



# Photoinduced Water Oxidation in Chitosan Nanostructures Containing Covalently Linked Ru<sup>II</sup> Chromophores and Encapsulated Iridium Oxide Nanoparticles

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**Abstract:** The luminophore Ru(bpy)<sub>2</sub>(dcbpy)<sup>2+</sup> (bpy = 2,2'-bipyridine; dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) is covalently linked to a chitosan polymer; crosslinking by tripolyphosphate produced Ru-decorated chitosan fibers (NS-RuCh), with a 20:1 ratio between chitosan repeating units and Ru<sup>II</sup> chromophores. The properties of the Ru<sup>II</sup> compound are unperturbed by the chitosan structure, with NS-RuCh exhibiting the typical metal-to-ligand charge-transfer (MLCT) absorption and emission bands of Ru<sup>II</sup> complexes. When crosslinks are made in the presence of IrO<sub>2</sub> nanoparticles, such species are encapsulated within the nanofibers, thus generating the IrO<sub>2</sub>⊂NS-RuCh system, in which both Ru<sup>II</sup> photosensitizers and IrO<sub>2</sub> water oxidation catalysts are within the nanofiber structures. NS-RuCh and IrO<sub>2</sub>⊂NS-RuCh have been characterized by dynamic light scattering, scanning electronic micro-

scopy, and energy-dispersive X-ray analysis, which indicated a 2:1 ratio between Ru<sup>II</sup> chromophores and IrO<sub>2</sub> species. Photochemical water oxidation has been investigated by using IrO<sub>2</sub>⊂NS-RuCh as the chromophore/catalyst assembly and persulfate anions as the sacrificial species: photochemical water oxidation yields O<sub>2</sub> with a quantum yield ( $\Phi$ ) of 0.21, definitely higher than the  $\Phi$  obtained with a similar solution containing separated Ru(bpy)<sub>3</sub><sup>2+</sup> and IrO<sub>2</sub> nanoparticles (0.05) or with respect to that obtained when using NS-RuCh and "free" IrO<sub>2</sub> nanoparticles (0.10). A fast hole-scavenging process (rate constant,  $7 \times 10^4 \text{ s}^{-1}$ ) involving the oxidized photosensitizer and the IrO<sub>2</sub> catalyst within the IrO<sub>2</sub>⊂NS-RuCh system is behind the improved photochemical quantum yield of IrO<sub>2</sub>⊂NS-RuCh.

## Introduction

The development of artificial photosynthetic systems, that is synthetic systems capable of efficiently converting light energy into chemical energy inspired by the photosynthetic process

performed by natural organisms, is attracting a large interest nowadays, for both fundamental and applicative reasons, in particular because of the potential impact on renewable energy research.<sup>[1]</sup> Within this general frame, the development of new nanomaterials that integrate all necessary components (i.e., light-harvesting, charge separation and catalyst subunits) into a restricted environment is a promising research field,<sup>[2]</sup> as a restricted environment can speed up the rate (and efficiency) of photoinduced electron transfer processes, when bimolecular reactions are involved.

In this work, an abundant natural polymer, chitosan, is exploited as a useful environment to integrate light harvesting systems—which can also play the role of initiator of the photoinduced charge separation process, that is the charge separation unit—and catalysts in order to achieve photoinduced water oxidation, considered one of the bottlenecks of water splitting. Chitosan is a well-known amino-polysaccharide (Figure 1) characterized by interesting biological and chemical properties, including biocompatibility, biodegradability, non-toxicity, physiological inertness and antibacterial properties.<sup>[3]</sup> Whereas most of these properties are not relevant to our scopes, we planned to take advantage of the supramolecular structure of chitosan, in particular of its ability to incorporate small molecules into its fiber-like nanostructures.<sup>[4]</sup> Indeed, the polymeric structure of chitosan, in the presence of various agents, like tripolyphosphate (TPP), can rearrange to form

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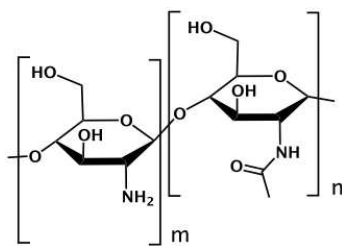


Figure 1. Representation of a chitosan repetitive unit.

nanosized superstructures that can encapsulate several substrates.<sup>[4]</sup>

Herein, we describe the synthesis and characterization of hybrid nanosystems made of chitosan nanostructures decorated with Ru<sup>II</sup> polypyridine complexes and loaded with iridium oxide nanoparticles as well-known water oxidation catalyst.<sup>[5,6]</sup> The photophysical properties and the photocatalytic performances of these hybrid nano-systems as far as photoinduced water oxidation is concerned are presented and discussed.

