



HAL
open science

Semiconducting overoxidized polypyrrole nano-particles for photocatalytic water splitting

Xiaojiao Yuan, Girlie Eunice Lopez, Viet-dung Duong, Samy Remita, Diana Dragoë, Dris Ihiawakrim, Ovidiu Ersen, Yannick Dappe, Winfried Leibl, Hynd Remita, et al.

► To cite this version:

Xiaojiao Yuan, Girlie Eunice Lopez, Viet-dung Duong, Samy Remita, Diana Dragoë, et al.. Semiconducting overoxidized polypyrrole nano-particles for photocatalytic water splitting. *Small*, 2025, pp.2407364. <10.1002/smll.202407364>. <hal-04976967>

HAL Id: hal-04976967

<https://hal.science/hal-04976967v1>

Submitted on 4 Mar 2025

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Semiconducting Overoxidized Polypyrrole Nano-Particles for Photocatalytic Water Splitting

Xiaojiao Yuan,^[a] Girlie Eunice Lopez,^[a] Viet-Dung Duong,^[a] Samy Remita,^[a] Diana Dragoe,^[b] Dris Ihiawakrim,^[c] Ovidiu Ersen,^[c] Yannick Dappe,^[d] Winfried Leibl,*^[e] Hynd Remita,*^[a] and Ally Aukauloo*^{[b][e]}

Dedicated to Akira Fujishima

Abstract: Capturing sunlight to fuel the water splitting reaction (WSR) into O₂ and H₂ is the leitmotif of the research around artificial photosynthesis. Organic semiconductors have now joined the quorum of materials currently dominated by inorganic oxides, where for both families of compounds the band gaps and energies can be adjusted synthetically to perform the WSR. However, elaborated and tedious synthetic pathways are necessary to optimize the photophysical properties of organic semiconductors. We report here, that when pyrrole dissolved distilled water is exposed to high energy radiation, this leads to the formation of nanostructured spherical polypyrrole (Nano-PPy) particles that were characterized as overoxidized polypyrrole. Electrochemical studies and Tauc's plot highlight the production of a semiconducting material with a band gap of ca. 1.8 eV with the conduction band at ca. -0.5 V and a valence band at around +1.3 V vs NHE. When suspended in water and under irradiation at wavelengths higher than 420 nm, Nano-PPy materials lead to O₂ evolution, while electrons and protons can be recovered in the form of reduced quinone. Interestingly, we observe upon intermittent visible irradiation and dark phases, a consumption of the evolved O₂ from oxidation of water. This concomitant O₂ reduction is found to produce H₂O₂.

All the lessons from intercepting sunlight photons to drive the synthesis of energy rich compounds are contained in the photosynthetic apparatus. Chemists are currently at work to uncover the principles behind these light-driven processes. The ongoing burden in this research is undoubtedly the photooxidation of water to recover the electrons and protons for the production of H₂, or to convert CO₂ to reduced carbon forms. Yet, after decades of efforts, the primary task of capturing light to oxidize water is deceptively still not solved, to expect a grand scale technological deployment. Nevertheless, this research field has been overwhelmed, and still is, by the development of inorganic semiconducting materials. This comes from the

seminal work of Honda-Fujishima showing that TiO₂ can photooxidize water upon irradiation in the UV region and that the electrons and protons can be conveyed to a platinum electrode for H₂ production.^[1] Although excellent results have been achieved, challenges ahead include the difficulty to adjust the band gap to lower than 2.0 eV as well as their corresponding band edges for overall water splitting, stability issues, fabrication cost, and low efficiencies.

