Nanocrystal-Molecular Hybrids for the Photocatalytic Oxidation of Water

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ABSTRACT

A modular molecular hybrid colloidal photocatalyst composed by TiO₂ nanocrystals (TiO₂-NCs) as light-absorber and the molecular complex [Ru(tda)(pypyr)₂], Ru-tda, as a water oxidation catalyst precursor, both anchored onto Single-Walled Carbon Nanotubes (SWCNTs) is described. This colloidal molecular hybrid photocatalyst, labeled as Ru-tda/SWCNT/TiO₂-NCs, is a robust material that can be easily prepared and scaled up. At neutral pH, in the presence of 3 suns illumination, the molecular hybrid material Ru-tda/SWCNT/TiO₂-NCs is capable of achieving the photocatalytic oxidation of water to dioxygen in the presence of persulfate, giving an unprecedented turnover number (TON) of 229.

Keywords

Photocatalysis, Water Oxidation, TiO₂ Nanocrystals, Ru Molecular Catalyst, Carbon Nanotubes, Hybrid Systems.

TOC GRAPHICS

The health and the environmental impact of fossil fuel usage by modern societies have urged the scientific community to find alternative fuels that can sustain current energy demands using carbon-neutral, clean, and sustainable sources.¹ Inspired by nature, artificial photosynthesis aims at capturing and storing the energy from solar photons into chemical bonds, generating clean and sustainable fuels, that obtained in this manner are termed solar fuels.² Light-induced water splitting ($h\nu$ -WS), where photons are stored into H-H and O-O bonds, can be considered a model case.³ Many scientific challenges still need to be overcome to be able to implement $h\nu$ -WS as a widespread technology. One of the most critical challenges include the performance of low-cost catalysts in terms of efficiency and stability, as well as their capacity to harmoniously interact with the light absorber.⁴

From a fundamental perspective, $h\nu$ -WS is a complex process involving a series of steps working in a synchronized manner, starting with the absorption of light, followed by charge separation, charge transfer, and finally, the corresponding proton reduction (PR) and water oxidation (WO) reactions. The WO reaction is particularly challenging because it involves the removal of four electrons and four protons from two water molecules and the formation of an O-O bond. Further, it is a thermodynamically very unfavorable reaction with a formal redox potential of 1.23 V vs. RHE.⁵ Semiconductor

Nanocrystals (NCs) with suitable bandgaps are excellent materials for light absorption and charge pair generation.⁶ However, high quantum efficiencies are not always translated into high water splitting activity due to the slow kinetics of the coupled PR and WO. The slow chemical reactions act as a bottleneck that will ultimately lead to charge recombination and photodegradation of the semiconductor NCs.⁷⁻⁸

Pure inorganic hybrid colloidal photocatalysts enclosed in aqueous reactor beds are highly promising due to their simplicity in reactor design, economic viability, and scalability.⁹ These systems involve colloidal photocatalyst based on wide-bandgap semiconductor NCs on top of which specific metal oxide domains -such as iridium, ruthenium, nickel or cobalt oxides- are deposited and employed as water oxidation catalysts (WOCs), leading to improved solar to fuel conversion efficiencies (STF).¹⁰⁻¹³ Despite their interest, their functionality and stability are mostly limited to extreme pH,¹⁴ which limits their use in realistic scenarios.

To overcome these limitations, molecular catalysts based on transition metal complexes can be employed. For the case of WO, some coordination complexes have been reported with very high turnover frequencies (TOFs), up to $50,000\text{ s}^{-1}$, and turnover numbers (TONs) higher than one million.¹⁵⁻¹⁶ Their proper design also allows them to work at mild pH conditions, close or equal to neutral pH.⁵ In this regard, the combination of highly active molecular catalysts and semiconductor NCs are promising candidates to perform solar-driven WO provided they have adequate electronic communication between them.¹⁷ Besides, as has recently been shown for a related molecular hybrid system, the swift hole transfer between the absorber and the molecular catalyst can act as a protective shield for the absorbing material against degradation due to the highly reactive generated holes upon light-induced charge separation.¹⁸