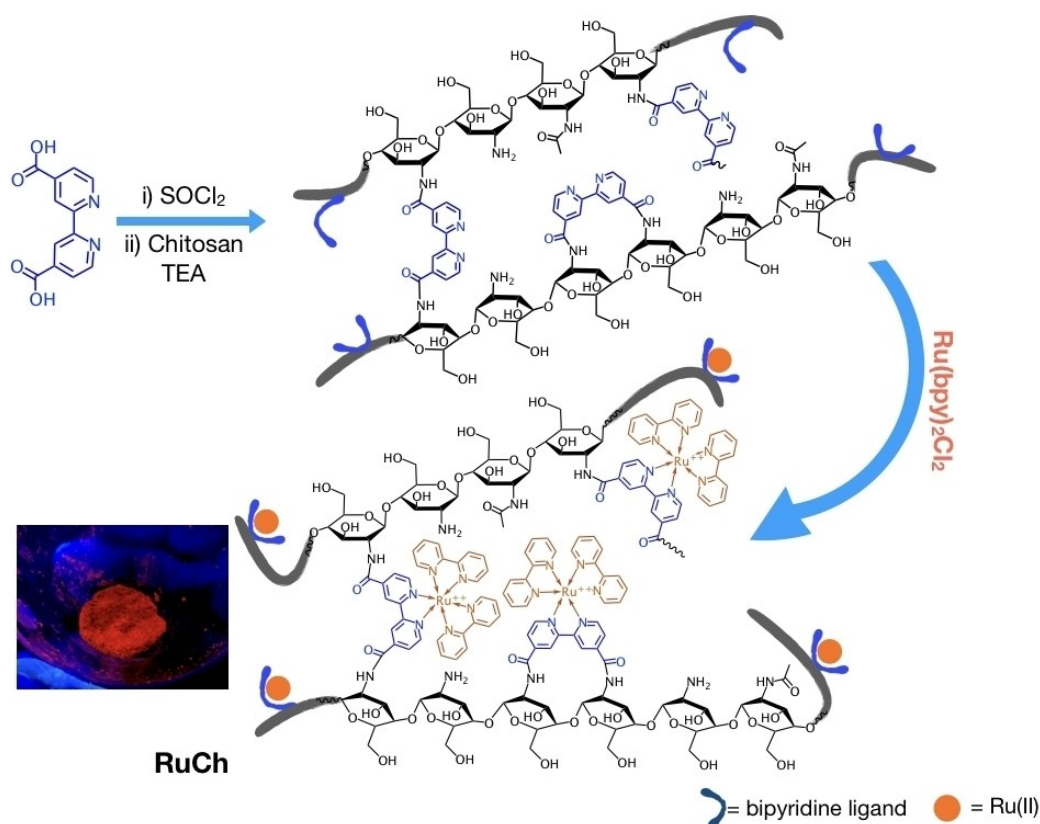
## Results and Discussion

### Synthesis of chitosan containing covalently linked Ru(bpy)<sub>3</sub><sup>2+</sup>-type subunits (polymeric RuCh)

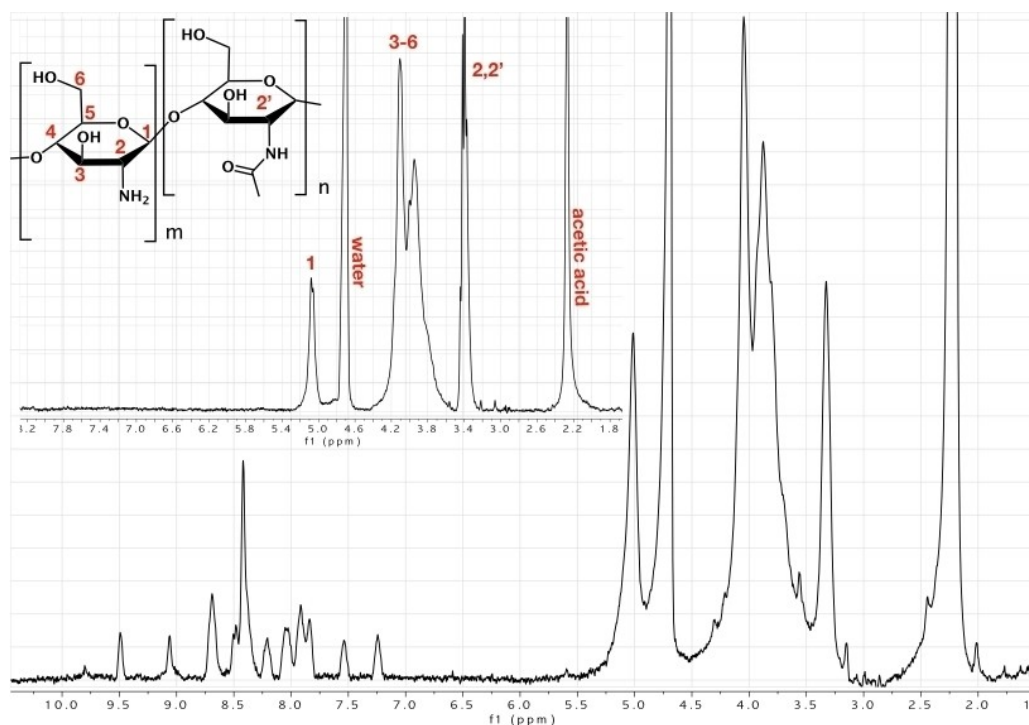
In order to prepare nanostructures of chitosan decorated with Ru<sup>II</sup> polypyridine complexes, it is necessary to find a synthetic way to covalently link Ru<sup>II</sup> complexes to the chitosan structure via a NH bond. This necessity arises from the fact that positively charged species, such as Ru(bpy)<sub>3</sub><sup>2+</sup> (bpy = 2,2'-bipyridine), are not easily incorporated into chitosan nanostructures because of the positive nature of the chitosan structure itself; in any case, the non covalently linked sensitizer possibly incorporated into the chitosan structure would easily be released in water. In fact, this is what happened in preliminary experiments (not reported) of this study. This prompted us to functionalize the chitosan basic molecules to allow the incorporation of Ru(bpy)<sub>3</sub><sup>2+</sup>-like species by direct link to the chitosan structure.