Organic semiconductors have been mainly developed with the focus for organic solar cell devices and much less to perform photocatalytic transformation of small molecules. A real breakthrough came with the discovery by Domen and Antonetti that melon, generally referred as graphitic carbon nitride g-C₃N₄, was acting as a photocatalyst for the hydrogen evolution reaction with added co-catalyst and in the presence of a sacrificial electron donor.^[2] This report has captured an immense attention on the photocatalytic properties of g-C₃N₄, leading Lifshitz-Lee-Kang and coworkers to discover a totally metal free system made of g-C₃N₄ and carbon nanodots that could split water to O₂ and H₂ with an apparent quantum yield of 2%.^[3] In parallel, synthetic efforts have been engaged to design and prepare novel semiconducting organic materials to tailor the bandgaps and energies for the water splitting reaction. Cooper et al. have pioneered this field with the preparation of conjugated microporous materials by stitching polycyclic aromatic units through conjugated molecular struts.^[4] The group of Xu has elaborated a 2D conjugated microporous organic polymers based on the formation of orchestrated 1,3-diyne links between aromatic rings. These materials were gifted with the right band gaps and energies for the complete photo-splitting of water reaching an apparent quantum efficiency up to ca. 10%.^[5] Wang and coworkers have designed conjugated triazine polymers with adjustable band gaps and energies to photo-oxidize water and produce hydrogen with cobalt species as added co-catalysts.^[6] An additional challenge to overcome concerns the activation barrier for the two multi-electronic catalysis i.e., water oxidation and reduction reactions. This segment of the research is still a major hurdle and in many cases metal-based co-catalysts are still needed to realize the multielectron catalytic reactions and often the addition of sacrificial agents is compulsory to bypass either the oxidative or reductive chemical reaction. The effervescence in this research field can also be gauged by many recent reviews on different aspects in the development of organic semiconductors as photoelectrodes for water splitting.^[7,8] Elegant synthetic tactics are being actively pursued and sometimes helped through robot assisted synthetic output to elaborate new organic semiconducting materials.^[9,10]

Pyrrole, a byproduct in the petroleum distillate, has been extensively studied in many polymeric forms and has been

[a] Dr. X. Yuan, G. E. Lopez, Dr. S. Remita, Dr. H. Remita
Université Paris-Saclay, UMR 8000 CNRS, Institut de Chimie
Physique, 91405, Orsay, France.

[b] Dr. Diana Dragoe, Prof. A. Aukauloo
Université Paris-Saclay, UMR 8182, CNRS, Institut de Chimie
Moléculaires et des Matériaux d'Orsay, 91405, Orsay, France
E-mail: ally.aukauloo@universite-paris-saclay.fr

[c] Dr. Dris Ihiawakrim, Prof. Ovidiu Ersen
IPCMS – DSI, UMR 7504, CNRS-Université de Strasbourg, 23 rue
du Loess, 67000 Strasbourg

[d] Dr. Y. Dappe, IRAMIS, CEA-Saclay

[e] Dr. W. Leibl, Prof. A. Aukauloo
Université Paris Saclay, CEA, CNRS, Institut de Biologie Intégrative
de la Cellule (I2BC),
91198 Gif-sur-Yvette, France
E-mail: winfried.leibl@cea.fr

implemented in different electronic, optics devices and for sensing applications.^[11] We found here that the radiolytic polymerization of pyrrole in an aqueous medium led to the formation of nano-spherical polypyrrole material (termed as Nano-PPy) without the need of a templating agent. Nano-PPy was found to contain overoxidized pyrrole units. When dispersed in water and irradiated in the visible spectrum, Nano-PPy led to the photocatalytic evolution of O₂ without any added co-catalyst. The formation of H₂O₂ was also evidenced that stems from the partial reduction of formed O₂. Importantly, part of the expelled electrons and protons could be recovered in the form of reduced quinones delayed in time. In what follows, we discuss these findings.

Nano-PPy was prepared by the radiolytic polymerization of pyrrole monomers dissolved in distilled water under an N₂O atmosphere to enhance the formation of HO[•] oxidizing species (see Experimental section in the SI).^[12–15] The as-synthesized Nano-PPy material was isolated as a black powder and was stable in air. Transmission Electron Microscopy study (Figure 1a) reveals that the material is constituted of dispersed spherical particles. With increasing absorbed irradiation dose and at a given pyrrole concentration, Nano-PPy particles of varying sizes from 150 to 400 nm in diameter were obtained (See SI, Fig. S1). At high absorbed irradiation dose (77 kGy), we observed that the Nano-PPy particles are highly coalesced (Fig. S1-c). After fixing the Nano-PPy powders in a resin, STEM technique was used to interrogate the inner structure of these particles. Fig.1b shows the STEM image of a sliced nanoparticle which reveals that the inside of these particles constitutes a matrix encapsulating agglomerations of tiny black nano-particles of ca. 2.5 nm in diameter. As can be seen on the STEM image, these nanometric particles are distributed on both the surface and within the inside of the spherical particulates while a network of tunnels run through the Nano-PPy.