To combine molecular catalysts with semiconductor NCs different strategies have been employed. The most straightforward methodology involves the simple deposition (drop casting, spin coating, etc.), which is based on van der Waal interaction. Despite its simplicity, it might suffer from catalyst leaching or bad electronic communication between components. A promising alternative is the direct linkage of the molecular catalyst on the surface of the semiconductor NCs employing organic linkers.^{17,19} However, its performance will directly depend on the stability of the bond between the linker and the surface in aqueous solutions as has been described in the literature.^{19,20}

To overcome these limitations, we herein describe a molecular colloidal hybrid photocatalyst containing three different components, each selected according to its specific functionality (**Fig. 1**). Suitable light-absorbing TiO₂-NCs²¹ and an efficient molecular Ru complex¹⁶ providing an efficient light absorption and fast WO kinetics were selected (**Fig. 1**). Both were deposited onto Single-Walled Carbon Nanotubes (SWCNTs, see S1.1. and **Fig. S1**), which work as charge transfer platforms favoring the catalytic process²² due to their high conductivity (theoretically estimated to be 10⁶ S·cm⁻¹).²³

Figure 1. Schematic representation of the synthetic steps to obtain the colloidal photocatalyst Ru-tda/SWCNT/TiO₂-NCs, starting with the attachment of TiO₂-NCs to SWCNTs followed by the final loading of the molecular WOC. The upper right inset shows how the light-induced water oxidation reaction occurs on the particulates. TiO₂-NCs are responsible for absorbing the light and generate electrons and holes, which will diffuse through the SWCNT to the WOC and perform the desired water oxidation. On the other hand, the electrons will reduce protons, PR, or the sacrificial electron acceptor, SEA.

Highly monodisperse TiO₂ anatase tetragonally distorted square bipyramidal NCs of 9.3 ± 1.5 nm edge (**Fig. S2-S4**) with a high-intense UV light absorption spectra were synthesized following a non-aqueous surfactant-assisted approach previously reported by Murray and co-workers.²¹ In that approach, TiO₂-NCs were obtained by injecting a 1:1 mixture of TiF₄:TiCl₄ solutions in a liquid mixture of surfactants and co-reagents under a controlled atmosphere. The use of TiF₄ as a precursor leads to reduced (substoichiometric) TiO₂ (TiO_{2-x}, $0 < x < 0.2$) NCs with a high percentage of highly active {101} facets and a large number of oxygen vacancies.²⁴ This is translated into a deep-blue color colloidal solution and reported as more photoactive than stoichiometric TiO₂.²⁴⁻²⁵

Representative images of transmission electron microscopy (**Fig. 2A-B**) of as-obtained TiO₂-NCs reveal highly uniform particles with well-defined morphologies. Optical characterization by UV-Vis spectroscopy shows a sharp absorption edge at 300 nm (3.2 eV), which broadens beyond this wavelength into the visible region, as manifested by the deep-blue color (**Fig. S3**).²⁶⁻²⁷ Structural characterization by X-ray diffraction (**Fig. S4**) shows well-defined peaks accordingly with the high crystallinity of the sample. Crystal texture is observed in the relative enhanced intensity of 37.5° and 48° peaks,

corresponding to the elongation of the “*a*” axis forming the bipyramids. Broadening of the peaks is attributed to finite crystal size and defects in the crystal structure as a result of the oxygen vacancies.^{21, 25}

Figure 2. A) Representative Transmission Electron Microscopy (TEM) images of as-synthesized TiO₂ anatase square bipyramidal NCs. B) High magnification HAADF-STEM microscopy of the SWCNT/TiO₂-NCs. C) Schematic representation of the SWCNT/TiO₂-NCs hybrid structure. D) Cyclic Voltammetry at scan rate of 100 mV·s⁻¹ in pH 7 phosphate buffer solution (I = 0.1M) from 0.25 to 1.45 V (vs NHE). In blue, a blank of SWCNT/TiO₂-NCs drop-casted on glassy carbon, GC, as the working electrode and in red the freshly prepared Ru-tda/SWCNT/ TiO₂-NCs on GC as a working electrode. In both cases, Pt was used as counter electrode and Hg/Hg₂SO₄ as reference electrode. E) TEM microscopy of the Ru-tda/SWCNT/TiO₂-NCs hybrid structure. F) EDX spectra from the sample in E revealing the presence of atomic Ru in the hybrid structures.

