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Towards electrochemical regeneration of redox photocatalysts? The example of the tris(2,2'-bipyridine)ruthenium(II)/methylviologen system

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ABSTRACT

The regeneration of redox photocatalysts usually requires the use of sacrificial reagents that are added to the medium in stoichiometric amounts, either as an electron donor or as an electron acceptor, to act as an electron relay to the photocatalyst to ensure its effective regeneration. In the present work, we consider the possibility of direct electrochemical regeneration of the catalyst using a model system made of tris(2,2'-bipyridine)ruthenium (II) ([Ru(bpy)₃]²⁺) as photosensitizer and methylviologen (MV²⁺) as quenching substrate. Based on hydrodynamic amperometry experiments, we demonstrate that this can indeed be possible provided that appropriate potential values are applied to ensure the electrochemical reduction of [Ru(bpy)₃]³⁺ back to [Ru(bpy)₃]²⁺ while avoiding interfering processes arising from electron transfer reactions involving the quencher and/or the products/intermediates generated in the course of the photocatalytic event. Furthermore, using EDTA as a sacrificial electron donor, we show that photocurrents can also be exploited for regenerating the quenching substrate by reduction of the reaction product MV^{•+} (back into MV²⁺).

1. Introduction

Photoredox catalysis has become an emerging field in organic synthesis thanks to the new opportunities offered by photochemical catalytic processes to accelerate a wide range of chemical reactions under mild conditions by exploiting the ability of photocatalysts to harvest visible-light energy [1–3]. This has led to the development of efficient synthetic methodologies, considering selectivity, yields and environmental impact, via photochemical transformations requiring low energetic light activation (see many examples in a recent thematic issue of *Chemical Reviews* [4]).

The basic principle of photoredox catalysis is illustrated in *Scheme 1*. It relies on the photoexcitation of a catalyst (named as PCat in *Scheme 1*) giving an excited state with unique properties that are likely to be exploited for oxidative or reductive quenching processes involving an electron transfer reaction with the substrate (Sub), forming

intermediates Sub^{•+} or Sub^{•-}, corresponding to a quenching of the excited state of the photocatalyst (*PCat) [5]. These radical intermediates can be exploited for a myriad of synthetic transformations in organic chemistry [1–4]. The regeneration of the photocatalyst most often requires the use of sacrificial redox partners (either electron donor, D, or electron acceptor, A) selected for their ability to either reduce PCat^{•+} or oxidize PCat^{•-} into the pristine PCat species [6,7]. The generated D^{•+} and A^{•-} radicals can be also involved in cross-coupling organic transformations [8] or they are simply used as sacrificial reagents (as in artificial photosystems [6]). To be effective, redox partners (D or A) should be added to the medium in stoichiometric amounts relative to the substrate [9], and they also could have undesired roles (competing reagents) [10]. In order to use them in catalytic quantities, one needs to find a regeneration step to reduce D^{•+} back to D or oxidize A^{•-} back to A, and electrochemistry may provide the solution [11]. Better yet, with the idea of improving the sustainability of such a photochemical process

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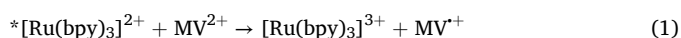
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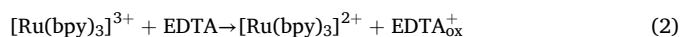
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while reducing waste and costs, would be the direct electrochemical regeneration of the catalyst (*i.e.*, inducing a shuttle of electrons to PCat^{•+} or from PCat^{•-} to get back PCat) [12]. We would like to investigate this hypothesis in the present work using a model system made of [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) as photocatalyst and methylviologen (MV²⁺) as substrate.

Among the wide range of photocatalysts, [Ru(bpy)₃]²⁺ is indeed a well-known redox-active compound offering unique opportunities to trigger formation of chemical bonds under illumination, even if its interest for preparative organic chemistry exploiting visible light photoredox catalysis gained widespread recognition mainly in the past two decades [8,13–17]. [Ru(bpy)₃]²⁺ can absorb light in the visible domain (maximum absorbance at 452 nm), forming an excited triplet Metal-to-Ligand Charge Transfer state (*PCat = *[Ru(bpy)₃]²⁺, also noted *Ru²⁺ for simplicity) that is quite long lived (from 100 ns of nanoseconds to microsecond range depending on conditions [15,17]), which can be involved in single-electron oxidation or reduction reactions with a wide range of reductive or oxidative quenchers, triggering photoreduction or photooxidation processes [17]. If considering the oxidative quenching cycle, *[Ru(bpy)₃]²⁺ can act as a strong reductant and the end form of the catalyst is [Ru(bpy)₃]³⁺. The electrochemistry of the [Ru(bpy)₃]^{3+/2+} redox couple is well known (E⁰ = +1.26 V in 1 M H₂SO₄ [18,19]), yet with redox properties being affected by the solvent and electrolyte [20,21], and the reversible interconversion between [Ru(bpy)₃]³⁺ and [Ru(bpy)₃]²⁺ species is basically possible by adjusting potentials respectively below and above E⁰ values. In contrast, the redox potentials associated with the photocatalyst in its excited state (*[Ru(bpy)₃]²⁺) cannot be measured experimentally but they can be estimated by calculations, giving values ranging from –0.62 V to –0.86 V (depending on the simulations method used) for the [Ru(bpy)₃]^{3+/*[Ru(bpy)₃]²⁺ redox system [14,22,23]. This confirms its strong reductive properties and the possibility of effective oxidative quenching in the presence of a substrate like methylviologen (E⁰ = –0.65 V vs. 3 M Ag/AgCl electrode for the MV²⁺/MV^{•+} redox couple [24], or –0.45 V vs. normal hydrogen electrode [25]), which is used as electron-acceptor quencher in the photoredox reaction (Eq. 1) occurring under illumination of a solution containing both [Ru(bpy)₃]²⁺ and MV²⁺ [26]. Note also that MV^{•+} rapidly oxidizes into MV²⁺ in the presence of molecular oxygen [25].}