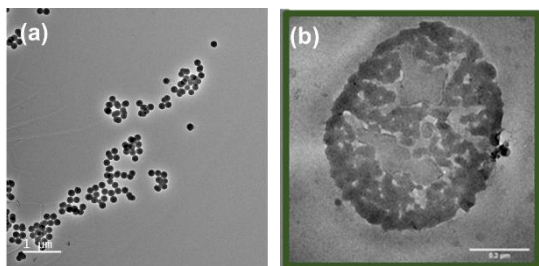


Figure 1. (a) TEM image of Nano-PPy particles (22 kGy) (b) STEM image of a sliced Nano-PPy fixed in resin showing the presence of small particles.

Previ
ous
therm

ogravimetric analysis indicated a loss of around 6% of the mass before reaching 100°C which we attribute to the presence of a low boiling point solvent EtOH used to wash the isolated nanoparticles. The continual loss of mass till reaching a plateau at 650°C supported the pure organic nature of the Nano-PPy material.^[12]

Further insight into the chemical state and elemental composition of Nano-PPy was given by X-ray Photoelectron Spectroscopy. The wide-scan spectrum (Figure 2a) shows the presence of C, N and O elements with the relative atomic concentrations of 71, 15 and 14, respectively. The nitrogen oxygen ratio obtained by XPS is 1.1 which is close to that obtained from elemental analysis (0.9), indicating a high degree of oxygenated form of the pyrrole units within Nano-PPy.

The C1s, N1s and O1s core-level spectra are shown in Figure 2b-d together with their components. The C1s spectrum was decomposed into six components corresponding to β -C and α -C at 284 eV and 284.8 eV, respectively, the polaron (=C-N^{•+}) at 285.8 eV, and the two contributions related to the presence of oxygen at 286.3 eV, attributed to C-O and the one at 287.7 eV corresponding to C=O. One last component at higher binding energies (291.6 eV) is due to the shake-up of π electrons.^[16] The higher intensity of α -C peak relative to β -C is due to the hydro-carbon contamination.

The two main contributions to N1s core-level spectrum located at 399.6 eV and 400.4 eV are assigned to pyrrolic and =C-N^{•+}, respectively. Besides, there are two small contributions reported for Nano-PPy^[16]: one at low Binding energy (BE), around 398 eV attributed to the imine-like nitrogen (-N=) and the second at high BE (~ 402 eV) attributed to the bipolaron (-C=N^{•+}). This high BE contribution is significantly reduced in the case of overoxidized PPy and was neglected.^[17]

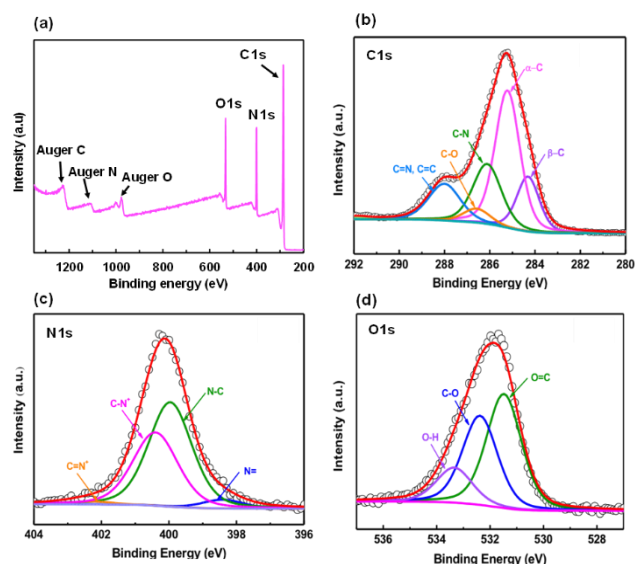


Figure 2. XPS survey of Nano-PPy (77 kGy) and high resolution C1s, N1s and O1s spectra.