The synthetic route to obtain a ruthenium polypyridine complex linked to the chitosan structure (RuCh), is described in Scheme 1.

In the first step of the synthetic scheme, 4,4'-dicarboxy-2,2'-bipyridine (dcbpy) is transformed in the corresponding acyl chloride, in order to easily react with the amino group of chitosan. The so-formed bpyNHCH is then reacted with the ruthenium complex [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>] (bpy = 2,2'-bipyridine) to obtain



Scheme 1. Schematic representation of the synthesis of RuCh. Inset: Photo of RuCh powder under UV light.



**Figure 2.**  $^1\text{H}$  NMR spectrum of RuCh in  $\text{D}_2\text{O}$  ( $\text{CD}_3\text{COOD}$ , 1% v/v). The  $^1\text{H}$  NMR spectrum of low-molecular-weight chitosan in  $\text{D}_2\text{O}$  ( $\text{CD}_3\text{COOD}$ , 1% v/v) is shown in the inset. Spectra were recorded at  $40^\circ\text{C}$ .

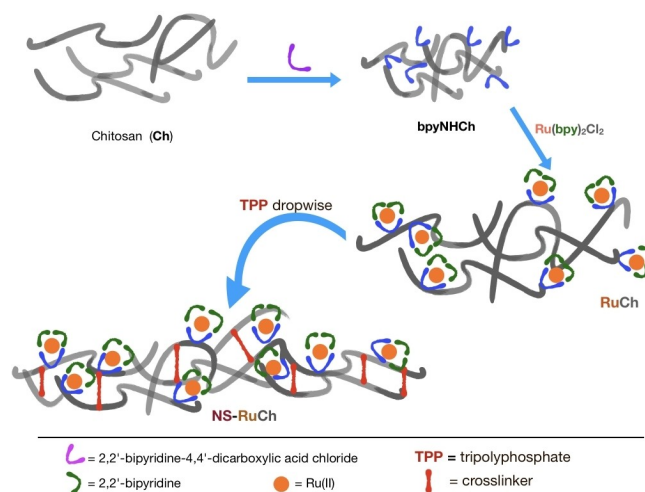
a modified chitosan containing covalently linked  $\{\text{Ru}(\text{bpy})_3\}^{2+}$  subunits, RuCh.

We characterized RuCh by H NMR in acidic conditions, at  $40^\circ\text{C}$ , because of its low solubility; its H NMR spectrum, in comparison with the H NMR spectrum of “free” chitosan (i.e., the chitosan missing the bpy functionalization and the ruthenium complex), is reported in Figure 2.

As shown in Figure 2, the various peaks in the range 5–1.8 ppm can be assigned to the chitosan structure and the peaks in the range 10–7 ppm are attributed to the bpy ligand of the ruthenium complex linked to chitosan. Moreover, from the NMR data it is also possible to establish a chitosan/Ru ratio of 20:1 (Figure S1 in the Supporting Information) so it can be stated that, on average, one ruthenium complex is linked per 20 units of chitosan monomer, by considering the monomer as reported in Figure 2.

### Nanosized superstructures prepared from RuCh (NS-RuCh and $\text{IrO}_2\text{@NS-RuCh}$ )

We prepared nanosized superstructures starting from RuCh by using a modification of methods already known in literature,<sup>[4]</sup> taking advantage of the fact that RuCh maintains the same reactivity of the free chitosan. In particular, we used TPP as the crosslinker, so obtaining nanoparticles containing the  $\{\text{Ru}(\text{bpy})_3\}^{2+}$  subunits (NS-RuCh). The synthetic method is schematized in Scheme 2.