The regeneration of [Ru(bpy)₃]²⁺ photocatalyst is usually achieved by using a sacrificial electron donor (such as ethylenediaminetetraacetate, EDTA [27–29]), which is able to reduce [Ru(bpy)₃]³⁺ species (Eq. 2), forming an oxidized form EDTA_{ox}⁺ that is known to undergo irreversible degradation [30].



Here, we would like to analyse the conditions (in particular the applied

potential and the medium composition) that would lead to a possible electrochemical regeneration of the photocatalyst or the quenching molecule, by measuring the amperometric response and the photocurrents recorded at a glassy carbon electrode (GCE) immersed in several stirred solutions of distinct composition. In order to distinguish the various reactions that are likely to be involved, the investigated solutions will contain [Ru(bpy)₃]²⁺ and MV²⁺, [Ru(bpy)₃]²⁺ and EDTA, or the three reagents ([Ru(bpy)₃]²⁺, MV²⁺, EDTA) in mixture, both in the presence of oxygen (aerated media) and after purging with nitrogen (deaerated media), and also [Ru(bpy)₃]²⁺ alone for comparison purposes. The investigated potential window will be between the characteristic values of the two redox couples (MV^{2+/*} and [Ru(bpy)₃]^{3+/*2+}).

2. Material and methods

2.1. Reagents

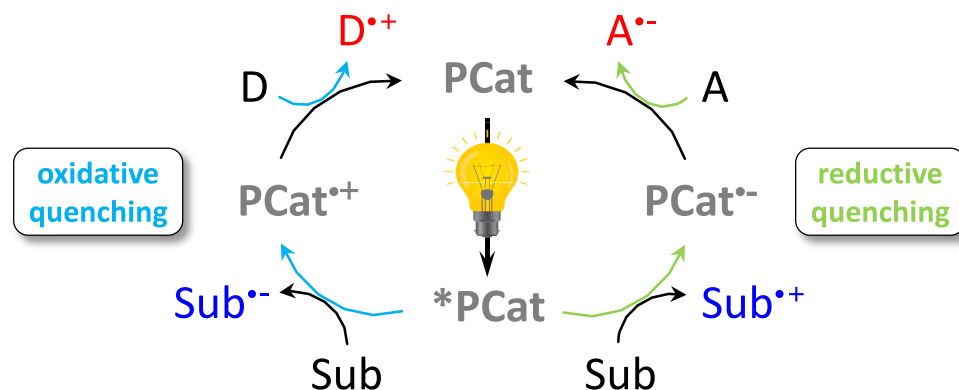
Tris(2,2'-bipyridine)ruthenium(II) chloride hexahydrate ([Ru(bpy)₃]Cl₂·6H₂O, 99 %, Merck), 1,1-dimethyl-4,4-bipyridinium dichloride (methylviologen, 98 %, Merck), ethylenediaminetetraacetic acid disodium salt (EDTA, 99 %, Prolabo) and sodium nitrate (NaNO₃, 99 %, Merck) were used as received. All solutions were prepared with high-purity water (18.2 MΩ cm) obtained from a Purelab Option-Q from ELGA.

2.2. Apparatus

Cyclic voltammetry experiments and amperometric measurements were performed using the AutoLab/PSTAT 101 A potentiostat monitored by the NOVA software (Metrohm). A three-electrode configuration was used, including a glassy carbon plate (SIGRADUR G, 20 mm × 10 mm × 1 mm, from HTW, Germany) as working electrode, an Ag/AgCl reference electrode (Metrohm) and a platinum rod acting as counter electrode. They were arranged in a configuration allowing placing the GCE surface normal to the incident light beam provided by Lightning Cure LC8 Spot Light-source apparatus (Hamamatsu) with a maximal power of 4.5 W (used here). A rotating disk electrode (RDE, Tacussel) was added to the device in order to ensure uniform stirring of the medium. All experiments were performed at room temperature.

2.3. Procedures

The electrochemical cell was filled with an aqueous solution containing the supporting electrolyte (0.1 M NaNO₃) in the presence of either: 1.0 mM [Ru(bpy)₃]²⁺ alone; a 1.0 mM [Ru(bpy)₃]²⁺ and 1.0 mM MV²⁺ mixture; a 1.0 mM [Ru(bpy)₃]²⁺ and 1.0 mM EDTA mixture; or the three reagents all together ([Ru(bpy)₃]²⁺, MV²⁺ and EDTA at 1.0 mM each). The choice of 1.0 mM concentration is arbitrary and selected



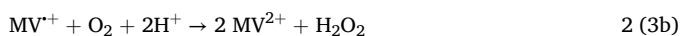
Scheme 1. Illustration of photocatalysis redox processes involving a photocatalyst (PCat), a substrate (Sub), and either an electron donor (D) or electron acceptor (A).

here for purpose of proof-of-concept, but few experiments were performed in more diluted solutions to point out possible concentration effects. All experiments were carried out under either aerated (O_2) or inert atmosphere, this latter being achieved by purging the solution with nitrogen (N_2) for 40 min. The amperometric responses were recorded in hydrodynamic conditions (rotating RDE at 150 rpm), by applying successive constant potential steps of 100 mV for typically 20 s, in a wide range of negative (from 0.0 V down to -0.6 V) and positive (from 0.0 V up to $+0.8$ V) potentials, and recording the corresponding transient currents. The wavelength of the visible light source was fixed at 400 nm to monitor the generation of photocurrents at the glassy carbon working electrode while performing the chronoamperometry experiments at increasing or decreasing potential values. The irradiation was applied through the whole cell (5 cm) in the direction of the GCE surface for 5 s in the middle of each potential step, beginning at 8 s and ending at 13 s. Photocurrents were calculated by difference between currents observed when turning light from off to on.