The FTIR spectrum of Nano-PPy (Fig. 3a) is dominated by an intense absorption band at 1685 cm⁻¹ that was not detected in a chemically synthesized polymer (see Fig. S12-a). We assigned this band to the stretching modes of both C=N and C=O functions. The presence of C=O fragments can be explained by the formation of overoxidized units of pyrrole within the Nano-PPy coming from the attack of HO[•] on the β -positions of the pyrrole ring upon radiolytic polymerization, in agreement with literature.^[12] The stretching modes of pyrrole are shown in the region 1600-1400 cm⁻¹ (Figure 3a). The band located at 1531-1561 cm⁻¹ is attributed to the C=C/C-C stretching vibration of the PPy chains. The band at 735 cm⁻¹ is assigned to -NH (out-of-plane) vibration. The shift of this band to a higher frequency indicates the presence of a shorter conjugation length of the conjugated PPy system. Finally, the band at 3316, 1045 and 1407 cm⁻¹ corresponds to the N-H stretch, C-C out-of-plane deformation vibration and C-N vibrations in the PPy ring.

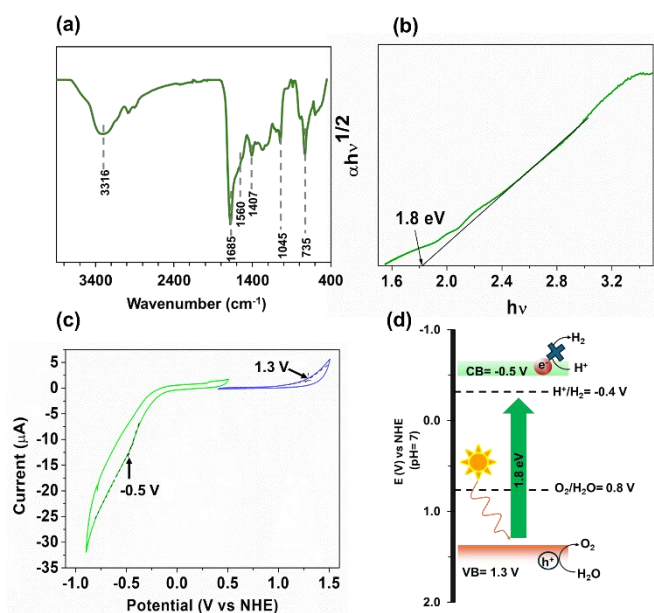


Figure 3. (a) FTIR spectrum, (b) Tauc plot, and (c) Cyclic voltammogram of PPy recorded at 20 mV/s in 0.1 M potassium phosphate buffer (pH 7); (d) Schematic band structure of PPy (77 kGy).

In a buffer solution at pH 6, the zeta potential of PPy was -23 mV, indicating a net negative charge (Fig. S2). The isoelectric point was found at around pH 4. The presence of amine, carbonyl, and hydroxyl groups makes the nano PPy responsive to pH changes, resulting in a change in zeta potential values from pH 2 to 12. Adsorption tests at different pH were performed to verify the surface charge behavior of PPy (Fig S3). Using methylene blue (MB) as probe molecule, we observed a dependence of MB adsorption with pH which is consistent with the surface charge of PPy at different pH.

The absorption spectrum in the solid state shows a broad band extending in the visible region (Fig. S4).^[13] The optical band gap of Nano-PPy was estimated from the Tauc's plot with an indirect band-gap (E_g) value of 1.8 eV (Figure 3b). The energy levels of the band (CB) and the valence band (VB) of Nano-PPy were estimated from cyclic voltammetry at ca. -0.5 and 1.3 V vs. NHE, respectively (Fig. 3c). Put together the approximated optical bandgap, the CB and VB edges of Nano-PPy can be portrayed as depicted in Figure 3d. Irradiating the suspension of PPy under visible light in the presence of triethanolamine (TEOA) as sacrificial electron donor and methyl viologen (MV^{2+}) as electron acceptor in acetonitrile solvent leads to the fast blue coloration of the solution, characterized by the formation of methyl viologen radical $MV^{\cdot+}$. (Figure 4a). Considering the potential of TEOA (0.84 - 1.14 V vs. NHE) and MV^{2+} (-0.45 V vs. NHE), the result is consistent with the estimated oxidation and reduction onsets of Nano-PPy. As such, the band edge positions show that Nano-PPy is thermodynamically apt to perform the water splitting reaction. However, no H_2 formation was detected by gas chromatography which can be assigned to kinetic issues for H_2 formation (Fig. S5).