**Scheme 2.** A cartoon representation of NS-RuCh synthesis by using the RuCh polymer.

The absorption and emission spectra of NS-RuCh in phosphate buffer are dominated by the spectra of its  $\text{Ru}(\text{bpy})_3^{2+}$ -type subunits (Figure 3): the UV region is characterized by the bpy-centered band at around 280 nm and the visible region exhibits the typical metal-to-ligand charge-transfer (MLCT) band of  $\text{Ru}^{\text{II}}$  polypyridine complexes.<sup>[7–8]</sup> The emission is attributed to the  $^3\text{MLCT}$  excited state of the  $\text{Ru}(\text{bpy})_3^{2+}$ -type subunits. Both the maxima of the visible absorption spectrum (465 nm) and of the emission band (645 nm) are slightly red-

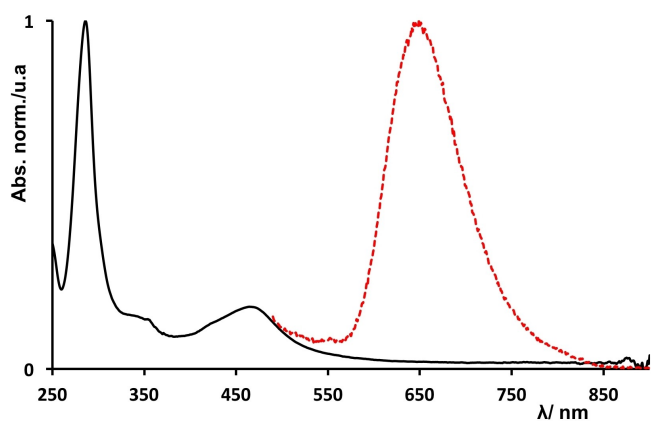


Figure 3. Absorption and emission spectra of NS-RuCh in phosphate buffer (20 mM, pH 7).

shifted compared to those of the model  $\text{Ru}(\text{bpy})_3^{2+}$  species (e.g., the emission spectrum of the model species exhibits a maximum at 625 nm in the identical experimental condition<sup>[7]</sup>), as expected since the acceptor of the MLCT transition in the present case is the modified bpy ligand, which has a lower lying  $\pi^*$  orbital than unsubstituted bpy. The emission lifetime in phosphate buffer at pH 7 is 305 ns, also in agreement with the  $^3\text{MLCT}$  assignment. The spectroscopic and excited state data indicate that the  $\text{Ru}(\text{bpy})_3^{2+}$ -type chromophores maintain their characteristic photophysical properties in the NS-RuCh assemblies.

Once verified that the properties of the Ru-based chromophores are maintained in the NS-RuCh assemblies, we performed the preparation of crosslinked Ru-decorated chitosan nanostructures in the presence of  $\text{IrO}_2$  nanoparticles in solution, which are known to be efficient water oxidation catalysts.<sup>[9–11]</sup> The assemblies so prepared contain both  $\text{Ru}(\text{bpy})_3^{2+}$ -type chromophores, covalently linked to the chitosan structure, and  $\text{IrO}_2$  nanoparticles, encapsulated within the superstructure of NS-RuCh (i.e., a  $\text{IrO}_2\text{CNS-RuCh}$  system), as demonstrated by dynamic light scattering (DLS), scanning electronic microscopy (SEM), and energy-dispersive X-ray analysis (EDX).

Dynamic light scattering analysis revealed an average size of 340 nm for  $\text{IrO}_2\text{CNS-Ru}$ , significantly larger than that observed in the case of NS-RuCh missing the  $\text{IrO}_2$  nanoparticle, that was 250 nm (Figure 4). The SEM images shows (Figure 5) a three dimensional porous net with a smooth surface. The nanofibers have an average diameter of about 250 nm and are spatially dispersed in random orientations. EDX analysis of such structures revealed the presence of both Ru and Ir atoms and allowed to estimate a Ru/Ir ratio of 2:1 in  $\text{IrO}_2\text{CNS-RuCh}$ , confirming the efficient encapsulation of  $\text{IrO}_2$  nanoparticles in the assemblies (Figure S2). Interestingly, once synthetically prepared in  $\text{IrO}_2\text{CNS-RuCh}$ ,  $\text{IrO}_2$  nanoparticles are not released in solution, as clearly demonstrated by the absence of any traces of “free”  $\text{IrO}_2$  nanoparticles in the DLS experiments on  $\text{IrO}_2\text{CNS-RuCh}$ . Probably, the several hydroxy groups which are present in the chitosan structure further stabilize the  $\text{IrO}_2$  nanoparticles within the structure.