3. Results and discussion

3.1. Preliminary considerations

Fig. 1 exhibits the characteristic cyclic voltammetry behaviour of $[Ru(bpy)_3]^{2+}$ and MV^{2+} on GCE. One can see on part A of the figure the well-established quasi-reversible response of the $[Ru(bpy)_3]^{3+/2+}$ redox couple at $+1.08$ V ($E_{pa} = +1.12$ V and $E_{pc} = +1.04$ V), and on part B the reversible signal attributed to the $MV^{2+/+}$ system ($E_{pc} = -0.70$ V and $E_{pa} = -0.61$ V) which is typical of this redox probe in deaerated aqueous medium [25]. Although the MV^{+} species can be reduced to neutral MV^0 by an additional one-electron transfer occurring below -1 V [25], it is better to avoid this because of possible comproportionation between MV^0 and MV^{2+} to generate $2 MV^{+}$ [31] (MV^0 is not considered as only MV^{2+} and MV^{+} are involved in the photoredox process, Eq. 1). In the presence of molecular oxygen, an additional pre-peak appeared at -0.39 V (Fig. 1B), which is due to the methylviologen mediated electrocatalytic reduction of O_2 (as evidenced previously on other electrodes [32–35]) via its reaction with MV^{+} (Eq. 3), leading to the production of transient O_2^- (Eq. 3a) and then hydrogen peroxide (Eq. 3b) because the oxidation of MV^{+} by O_2^- is fast in aqueous media [36].



For the $[Ru(bpy)_3]^{3+/2+}$ system, if operating in the presence of EDTA, the reversible signal evolved progressively to an irreversible

anodic peak/wave with the disappearance of the cathodic counterpart (Fig. 1A), which is indicative of the mediated electrocatalytic oxidation of $[Ru(bpy)_3]^{2+}$ as a result of reaction between EDTA and electro-generated $[Ru(bpy)_3]^{3+}$ (Eq. 2). This catalytic wave was even more intense as the EDTA concentration in the medium increased. Similar behaviour was reported for the electrooxidation of $[Ru(bpy)_3]^{2+}$ in the presence of bromide ions, also exhibiting a catalytic regeneration electro mechanism [37].

Based on these observations, one could think about regenerating either the photocatalyst (by reduction of $[Ru(bpy)_3]^{3+}$) or the quencher (by oxidation of MV^{+}) in the potential window lying between these two redox systems, depending on the conditions (aerated or deaerated medium, presence of EDTA or not), but this is also questionable regarding the various intermediate species that are likely to (co)exist under illumination, as discussed below.

3.2. Influence of applied potentials on generated photocurrents

3.2.1. $[Ru(bpy)_3]^{2+}$ and MV^{2+}

Fig. 2A shows the current variations observed when applying potential steps of 100 mV (respectively up to $+0.9$ V (Fig. 2A1) and down to -0.6 V (Fig. 2A2)) for 20 s to a GCE plate immersed in a stirred solution containing 1 mM $[Ru(bpy)_3]^{2+}$ and 1 mM MV^{2+} . The solutions were either aerated (black curves) or deaerated (pink/violet curves), and photoirradiation (400 nm) was applied for 5 s in the middle of each potential step, generating an increase or decrease in current that corresponds respectively to anodic or cathodic photocurrents, which are depicted as a function of the applied potentials in Fig. 2B. As a first observation, background currents (i.e., without irradiation) were similar in aerated and deaerated media in the positive potential window (Fig. 2A1), whereas larger cathodic currents were observed in an aerated medium at potentials lower than -0.4 V (Fig. 2A2) due to oxygen electroreduction.

When illuminating (i.e., light ‘on’) the aerated solution containing both $[Ru(bpy)_3]^{2+}$ and MV^{2+} , one can clearly see cathodic photocurrents (see black bars on Fig. 2B) corresponding to the electrochemical reduction of $[Ru(bpy)_3]^{3+}$ resulting from the oxidative quenching of the excited state of the photocatalyst by methylviologen (reaction of $[Ru(bpy)_3]^{2+}$ with MV^{2+} , Eq. 1) [26,38]. Such electrochemical regeneration of the photosensitizer (Eq. 1) is possible due to dissolved molecular oxygen acting as an electron relay to oxidize MV^{+} back to MV^{2+} while producing H_2O_2 (Eq. 3b) [23]. The various reactions are schematically depicted in Fig. 2C. It is noteworthy that cathodic photocurrents are mainly visible at potentials lower than $+0.4$ V because at more positive values the electrochemical oxidation of H_2O_2 at the GCE surface [39]