After purification, TiO₂-NCs were mixed at room temperature with a suspension of SWCNTs in a methanolic solution. The decrease in surfactant concentration results in the progressive depletion of surfactant in the NCs' surface, destabilizing the system favoring aggregation. In a control experiment, NCs slowly aggregate in a relatively long period of time (> 6 h) in these conditions. The addition of SWCNTs to the system allows the NC naked surfaces to attach to them in a randomly distributed manner before aggregation takes place. As it can be seen in **Figs. 2B** and **S5**, the process leads to SWCNTs homogeneously coated with high densities of TiO₂-NCs ($3 \cdot 10^{15}$ NCs·mg⁻¹ SWCNT), in the c.a. 80% of the SWCNT coated surface (see supporting information for details). Remarkably, the SWCNT/TiO₂-NCs structures can undergo ultra-sonication in a bath for up to 6 h without any observable NCs detachment or change in morphology. This endurance experiment corroborates the stable and robust contact between both species indicating their direct contact, as microscopy analysis reveals (**Fig. 2B-C**). The method is fast, straightforward, versatile, highly reproducible, and scalable, thereby representing an exciting approach for the modular development of inorganic carbon-supported hybrid structures.

As molecular Water Oxidation Catalyst (WOC) precursor in this work we used the Ru complex [Ru(tda)(pyrpyr)₂], where tda²⁻ = [2,2':6',2''-terpyridine]-6,6''-dicarboxylato and pyrpyr = 4-(pyren-1-yl)-N-(pyridin-4-ylmethyl)butanamide) reported earlier⁹ and abbreviated as “Ru-tda” from here on (inset **Fig. 1**). The tda²⁻ ligand coordinates equatorially to the Ru metal center and is the key for achieving TOFs in the range of 8.000 s⁻¹ at neutral pH, thanks to the capacity of one of the carboxylate groups to act as an intramolecular proton acceptor during the O-O bond formation step.²⁸⁻²⁹ The axial positions are occupied by two pyridyl ligands that are functionalized with pyrene units, which are responsible for the anchoring on the SWCNTs via π,π -stacking interactions

(**Fig. 1**).¹⁶ The anchoring process, schematically represented in **Fig. S1**, consists of soaking the SWCNT/TiO₂-NCs material in a 1mM methanolic solution of the Ru-tda catalyst precursor. After 8h of stirring, the sample was centrifuged and washed with methanol. The resulting molecular hybrids Ru-tda/SWCNT/TiO₂-NCs were analyzed by cyclic voltammetry (CV), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) (**Fig. 2D-F**), confirming the successful incorporation of the ruthenium complex without changing neither the morphology of the SWCNT/TiO₂-NCs nor the molecular structure of the catalyst precursor. Particularly for the latter, CV experiments were very useful to electrochemically corroborate the presence of the molecular Ru compound on top of the conductive SWCNTs. By drop-casting the Ru-tda/SWCNT/TiO₂-NCs molecular hybrids onto a glassy carbon working electrode and carrying out a CV at pH 7, two redox waves at $E_{1/2} = 0.61$ V and $E_{1/2} = 1.06$ V (vs. NHE) appeared, corresponding to the characteristic Ru^{III/II} and Ru^{IV/III} couples, respectively (**Fig. 2D**).²⁸ We calculated coverage of $\Gamma = 2.18 \cdot 10^{-8}$ mol_{Ru}·g_{molecular hybrid}⁻¹, based on the charge under the anodic Ru^{III/II} wave, which accounts for a ratio of 10⁴:1 TiO₂-NCs:Ru-tda (see supporting information for details). A high ratio of semiconductor NCs versus catalyst is desirable to perform light-induced water oxidation efficiently, as previously observed in photocatalytic molecular systems.³⁰⁻³²

