON[g]	TOF[h]
A[b]	1[d]	6	250	100	0.33	63	12	3
B[c]	0.3[d]	15	119	104	0.53	98	31	16

[a] 1 cm^2 glassy carbon modified electrode. [b] $\Gamma_{Ru} = 5.0 \times 10^{-8}$ mol cm^{-2}, $\Gamma_{MoSx} = 2.7 \times 10^{-8}$ mol cm^{-2}. [c] $\Gamma_{Ru} = 3.1 \times 10^{-8}$ mol cm^{-2}, $\Gamma_{MoSx} = 1.7 \times 10^{-8}$ mol cm^{-2}. [d] aqueous H_2SO_4. [e] Bias 0.1 V vs Ag|AgCl (3 M KCl); [f] Determined by GC. [g] The mol of H_2 on mol of MoS_x ratio. [h] Turn over frequency per hour.

$$[MoS_x]^- + H^+ \rightarrow MoS_x + 1/2H_2 \qquad (3)$$

An important point is that poly[pyrrole-tris(bipyridyl)ruthenium(II)] films are known to be stable under visible irradiation, and also in their one-electron oxidized form.[21] Moreover, although the lifetime of the excited state of a tris(bipyridyl)ruthenium(II) complex in a functionalized polypyrrole matrix is about ten times shorter than that of pyrrole-Ru complex monomer,[27] probably because of self-quenching phenomena, it is long enough to be engaged in an electron transfer reaction with an external acceptor. The proposed mechanism is in agreement with the fact that the driving force of the whole catalytic process clearly depends on pH. Taking into account that the oxidation potential of the complex in its excited state is about −1 V vs Ag|AgCl,[28] this mechanism is consistent with the fact that the polarization curves recorded at different pHs clearly show that a pH lower than 2 is required to obtain a significant catalytic activity around −1 V (see Figure 2).

To provide further evidence for the suggested photoinduced oxidation of $Ru(L)_3^{2+}$ by MoS_x (eq 1), in a separate experiment we have studied the evolution of the intensity of the visible absorption of a polyRu-MoS_x composite film coated onto an ITO surface during the course of its visible irradiation in acidic media, without applying a bias voltage (see Figure S7 in the Supporting Information). Illumination of the film at pH 4 does not lead to noticeable change in the spectra of the film. In contrast, under irradiation in more acidic (pH 0.3) solutions its absorption intensity significantly deceased. Taking into account that $Ru^{III}(L)_3^{3+}$ species exhibit only a very weak absorption in the visible region,[21] these observations strongly suggest the irreversible oxidative quenching of $Ru(L)_3^{2+*}$ by MoS_x in the composite film under acidic conditions, leading to a net buildup of $Ru^{III}(L)_3^{3+}$ species because the electrode was not biased in this experiment.

In conclusion, we have developed a novel, straightforward and versatile strategy to fabricate photosensitive cathode materials for the HER. The electrochemically synthesized MoS_x-incorporated polyRu composite films exhibit stable photocatalytic activity for hydrogen evolution from water under visible light. The HER process certainly occurs via the oxidative quenching of the excited state of the ruthenium complex by the molybdenum sulfide catalyst. To the best of our knowledge this is the first example of a composite photocathode using a poly[tris(bipyridyl)ruthenium(II)] film as photosensitive support material for a MoS_x cocatalyst. This result provides a starting point for further synthesis of composite electrode materials that should have great potential in the fabrication of photoelectrochemical cells for the HER.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section: materials and general procedures; electrosynthesis and electrochemical characterization of poly[pyrrole-$Ru(L)_3^{2+}$]-MoS_x composite films and MoS_x films; AFM; UV−vis characterizations of composite films; Tafel plots for HER. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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