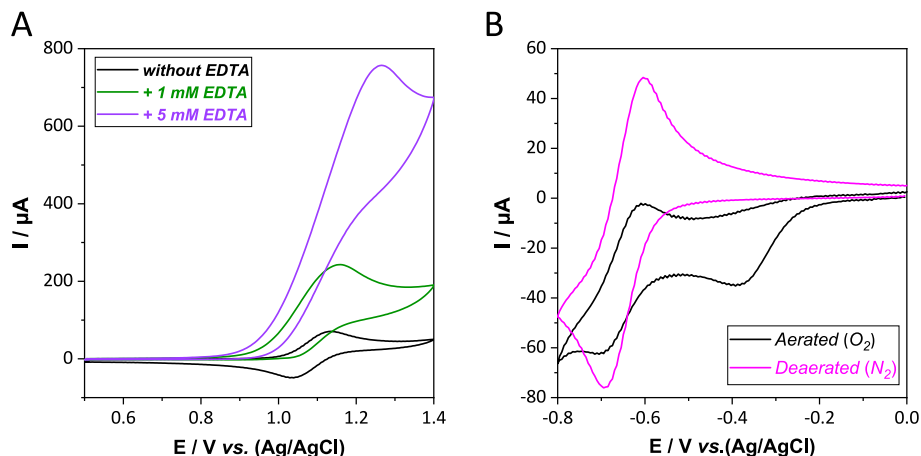


Fig. 1. Cyclic voltammetry (CV) characterization of $[Ru(bpy)_3]^{2+}$ (A) and MV^{2+} (B) at GCE. (A) CV curves recorded at 100 mV/s in 1 mM $[Ru(bpy)_3]^{2+}$ without and with 1 mM or 5 mM EDTA added to the medium, respectively. (B) CV curves recorded at 100 mV/s in 1 mM MV^{2+} before (aerated) and after purging with nitrogen (deaerated). Supporting electrolyte: 0.1 M $NaNO_3$.

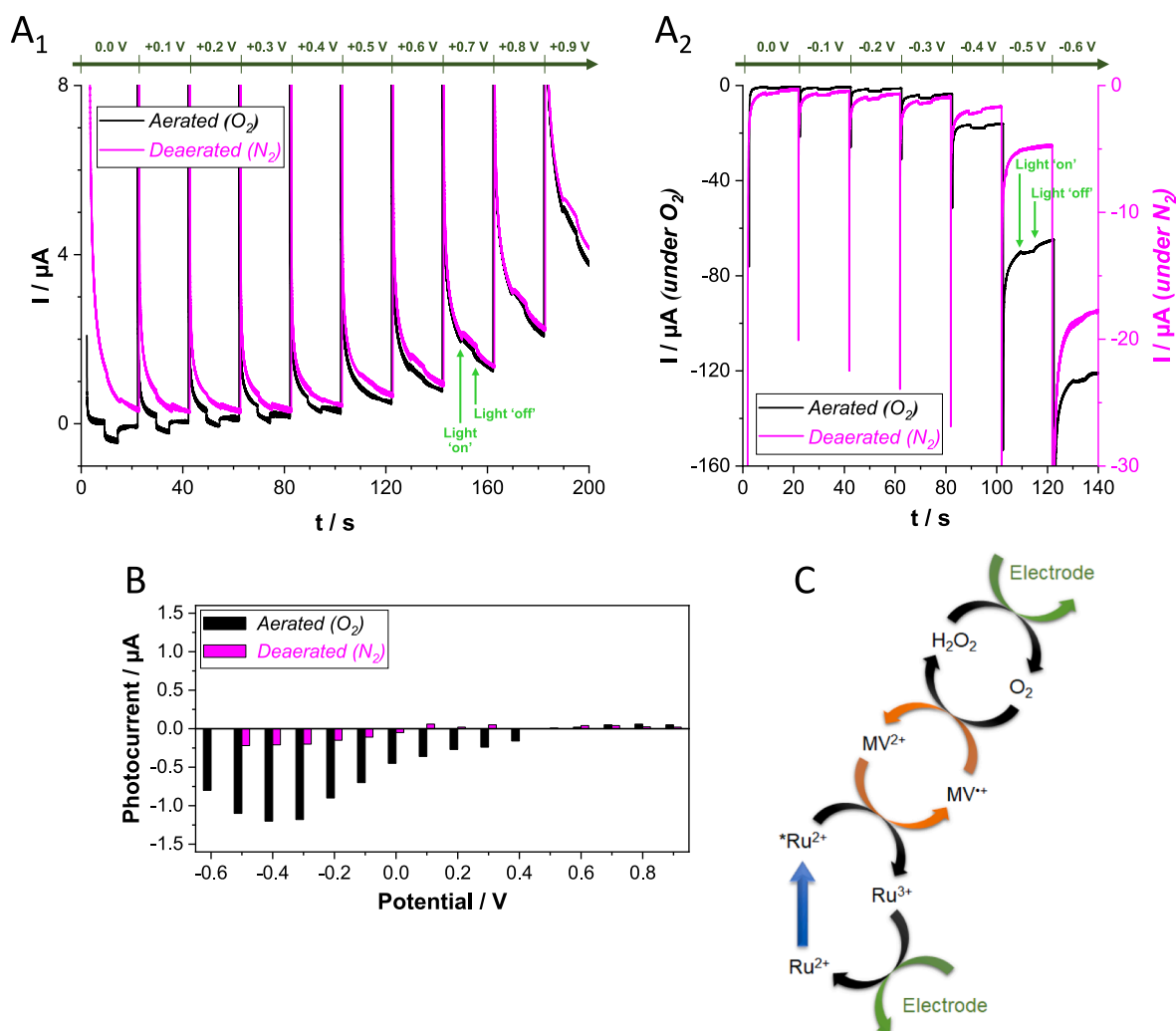


Fig. 2. (A) Hydrodynamic amperograms recorded in a stirred solution containing 1 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ and 1 mM MV^{2+} (+0.1 M NaNO_3), before (aerated, black line) and after purging with nitrogen (deaerated, pink line), by applying successive potential steps (100 mV each) to GCE for 20 s towards positive (A_1) or negative (A_2) values, and irradiating at 400 nm between the 8th and 13th second in each step. (B) Corresponding photocurrents expressed as a function of the applied potential. (C) Scheme illustrating the possible reactions and origin of photocurrents (in aerated medium).