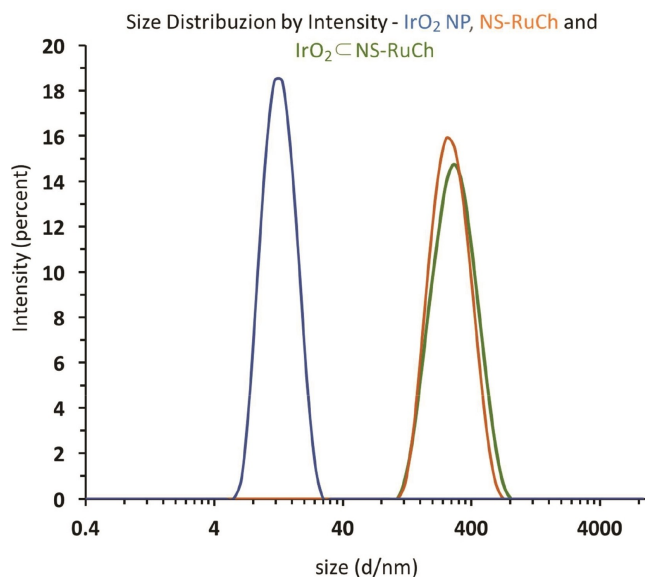


Figure 4. DLS analysis of  $\text{IrO}_2$  nanoparticles (blue), NS-RuCh (orange) and  $\text{IrO}_2\text{CNS-RuCh}$  (green). Note that the x-axis is drawn on a logarithmic scale.

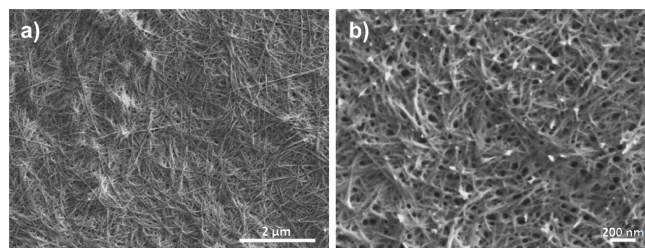


Figure 5. SEM analysis of  $\text{IrO}_2\text{CNS-Ru}$  at different scales.

The absorption spectrum of  $\text{IrO}_2\text{CNS-RuCh}$  in phosphate buffer at pH 7 strongly overlaps with that of NS-RuCh (Figure 6), with the remarkable difference that the spectrum of  $\text{IrO}_2\text{CNS-RuCh}$

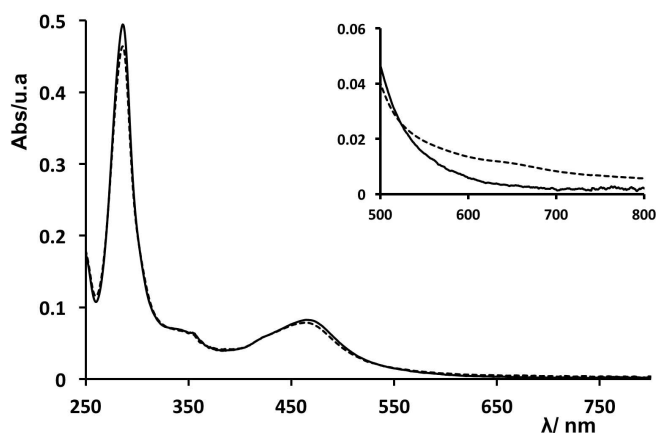


Figure 6. Absorption spectra of NS-RuCh (solid line) and  $\text{IrO}_2\text{CNS-RuCh}$  (dashed line) in phosphate buffer (20 mM, pH 7). The inset shows a zoomed area (500–800 nm) of the spectra.

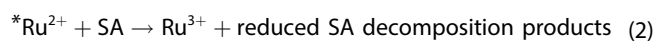
RuCh shows a small additional contribution at about 650 nm which can be attributed to the presence of IrO<sub>2</sub> nanoparticles.<sup>[9–12]</sup>

The emission spectrum of the IrO<sub>2</sub>CNS-RuCh is identical to that of NS-RuCh, and the emission lifetime is also very similar (315 ns): altogether, these data indicate that there is no significant interactions between the Ru-based chromophore and the IrO<sub>2</sub> catalyst, which thus behave as independent entities.

### Photo-induced water oxidation

Photoinduced water oxidation using Ru<sup>II</sup> polypyridine complexes has been explored by a catalytic cycle involving IrO<sub>2</sub> nanoparticles and sacrificial donor agents in solution.<sup>[9–11]</sup> Sacrificial agents have the role of extracting an electron from the MLCT excited state, simulating the effect of semiconductors, like nanostructured TiO<sub>2</sub>, in regenerative cells.<sup>[13]</sup> Whereas regenerative cells, for example dye-sensitized photosynthetic cells (DSPSC),<sup>[13b]</sup> are needed for effective water splitting, the use of sacrificial agents in solution allows to investigate the rate constants of the individual processes involved.