The capacity of the new molecular hybrid material, Ru-tda/SWCNT/TiO₂-NCs, to catalytically oxidize water to dioxygen induced by light was assessed in a thermostated reactor at 25 °C, under 3 suns irradiation, using peroxydisulfate (S₂O₈²⁻) as a sacrificial electron acceptor (SEA) in a pH 7 phosphate buffer solution. **Fig. 3A** displays the oxygen evolution profile in the presence (red trace) and the absence (blue trace) of the Ru-tda catalyst precursor under dark (light off, grey area) and light on conditions (yellow region). Once the sample is illuminated, electrons and holes are generated at the photoactive TiO₂-

NCs and are used to induce the chemical reactions that are responsible for final oxygen evolution (**Fig. 3B**).

In the absence of the Ru-catalyst, the SWCNT/TiO₂-NCs material upon illumination generates an increasing amount of oxygen during the first 50 minutes, via hydroxyl radical formation and its evolution (see eq. 4-8 in **Table 1**) as it has been previously described in the literature.³³ Then, during the next 2.5 h, the oxygen production continuously decreases until it fades away (See **Fig. 3A**, blue trace). This is consistent with the existence of a competing reaction pathway that degrades the TiO₂ or blocks its surface for further photoactivity in the present working conditions.

On the other hand, in the presence of the Ru-tda catalyst precursor, the molecular hybrid material Ru-tda/SWCNT/TiO₂-NCs generates no net molecular oxygen during the first 30 minutes when compared to the blank. However, and in sharp contrast, there is a sustained generation of O₂ over time afterward. This induction period is associated with the generation of the catalyst active species from the catalyst precursor as indicated in equations 3a-c in **Table 1**, where the precursor is progressively oxidized from Ru(II) to Ru(IV). The latter coordinates to a solvent OH⁻ generating a Ru seven-coordinated species, [Ru^{IV}(O)(tda)(pypyr)₂] (abbreviated as Ru^{IV}(O)-tda), responsible for water oxidation catalysis. This is a process that has been described previously in homogeneous phase and is known to be slow at pH 7.^{28, 30} Therefore, the initial molecular hybrid material containing the catalyst precursor Ru-tda/SWCNT/TiO₂-NCs, is progressively transformed into a new catalytically active molecular hybrid material, Ru^{IV}(O)-tda/SWCNT/TiO₂-NCs, that is responsible for the light-induced water oxidation catalysis. As mentioned earlier, the water oxidation to dioxygen reaction involves the removal of 4 H⁺ and four e⁻ from two water molecules and the formation of an O-O bond. The sequence of reactions responsible for all these processes is outlined in **Table 1**, in equations 3d-3h,

and are shown in a simplified manner with the green arrows in the energy scheme illustrated in **Fig. 3B**. This overall water oxidation reaction has been shown to occur very fast with TOFs in the range of 8.000 s^{-1} at pH 7 and it is the driving force that sustains the WO catalysis under illumination in the valence band of the TiO_2 -NCs. On the cathodic side, a large excess of peroxydisulfate is reduced to sulfate by the photoexcited electrons in the conduction band of the TiO_2 (eq. 4, 5a-b in **Table 1** and solid red arrows in **Fig. 3B**).