will compensate the electrochemical reduction of $[\text{Ru}(\text{bpy})_3]^{3+}$. Also, the slight decrease in photocurrent observed at potential values lower than -0.4 V (black bars in the left of Fig. 2B) is probably due to some consumption of O_2 being thus less available to react with MV^{+} . This is the reason why one cannot determine any yield of the electrochemical regeneration process. Interestingly, the system also worked in dilute $[\text{Ru}(\text{bpy})_3]^{2+}$ solution (6 μM), the photocurrents being proportional to the MV^{2+} concentration (see Fig. S1 in Supplementary Material). Regeneration efficacy is thus ensured over a wide range of quencher concentrations, which is advantageous compared to regeneration methods based on sacrificial reagents for which the concentration should be adjusted, without needing any additional separation step for purification when intended to be applied in organic synthesis. It would enable to translate a purely photoredox method into a photoelectrosynthesis one [12].

In the absence of oxygen in the medium (*i.e.*, after purging with N_2), the photoexcitation still produces $[\text{Ru}(\text{bpy})_3]^{3+}$ and MV^{+} species, but there is no more oxidant to react with MV^{+} , and the concomitant electroreduction of $[\text{Ru}(\text{bpy})_3]^{3+}$ and electrooxidation of MV^{+} leads to negligible net photocurrents (see pink/violet bars on Fig. 2B). Further, the direct reaction between $[\text{Ru}(\text{bpy})_3]^{3+}$ and MV^{+} species [40] cannot be excluded, but this reaction is anticipated to be very slow [41].

3.2.2. $[\text{Ru}(\text{bpy})_3]^{2+}$ and EDTA

In the absence of MV^{2+} , $^*\text{Ru}(\text{bpy})_3]^{2+}$ is also likely to be involved in photochemical processes and molecular oxygen is a possible alternative oxidative quencher [42]. In such a case, photocurrents can be observed (Fig. S2 in Supplementary Material), arising either from $[\text{Ru}(\text{bpy})_3]^{3+}$ reduction or from oxidation and reduction reactions involving the oxygen species originating from the quenching process ($\text{O}_2^{\cdot-}$, H_2O_2). In the presence of EDTA along with $[\text{Ru}(\text{bpy})_3]^{2+}$, one can also observe significant photocurrents in aerated medium (see Fig. 3). In this case, there is no contribution from the electrochemical reduction of $[\text{Ru}(\text{bpy})_3]^{3+}$ because such species are reduced by EDTA (Eq. 2) [30], consistent with the above observations by cyclic voltammetry (Fig. 1A). The resulting photocurrents (see black bars in Fig. 3B) are only due to the oxidation or reduction of the generated $\text{O}_2^{\cdot-}$ and/or H_2O_2 species (Fig. 3C). Compared to a medium containing $[\text{Ru}(\text{bpy})_3]^{2+}$ alone (*i.e.*, without EDTA), the photocurrents are less negative or more positive (compare black bars in Fig. 3B and Fig. S2), confirming the possible electrochemical regeneration of the photocatalyst in the absence of a sacrificial electron donor. It is also noteworthy that some photocurrents can be observed in a deaerated medium (see pink/violet bars in Fig. 3B), which might be due to some contribution of water photolysis in the presence of $[\text{Ru}(\text{bpy})_3]^{2+}$ as photosensitizer [43,44], even if its effectiveness usually requires additional catalysts and/or mediators [45,46].