Sodium persulfate is a quite convenient sacrificial agent, since it efficiently quenches the MLCT state of Ru<sup>II</sup> polypyridine complexes by oxidative electron transfer, leading to the oxidized form of the chromophore, which is able to oxidize a suitable multielectron transfer catalyst like IrO<sub>2</sub> nanoparticles.<sup>[9]</sup> The overall reaction process is summarized in Equations (1)–(3),<sup>[14]</sup> where Ru<sup>2+</sup> represents the Ru<sup>II</sup> polypyridine chromophore, SA is the sacrificial agent (sodium persulfate in this case), and C is the catalyst (IrO<sub>2</sub> nanoparticles). Moreover, the reduced form of persulfate (i.e., the reduced SA species in Equation (2)) is not stable, forming sulfate radical anion, which is even a better oxidant than persulfate and reacts with Ru<sup>II</sup> polypyridine complexes so contributing to produce the oxidized photosensitizer Ru<sup>3+</sup>. Therefore, in sacrificial schemes involving persulfate anions, two Ru<sup>3+</sup> equivalent species are produced by a single absorbed photon.



The reaction in Equation (3) is repeated, involving several oxidized forms of C, in a stepwise manner, represented by Equation (4), until the active catalytic species is formed – for example C<sup>4+</sup> – and finally water oxidation takes place, according to Equation (5).



Clearly, several poisoning reactions can take place, reducing the quantum yield of the overall process. Such poisoning processes include direct decay of <sup>\*</sup>Ru<sup>2+</sup> to the ground state, which competes with Equation (2), as well as any back electron transfer process, which anyway is minimized – at least for the back electron transfer involving SA – by the instability of the reduced form of persulfate anions. Please note that since persulfate anions can produce two Ru<sup>III</sup> polypyridine complexes per absorbed photons (see above), and probably C<sup>4+</sup> is needed to oxidize water, the maximum photochemical water oxidation quantum yield in systems involving Ru<sup>II</sup> polypyridine complexes, persulfate anions as SA and IrO<sub>2</sub> nanoparticles as catalyst is 0.5.

We studied the photoproduction of molecular oxygen by irradiating ( $\lambda = 450$  nm) 2 mL of a buffered solution (20 mM phosphate buffer at pH 7) of IrO<sub>2</sub>CNS–Ru ( $1 \times 10^{-4}$  M) and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (10 mM). The concentration of IrO<sub>2</sub>CNS–Ru refers to the concentration of Ru(bpy)<sub>3</sub><sup>2+</sup>-type subunit, calculated on the basis of the molar absorption coefficient of RuCh (assumed roughly identical to that of Ru(bpy)<sub>3</sub><sup>2+</sup> in aqueous solution, i.e.,  $14600 \text{ M}^{-1} \text{ cm}^{-1}$ <sup>[7b]</sup>). The amount of molecular oxygen evolved during the photocatalytic cycle as well as the quantum yield of the process have been determined as previously described.<sup>[11]</sup> A typical result is shown in Figure 7. Similar experiments have been made by using Ru(bpy)<sub>3</sub><sup>2+</sup> or NS-RuCh as photosensitizers and adding IrO<sub>2</sub> nanoparticles in solution, always in the presence of persulfate, for comparison purposes. The three set of systems are schematized as follows:

- Ru(bpy)<sub>3</sub>Cl<sub>2</sub>/IrO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. This system is very well known in literature and is here used as a benchmark.<sup>[9–11]</sup>
- NS-RuCh/IrO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. In this system, the IrO<sub>2</sub> catalyst is added in solution to the preformed NS-RuCh assemblies containing the photosensitizer.
- IrO<sub>2</sub>CNS-RuCh/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. In this system the IrO<sub>2</sub> catalyst is encapsulated within the nanostructured assemblies.

In all the experiments, the concentration of the photosensitizer and catalyst are chosen to be constant ( $1 \times 10^{-4}$  and

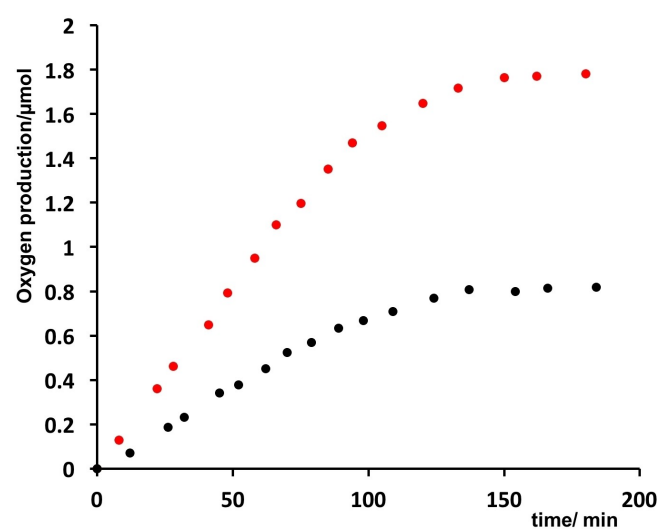


Figure 7. Oxygen evolution in the IrO<sub>2</sub>CNS–Ru/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (red) and NS-RuCh/IrO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems (black).