The fact that under the presence of Ru complex the photoactivity of the TiO_2 moiety is maintained throughout 2.7 h indicates that the Ru complex acts as a protecting agent for the surface of TiO_2 . Firstly, by avoiding the formation of $\text{HO}^\cdot$ and secondly, by reacting very fast with the holes generated upon excitation, thus avoiding TiO_2 surface degradation. The latter is a phenomenon that has recently been reported that occurs in the time scale of 300 fs in related systems.¹⁸

Figure 3. A) Oxygen evolution profile obtained during illumination of a mixture containing $2 \text{ mg} \cdot \text{mL}^{-1}$ Ru-tda/SWCNT/ TiO_2 -NCs (red) or $2 \text{ mg} \cdot \text{mL}^{-1}$ SWCNT/ TiO_2 -NCs (blue) in a photocatalytic reactor thermostated at 25°C , under 3 suns irradiation, and using 10 mM $\text{Na}_2\text{S}_2\text{O}_8$ as a sacrificial electron acceptor in a pH 7 phosphate buffer solution (I

= 0.1 M); B) schematic representation of the charge carrier dynamics and main reactions upon illumination.

Table 1. Set of reactions occurring on the Ru-tda/SWCNT/TiO₂-NCs molecular hybrid under light irradiation in the presence of a sacrificial electron acceptor in an aqueous phosphate buffer solution at pH 7.

Reactions		E / V vs NHE pH7	Eq.
Water Oxidation (WO)	$2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{O}_2 + 4\text{H}^+$	0.82	(1)
Proton Reduction (PR)	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	-0.41	(2)
Catalyst Precursor activation	$\text{Ru}^{\text{II}}\text{-tda} + \text{h}^+ \rightarrow \text{Ru}^{\text{III}}\text{-tda}$	0.61	(3a)
	$\text{Ru}^{\text{III}}\text{-tda} + \text{h}^+ \rightarrow \text{Ru}^{\text{IV}}\text{-tda}$	1.06	(3b)
WO Catalyst (WOC) generation	$\text{Ru}^{\text{IV}}\text{-tda} + \text{OH}^- \rightarrow \text{Ru}^{\text{IV}}(\text{O})\text{-tda} + \text{H}^+$		(3c)
WO Catalytic Cycle	$\text{Ru}^{\text{IV}}(\text{O})\text{-tda} + \text{h}^+ \rightarrow \text{Ru}^{\text{V}}(\text{O})\text{-tda}$	1.43	(3d)
	$\text{Ru}^{\text{V}}(\text{O})\text{-tda} + \text{H}_2\text{O} \rightarrow \text{Ru}^{\text{III}}(\text{OOH})\text{-tda} + \text{H}^+$		(3e)
	$\text{Ru}^{\text{III}}(\text{OOH})\text{-tda} + \text{h}^+ \rightarrow \text{Ru}^{\text{IV}}(\text{OO})\text{-tda} + \text{H}^+$		(3f)
	$\text{Ru}^{\text{IV}}(\text{OO})\text{-tda} + \text{H}_2\text{O} \rightarrow \text{Ru}^{\text{II}}(\text{H}_2\text{O})\text{-tda} + \text{O}_2$		(3g)
	$\text{Ru}^{\text{II}}(\text{H}_2\text{O})\text{-tda} + 2\text{h}^+ \rightarrow \text{Ru}^{\text{IV}}(\text{O})\text{-tda} + 2\text{H}^+$		(3h)
Sacrificial Electron Acceptor (SEA)	$\text{S}_2\text{O}_8^{2-} + \text{e}^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{\cdot-}$		(4)
	$\text{SO}_4^{\cdot-} + \text{e}^- \rightarrow \text{SO}_4^{2-}$		(5a)
	$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}$		(5b)

	$2\text{SO}_4^{\cdot-} + \text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + \text{OH}^{\cdot}$		(5c)
Hydroxyl radical evolution	$2\text{OH}^{\cdot} \rightarrow \text{H}_2\text{O}_2$		(6a)
	$\text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + \text{O}_2 + 2\text{e}^-$	-0.11	(6b)
Oxygen Reduction (OR) on TiO_2^{CB}	$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	-0.33	(7)
1 and 2e⁻ WO on TiO_2^{VB}	$\text{H}_2\text{O} + \text{h}^+ \rightarrow \text{HO}^{\cdot} + \text{H}^+$	2.39	(8)
	$2\text{H}_2\text{O} + 2\text{h}^+ \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+$	1.37	(9)