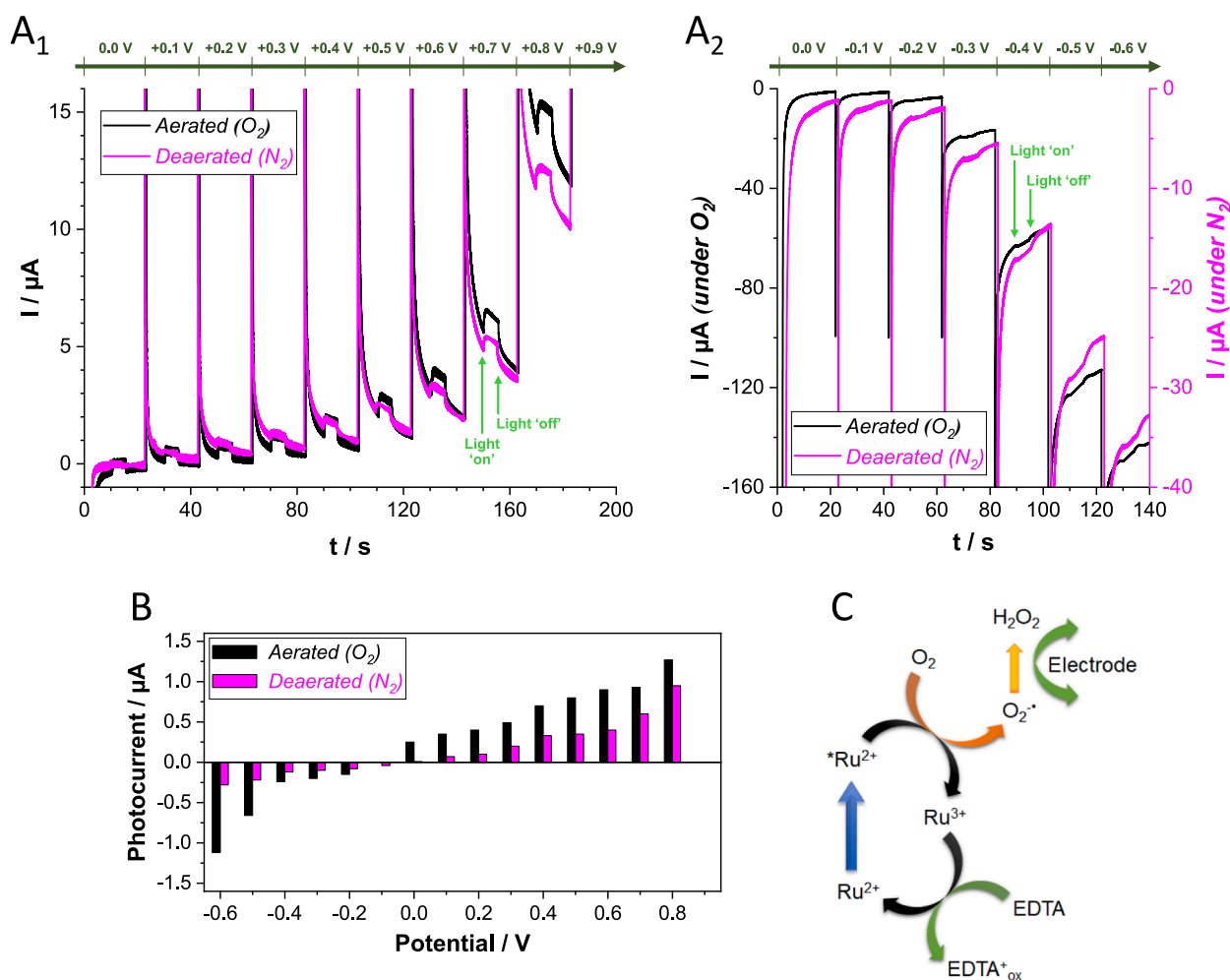


Fig. 3. (A) Hydrodynamic amperograms recorded in a stirred solution containing 1 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ and 1 mM EDTA (+0.1 M NaNO_3), before (aerated, black line) and after purging with nitrogen (deaerated, pink line), by applying successive potential steps (100 mV each) to GCE for 20 s towards positive (A₁) or negative (A₂) values, and irradiating at 400 nm between the 8th and 13th second in each step. (B) Corresponding photocurrents expressed as a function of the applied potential. (C) Scheme illustrating the possible reactions and origin of photocurrents (in aerated medium).

3.2.3. $[\text{Ru}(\text{bpy})_3]^{2+}$, MV^{2+} and EDTA

Fig. 4A shows typical hydrodynamic amperograms recorded in solutions containing an ensemble of photosensitizer ($[\text{Ru}(\text{bpy})_3]^{2+}$), quencher (MV^{2+}) and electron donor (EDTA), before and after nitrogen purging. By comparing pink/violet curves to the black ones in both positive (Fig. 4A1) and negative (Fig. 4A2) domains, one can immediately see that background currents are becoming continually more positive in deaerated medium. This is clearly due to the accumulation of $\text{MV}^{\cdot+}$ radical cations in larger amounts in the medium as well as increasing the number of light periods, as these species are not chemically oxidized in the absence of oxygen (Eq. 3 not occurring) and they are thus detected by electrochemical oxidation over a wide potential window (between -0.5 V to $+0.8$ V). This is also visible to the naked eye (see Fig. S3 in Supplementary Material), via the characteristic bluish colour of the $\text{MV}^{\cdot+}$ solution [47], being darker as the experiment is going on further. This is possible because the irradiation is imposed not only on the electrode surface but also into the bulk of the solution where EDTA is also present and thus likely to regenerate the photocatalyst by chemical reduction $[\text{Ru}(\text{bpy})_3]^{3+}$, contrary to the case of the electrochemical regeneration process taking place only on the electrode surface in the absence of EDTA in the medium (section 3.2.1).

Focusing now on the photocurrents (Fig. 4B), there are significant differences between aerated and deaerated media. In the absence of oxygen (see pink/violet bars in Fig. 4B), electrochemistry can be used to

regenerate the quencher by electrooxidation of the produced $\text{MV}^{\cdot+}$ radical cations back to MV^{2+} , leading to positive photocurrents of the same order of magnitude over the whole potential window, yet being kinetically limited at the beginning of the experiments (see shape of the pink/violet curve in Fig. 4A1 and differences in photocurrent values when measured at the beginning (Fig. 4B1) or the end (Fig. 4B2) of the irradiation). In the presence of oxygen, the anodic photocurrents (see black curve in Fig. 4A1 and black bars in Fig. 4B) are even larger due to the simultaneous direct electrochemical oxidation of $\text{MV}^{\cdot+}$ and its mediated oxidation by oxygen (i.e., regeneration of O_2 by electrochemical oxidation of H_2O_2 produced according to Eq. 3b). Of course, this is only possible in the anodic potential window where H_2O_2 can be readily electrooxidized. The reaction pathways for both aerated and deaerated media are summarized in Fig. 4C.