The addition of an electron acceptor such as dichlorobenzoquinone prior irradiation resulted in the formation of a pink solution as depicted in Figure 6b. The pink color is typical of the formation of quinhydrone, a dimer formed from the reduction of the quinone by strong interaction of quinone with

the doubly reduced quinol form.^[18–20] Put together, these results underpin that in the absence of the formation of H_2 with Nano-PPy, the electrons and protons are stored on the material. Such a storage of charges on both inorganic and organic semiconducting materials has already been reported in literature.^[21–24]

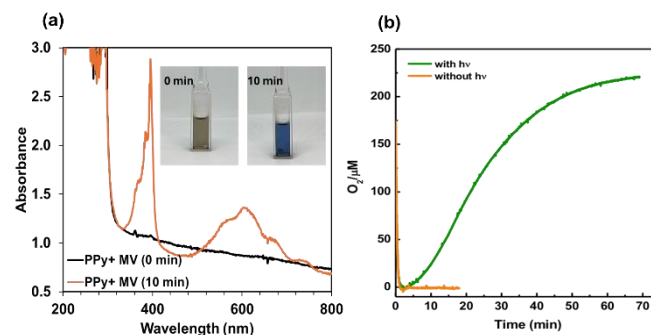


Figure 4. (a) UV vis spectra of PPy suspension irradiated under visible light ($\lambda \geq 420$ nm) and Ar purged conditions (100 μ M MV^{2+} and 10% TEOA in MeCN, inset: colour change due to formation of $MV^{\cdot+}$); (b) Time course of O_2 evolution from H_2O measured by Clark electrode with and without irradiation.

Due to extensive cross-linking and self-assembling of the polymers, nano-PPy is usually not soluble in classic organic solvents. It could, however, be sufficiently dispersed in a water/MeCN mixture to allow investigation by laser flash spectroscopy. Excitation by a nanosecond laser flash at 460 nm induced an excited state that showed emission centered at 530 nm. The rate of decay of this excited state was faster than the time resolution of our setup but can be estimated to be about 3 ns (Fig. S6). At longer times, weak emission from a strongly red-shifted state centered at 625 nm was detected. Transient absorption data showed laser flash-induced bleaching of the ground state absorption extending over the whole visible spectral range but did not reveal characteristic absorption features attributable to the product state (Fig. S7). The ground state absorption recovers with multi-exponential kinetics. We attribute the detected absorption transients to the formation of a charge separated state which decays with a lifetime of about 10 μ s and which is not quenched in the presence of O_2 . It is tempting to assign the long-lived emission band at 625 nm to photoluminescence from this charge-separated state which then should lie about 2 eV above the ground state. Together, the transient absorption data suggests that an emissive singlet excited state is evolving to a long-lived charge separated state with a lifetime of some microseconds.

In the first photocatalytic experiment, 2 mg of Nano-PPy was dispersed in 2 mL of distilled water at neutral pH in a Clark electrode cell jacketed with a refrigerating water source at 20°C (see SI). After degassing with N_2 to exclude all dissolved O_2 in water, the suspension was irradiated in the visible region ($\lambda > 435$, 150 W Halogen light source) under stirring. The time course of the evolution of oxygen is represented in Figure 4b. Remarkably, Nano-PPy was found to exhibit very high photocatalytic activity towards the formation of O_2 which rapidly increases to 220 μ M after 70 min irradiation. By contrast, no O_2 was observed under dark conditions, which indicates that O_2 comes from light-driven water oxidation. Isotopic labelling experiment with H_2O^{18} confirmed that the O_2 molecule originated from the oxidation of water (Figure S8). As mentioned above, based on the energy level of the conduction band of Nano-PPy,

COMMUNICATION

H_2 evolution was possible but was not observed, possibly due to kinetic issues. However, no change in pH of the solution was detected raising interrogation on the fate of the electrons and protons issued from the oxidation reaction.