Remarkably, the hybrid material $\text{Ru}^{\text{IV}}(\text{O})\text{-tda/SWCNT/TiO}_2\text{-NCs}$ achieves 229 TONs based on the Ru catalyst amount (see supporting information), which is the highest reported for these type of systems.³⁴ The apparent quantum yield (AQY) of the water oxidation reaction at pH 7 and 25 °C was measured to be approximately 0.9% at the peak of absorbance of $\text{TiO}_2\text{-NCs}$ at $\lambda = 310\text{ nm}$ (see S8). On the one hand, this low value can be attributed to the large excess of light absorber versus catalyst and, on the other hand, to the high complexity of these systems. Similar quantum yields, albeit a bit lower 0.10-0.27%, have been recently reported for related hybrid molecular photocatalytic material using a Ru complex as WOC and CdS as a light absorber,^{18, 35} although in this case TONs were below 1.

The large absorber excess versus molecular catalyst ($10^4\text{:}1\text{ TiO}_2\text{-NCs:Ru-tda}$) could help in promoting the light-induced oxidation of the catalyst into high oxidation states by multiple sites which is reminiscent of the quantasome that operates in the photosystem II of green plants and algae.³⁵⁻³⁶ Further, this cooperation will be favored by the high mobility of the catalysts within the SWCNT surface as recently proposed for related Ru complexes.³⁶ In fact, given the large excess of absorber vs. molecular catalyst, the AQY

is relatively high. This can be explained by the fact that all the TiO_2 moieties that are not accessible by the highly mobile anchored Ru will progressively lose their photoactivity, as we have observed in the blank experiment. Thus they will not be involved in the light-harvesting process.^{33, 37} Further it is worth mentioning that the amount of highly active Ru catalyst used is extremely low ($2.2 \mu\text{g}_{\text{Ru}} \cdot \text{g}_{\text{molecular hybrid}}^{-1}$), in line with the scarcity of that element on Earth and the need of a better atom-(circular) economy for the future.³⁸⁻

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The low quantum yield also reflects the complexity of the system studied here where a large number of reactions are operating at the same time. For instance, back electron transfer from the Conduction Band (CB) to the Valence Band (VB) upon light-induced charge separation, will consume photons but will not lead to productive reactions. An additional challenge of single colloidal devices, as compared to typical two-compartment photoelectrochemical cells (PECs), is that oxidation and reduction reactions are not spatially separated. Therefore, it can lead to non-productive redox reactions that again will be responsible for a decrease in quantum efficiency.

The system presented here is remarkable because it is capable of overcoming all the challenges just described at neutral pH. Although the AQY is low, it is still within the best values reported in the literature up to now³⁴. Under these conditions, the molecular hybrid material $\text{Ru}^{\text{IV}}(\text{O})\text{-tda/SWCNT/TiO}_2\text{-NCs}$ achieves a remarkable TON of 229 upon illumination, which is the highest reported for this type of device¹⁸, thanks to favorable overall kinetics. Furthermore, obtained results can be considered a proof-of-concept of a modular approach that paves the way to develop molecular-NC hybrid photocatalysts for the production of clean and renewable fuels. This unique architecture allows rational adjustments of each component independently. Based on this tunability, future work will be focused on optimizing the system by controlling the loading of semiconductor NCs

and catalyst onto SWCNTs or other graphitic surfaces (e.g., graphene, 3D aerographites), and on adding a hydrogen evolution reaction (HER) catalyst for full water splitting. the modular approach reported here establishes a very versatile platform. Each of the constituting entities, such as the light absorber, the holder/communicator, and the catalyst, can be easily and independently replaced. For this reason, it is an optimal and efficient methodology for device discovery to foster the production of clean and renewable fuels.

ASSOCIATED CONTENT

Supporting Information. Material synthesis, material characterization, photocatalytic performance, ratios and concentrations, AQY

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Notes

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