As the photosensitizer is regenerated in the photocatalytic process, one can in principle use it in a more dilute form and Fig. 5 demonstrates that it is indeed the case, showing photocurrents for a 0.1 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ solution comparable to those observed for a solution containing 1 mM of $[\text{Ru}(\text{bpy})_3]^{2+}$, along with 1 mM MV^{2+} and 1 mM EDTA in both cases (compare black curves in Fig. 5A and Fig. 4A1). However, repeating the measurements in the same solution led to significant decrease in the photocurrent intensities (see, e.g., 3rd and 5th amperograms in Fig. 5A). The reason for that is the progressive consumption of the sacrificial electron donor (EDTA) used to regenerate the

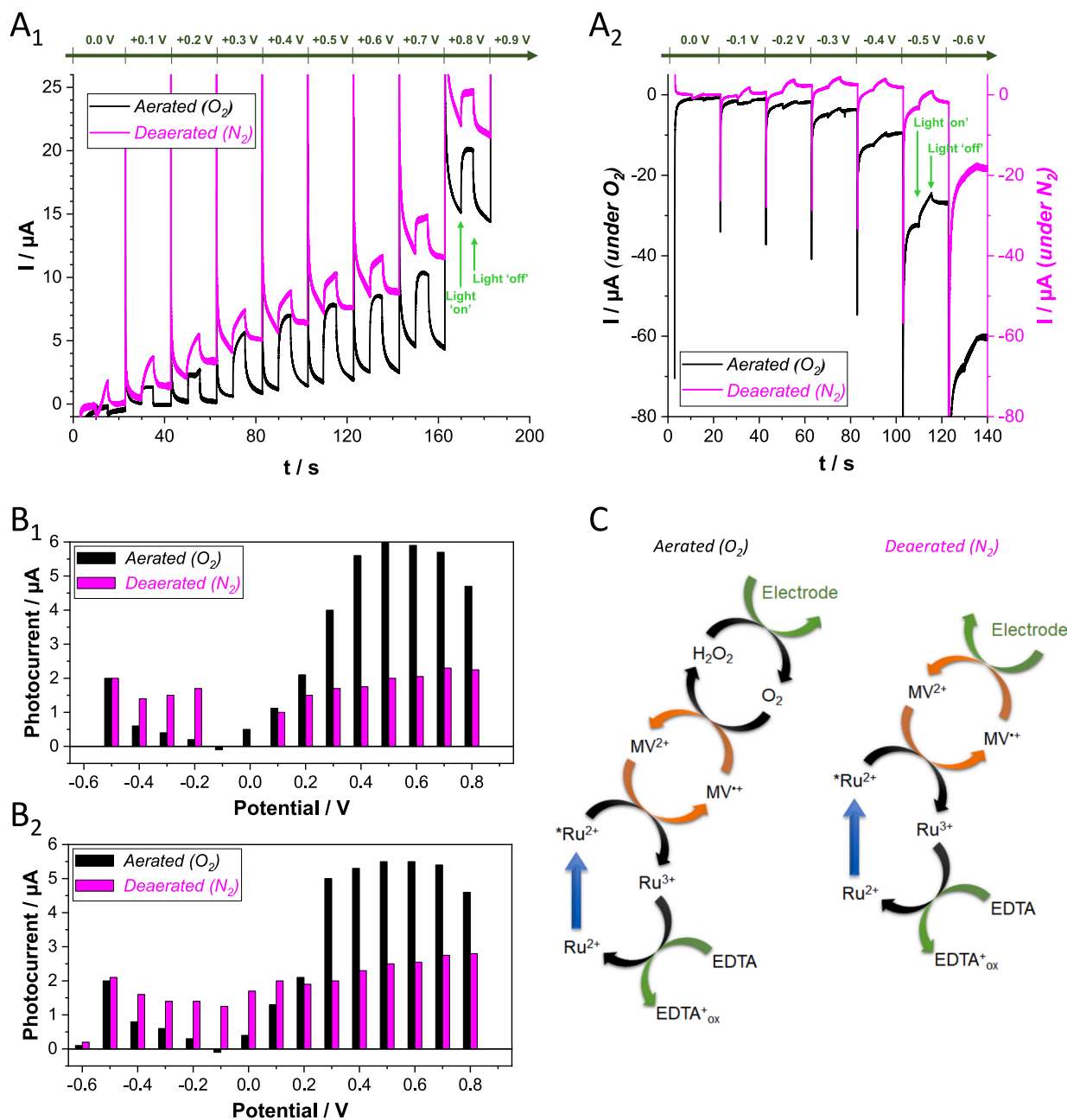


Fig. 4. (A) Hydrodynamic amperograms recorded in a stirred solution containing 1 mM $[\text{Ru}(\text{bpy})_3]^{2+}$, 1 mM MV^{2+} and 1 mM EDTA (+0.1 M NaNO_3), before (aerated, black line) and after purging with nitrogen (deaerated, pink line), by applying successive potential steps (100 mV each) to GCE for 20 s towards positive (A_1) or negative (A_2) values, and irradiating at 400 nm between the 8th and 13th second in each step. (B) Corresponding photocurrents expressed as a function of the applied potential, as measured at the beginning (B_1) or the end of the irradiation (B_2). (C) Scheme illustrating the possible reactions and origin of photocurrents (without and with oxygen in the medium, respectively).

photocatalyst in solution [48,49]. The intensity of photocurrents was indeed dependent on the EDTA content and using 20 mM EDTA instead of 1 mM EDTA in the same medium (as in Fig. 5A) gave rise to much larger photocurrents (Fig. 5B). This confirms the interest of avoiding the use of a sacrificial electron donor by applying an electrochemical regeneration method to recover the photocatalyst (as in Fig. 2).