Pursuing our investigation, we reasoned that the addition of a sacrificial electron acceptor would enable the extraction of charges from the conduction band to promote the accumulation of holes at the valence band for the light driven oxidation of water. The photocatalytic activity of Nano-PPy was then tested in a Clark electrode cell with minimal headspace. Nano PPy (2 mg) was dispersed in distilled water at pH 7 and an excess of sodium persulfate (10 mM) was added. The time course of the evolution of oxygen is represented in (Fig. 5a). To our surprise, we noticed an outburst of O_2 detected by the Clark electrode as soon as the irradiation was turned on, reaching a concentration of ca. 800 μM of O_2 within 2 minutes. This value is far beyond an air-equilibrated solubility of O_2 in water under our experimental conditions which is ca. 250 μM at ambient temperature. Upon turning the light off, we noticed a saturation regime due to the limit of detection O_2 concentration of the cell, followed by a continual decrease of O_2 concentration in the aqueous phase.

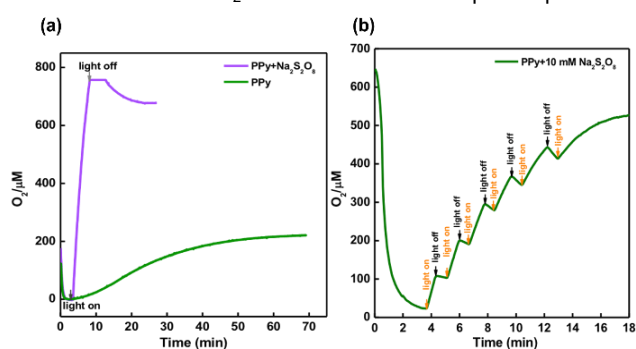
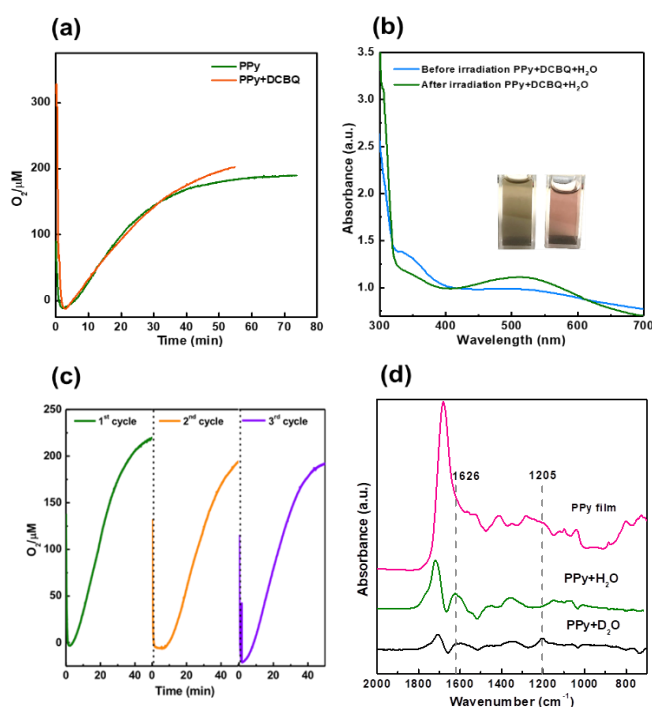


Figure 5. (a) Time courses of O_2 evolution in the presence of $\text{Na}_2\text{S}_2\text{O}_8$ (10 mM) and in the absence of electron acceptor using PPy irradiated at 77 kGy; (b) Alternate cycles of irradiation and dark periods.

In a subsequent experiment, we interrogated the effect of alternate light and dark phases for the photocatalytic O_2 production in presence of the persulfate salt. As clearly evidenced in Fig. 5b, O_2 is released only during the light excitation phases confirming that O_2 indeed comes from the light-driven oxidation of water. An intriguing observation comes from the dark phases where a systematic drop in the O_2 concentration is noted prior to the light is turned back on. Furthermore, a closer inspection shows that the drop in O_2 concentration for consecutive light and dark steps becomes more pronounced as the O_2 concentration in the solution increases. At this point, we can arguably postulate that during the dark phases there is a consumption of the produced O_2 . However, the rate of O_2 evolution outpaced the O_2 reduction resulting in net O_2 production under continuous irradiation with time. Hence, we reasoned that the consumption of O_2 may result in the formation of superoxide $\text{O}_2^{\cdot-}$, H_2O_2 or H_2O . It is likely that the formation of superoxide anion in the aqueous phase would rapidly lead to its dismutation to form H_2O_2 and O_2 . We thus investigated the presence of H_2O_2 by filtering the aqueous phase to remove the Nano-PPy. Upon the addition of a permanganate solution, we noticed a fading of the typical violet color associated with MnO_4^- ions (Fig S9).^[25] This interesting observation led us to verify the light-driven H_2O_2 production over PPy under O_2 purged, N_2 purged, and open-air conditions in pure water. We performed iodide oxidation to triiodide (I_3^-) to approximate the H_2O_2 amount. By monitoring the absorption band of I_3^- at 350