$5 \times 10^{-5}$  M, respectively, to respect the 2:1 photosensitizer/catalyst ratio estimated in  $\text{IrO}_2\text{CNS-RuCh}$ . Please note that concentration of  $\text{IrO}_2$  catalyst is referred to iridium atom content). Table 1 collects the photochemical quantum yields of molecular oxygen production recorded for the systems (a)–(c).

The larger photochemical quantum yield of molecular oxygen production in system (b) compared to that of system (a) can be justified by considering that an  $\text{IrO}_2$  nanoparticle which has been involved in one of the electron-transfer steps of Equations (3) and (4), so generating an intermediately oxidized form of  $\text{IrO}_2$ , is probably closer to other photosensitizers, so experiencing a higher local concentration of photosensitizers, making the overall photochemical process more efficient.

System (c), in which  $\text{Ru}(\text{bpy})_3^{2+}$ -type chromophores are covalently linked to the chitosan nanofibers and  $\text{IrO}_2$  nanoparticles are encapsulated within the nanostructure by the synthetic approach, experiences an even higher local concentration of both photosensitizers and catalyst: therefore it is not surprising that the photochemical quantum yield of molecular oxygen obtained using  $\text{IrO}_2\text{CNS-Ru}$  is larger than the other systems (a) and (b). The improved efficiency of the photocatalytic process in the case of  $\text{IrO}_2\text{CNS-Ru}$  can be thus attributed to kinetic advantages favored by the proximity of sensitizer and catalyst. This attribution is confirmed by flash photolysis experiments (see below).

It can be noted that the photostability of the systems based on  $\text{Ru}^{\text{II}}$  polypyridine complexes as photosensitizers is limited by the stability of the oxidized form of the photosensitizer, which can undergo oxidation of the polypyridine ligands.<sup>[15]</sup> This is evidenced by modification of the absorption spectrum of the photosensitizer during the photocatalysis. Noteworthy, system (c) exhibits a significant higher stability than system (a), probably connected with the faster reaction involving the oxidized form of the sensitizer (Figures S3–S5).

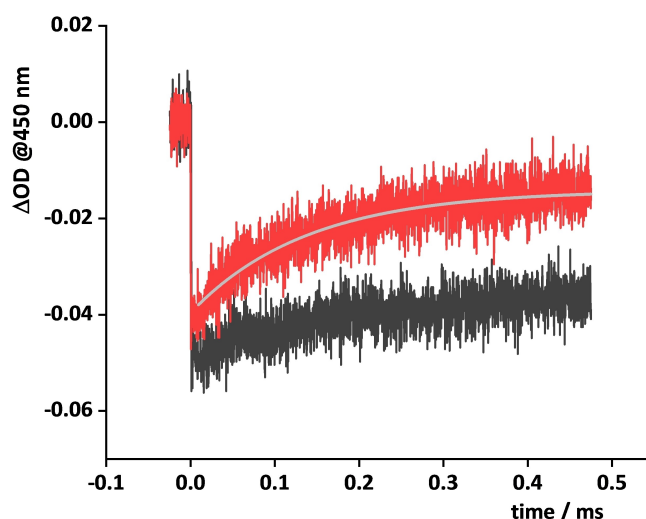
### Flash photolysis experiments

In order to better understand the photocatalytic performance of the  $\text{IrO}_2\text{CNS-Ru}$  system, we performed flash photolysis experiments in presence of  $\text{Na}_2\text{S}_2\text{O}_8$ . These experiments allow to gain kinetic information on the hole scavenging reaction between the oxidized photosensitizer and the catalyst, that is the key reaction in Equation (3).<sup>[9,10,13,16–19]</sup> Figure 8 shows the

**Table 1.** Quantum yield of oxygen production measured for each system reported.<sup>[a]</sup>

System	$\phi$
a) $\text{Ru}(\text{bpy})_3\text{Cl}_2 / \text{IrO}_2 / \text{Na}_2\text{S}_2\text{O}_8$	0.05
b) $\text{NS-RuCh} / \text{IrO}_2 / \text{Na}_2\text{S}_2\text{O}_8$	0.10
c) $\text{IrO}_2\text{CNS-RuCh} / \text{Na}_2\text{S}_2\text{O}_8$	0.21 <sup>[b]</sup>

[a] Each value is an average of three independent experiments in which a solution of 2 mL in buffer phosphate at pH 7 containing the photosensitizer ( $1 \times 10^{-4}$  M), the catalyst ( $5 \times 10^{-5}$  M) and  $\text{Na}_2\text{S}_2\text{O}_8$  (10 mM) was irradiated at  $\lambda = 450$  nm. [b] In this system the concentration of the catalyst is estimated to be  $5 \times 10^{-5}$  M by the determination of 2:1 Ru/Ir ratio obtained by EDX experiments (see text).