4. Conclusions

Using a known model system with $[\text{Ru}(\text{bpy})_3]^{2+}$ as photosensitizer, MV^{2+} as quencher and EDTA as sacrificial electron donor, we demonstrate on the basis of hydrodynamic amperometry experiments that electrochemistry can be envisaged as a mean to regenerate the

photocatalyst without the need to add sacrificial reagents in the medium. However, this is limited to a certain potential window and conditions in which no other electrochemical reactions are expected to take place (e.g., as those involving the quencher or the reaction products). For the present system, this is possible in an aerated medium containing $[\text{Ru}(\text{bpy})_3]^{2+}$ and MV^{2+} and applying potential values ranging from +0.4 V to -0.6 V (the optimum ones being between -0.2 V and -0.5 V) resulting in the electrochemical reduction of $[\text{Ru}(\text{bpy})_3]^{3+}$ back to $[\text{Ru}(\text{bpy})_3]^{2+}$. Note that it is also possible to regenerate the quencher (i.e., MV^{2+} , by electrochemical oxidation of MV^{+}), but this requires the use of the EDTA sacrificial electron donor to avoid the concomitant reduction of $[\text{Ru}(\text{bpy})_3]^{3+}$ and oxidation of MV^{+} onto the electrode surface resulting in no net photocurrents. The next step for practical

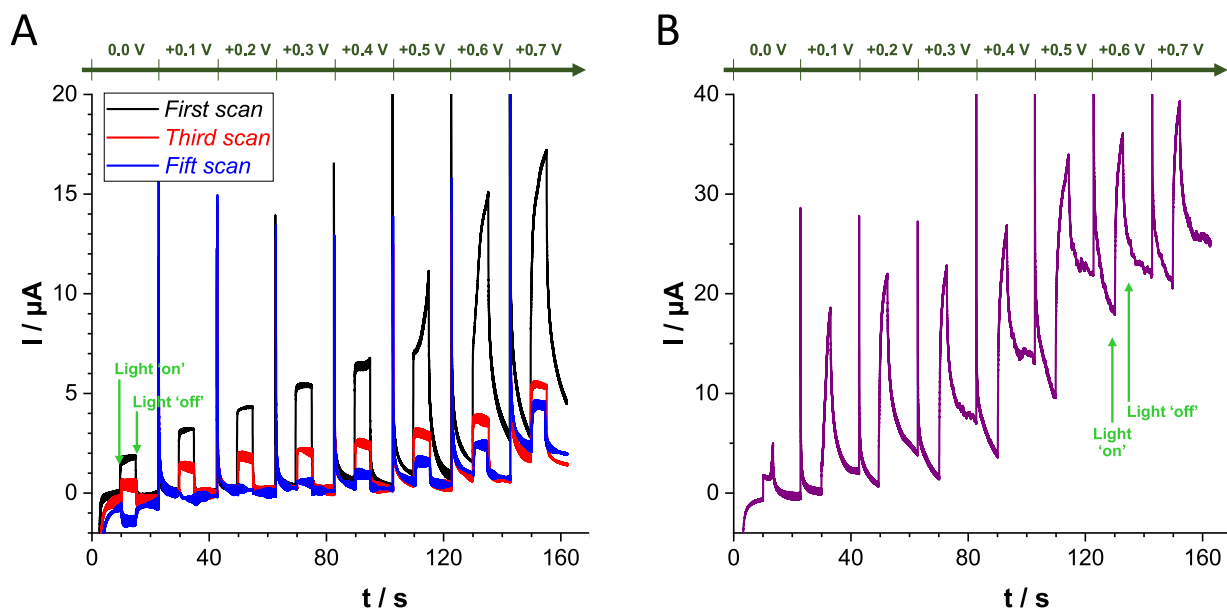


Fig. 5. (A) Hydrodynamic amperograms (1st, 3rd and 5th scans, respectively) recorded in a stirred and aerated solution containing 0.1 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ and 1 mM EDTA (+0.1 M NaNO_3), by applying successive potential steps (100 mV each) to GCE for 20 s towards positive values, and irradiating at 400 nm between 8th and 13th second in each step. (B) Same experiment (1st scan) as in (A) but performed with 20 mM EDTA in the medium (instead of 1 mM).

applications would be the immobilization of the photocatalyst onto an electrode surface in order to build a reagent-free electrochemical device likely to be used in organic synthesis without the need for adding neither the photosensitizer nor a sacrificial reagent in the medium.

CRediT authorship contribution statement

Mahmoud Rahal: Writing – original draft, Visualization, Methodology, Investigation. **Neus Vilà:** Writing – review & editing, Supervision, Conceptualization. **Christelle Despas:** Writing – review & editing, Validation, Conceptualization. **Malik Sebbat:** Investigation. **Nathan McClenaghan:** Writing – review & editing, Conceptualization. **Emmanuel Oheix:** Writing – review & editing. **Bénédicte Lebeau:** Writing – review & editing, Conceptualization. **Morgan Cormier:** Writing – review & editing, Conceptualization. **Jean-Philippe Goddard:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Alain Walcarius:** Writing – original draft, Validation, Supervision, Resources, Methodology, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jelechem.2024.118618>.

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