**Figure 8.** Flash photolysis experiments:  $\lambda_{\text{ex}} = 355$  nm;  $\text{Na}_2\text{S}_2\text{O}_8$  ( $1 \times 10^{-2}$  M).  $\text{IrO}_2\text{CNS-Ru}$  (red) and  $\text{NS-RuCh/IrO}_2$  ( $5 \times 10^{-5}$ ) systems (black).

kinetics of the bleaching and recovery of the MLCT absorption at 450 nm for the  $\text{IrO}_2\text{CNS-RuCh}$  system and for the  $\text{NS-RuCh}$  in the presence of  $5 \times 10^{-5}$  M of “free”  $\text{IrO}_2$ , which testifies the hole scavenging process. The bleaching of the MLCT band is produced upon excitation of the  $\text{Ru}$ -based chromophore followed by very fast oxidative electron transfer by 0.01 M persulfate anions, so generating the  $\text{Ru}^{\text{III}}$  species, which may undergo hole scavenging by the  $\text{IrO}_2$  catalyst, synthetically incorporated in  $\text{IrO}_2\text{CNS-RuCh}$  or present in solution in the case of  $\text{NS-RuCh}$ . The overall concentration of  $\text{IrO}_2$ , either incorporated or in solution, is identical for comparison purposes ( $5 \times 10^{-5}$  M). It is clear from Figure 8 that the hole scavenging process (associated to the bleach recovery due to the restoring of the  $\text{Ru}^{\text{II}}$  ground state) is faster in  $\text{IrO}_2\text{CNS-RuCh}$ . For this latter species, the rate constant of the hole scavenging process is  $7.4 \times 10^4 \text{ s}^{-1}$ . This is a remarkable value, when compared to the rate constant for the hole scavenging process in the  $[\text{Ru}(\text{bpy})_3]^{2+} / \text{IrO}_2 / \text{Na}_2\text{S}_2\text{O}_8$  system, which is reported to be  $8 \times 10^2 \text{ s}^{-1}$ ,<sup>[10]</sup> that is two orders of magnitude slower (this is consistent with the negligible hole scavenging of photogenerated  $\text{Ru}^{\text{III}}$  in  $\text{NS-RuCh}$  by “free”  $\text{IrO}_2$  within the measured time window at the  $\text{IrO}_2$  concentrations used; Figure S7). The relevant acceleration of the hole scavenging in  $\text{IrO}_2\text{CNS-RuCh}$  is attributed to the increase in proximity of both photosensitizer and catalyst subunits, thanks to the restricted environment promoted by the chitosan nanofibers which play the role of concentrators. Such a relevant acceleration of the hole scavenging process is therefore hold responsible for the improvement in the photochemical quantum yield of molecular oxygen production (Table 1), that is in the water oxidation process.

Nanosized fibers  $\text{IrO}_2\text{CNS-RuCh}$  made of crosslinked  $\text{Ru}$ -decorated chitosan have been prepared, with  $\text{IrO}_2$  nanoparticles encapsulated within the fibers by synthetic design. The  $\text{Ru}(\text{bpy})_3$ -type chromophores were covalently linked to the

chitosan scaffold. Absorption and emission spectroscopy showed that the Ru<sup>II</sup> polypyridine units keep their own spectroscopic and photophysical properties essentially unperturbed within the chitosan nanofiber. Photoinduced water oxidation takes place in the system in the presence of persulfate anions as sacrificial agents, with a quantum yield of 0.21, which is significantly higher than the quantum yield obtained for separated Ru<sup>II</sup> chromophores and IrO<sub>2</sub> catalyst in solution (0.05), as well as for the Ru-decorated chitosan nanofibers and non-encapsulated IrO<sub>2</sub> nanoparticle catalyst (0.10) investigated for comparison purposes. The more efficient photochemical water oxidation in the IrO<sub>2</sub>/CNS-RuCh system is attributed to the restricted environment experienced by the photosensitizers and catalysts, and in particular to kinetic reasons; actually, a remarkably fast hole-scavenging process between the oxidized photosensitizer and the catalyst occurs in IrO<sub>2</sub>/CNS-RuCh, with a rate constant of  $7.4 \times 10^4 \text{ s}^{-1}$ , which is about two orders of magnitude faster than the same process for isolated light-harvesting chromophore and catalyst species in solution. This result strongly confirms that restricted environments can play important roles in the design of functional supramolecular assemblies for achieving efficient photochemical water oxidation.

**Supporting Information available:** Details of materials, synthesis and characterization, instrumentation, oxygen evolving experiments.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** artificial photosynthesis · electron transfer · photochemical water oxidation · photochemistry; ruthenium

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