nm,^[25] we found ca. 380 μM , 273 μM and 45 μM H_2O_2 under O_2 purged, open air, and in N_2 conditions, respectively, after 2.5 hours of irradiation (Fig S10). This supports the reduction of O_2 as observed during water oxidation experiments and part of the charges is being consumed to reduce the produced O_2 to ultimately form H_2O_2 . In order to further verify that H_2O_2 stems from the reduction of O_2 , we added an electron acceptor, in this case, benzoquinone (BQ), that effectively competes with O_2 for electrons from the conduction band. As we evidenced in Figure S11, the pathway leading to H_2O_2 is inhibited implying that O_2 is reduced to form superoxide at the Nano-PPy particles that dismutates to form H_2O_2 . Henceforth, the formation of H_2O_2 from the water oxidation can be discarded.

The cyclability of Nano-PPy was tested after consecutive photocatalytic runs and no significant change in the O_2 evolution was observed (Figure 6c). The chemical stability of the Nano-PPy was monitored by XPS studies after photocatalytic experiments. Interestingly no marked changes were noticed between the starting material and the samples after photocatalysis, however aggregation of the particles was



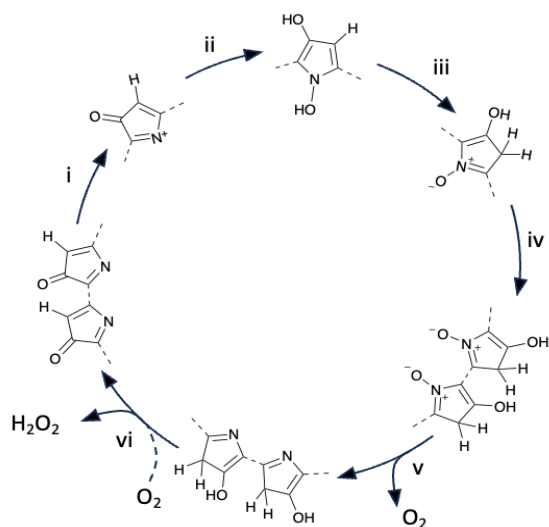
observed (Fig S12).

Figure 6. (a) Time courses of O_2 evolution in presence of DCBQ; (b) UV-Vis absorption before and after irradiation in presence of DCBQ; (c) recyclability tests after water oxidation and (d) FTIR monitoring in presence of H_2O and D_2O .

Additionally, we also monitored the spectral changes using Infrared spectroscopy upon photocatalysis in presence of H_2O and D_2O (Fig. 6d). The stretching modes of NanoPPy-film are shown in the region 1600-1400 cm^{-1} . The band located at 1666 cm^{-1} is attributed to the C=C/C-C stretching vibration of the PPy chains. No changes were observed in the C-C aromatic ring stretch region. The peak at 1626 cm^{-1} is attributed to the δ (H-O-H) bending. In the presence of D_2O , a new peak at 1205 cm^{-1} emerges, which is in accordance with the results of Belhadj and coworkers.^[27] The observed H/D isotopic effect can be tentatively attributed to alterations in electron density and the accumulation of protons/deuterons at the PPy.^[26]

With the objective of providing some insights on the structure/reactivity of the Nano-PPy, we performed comparative experiments with PPy obtained from the classic chemical oxidation method with FeCl_3 (Fig. S13). No O_2 was formed upon irradiation of the slurry of the PPy in water (Fig. S14) and only traces of H_2O_2 were detected (Fig. S15). These results tend to support the overoxidized nature and probably the polymerization pattern of Nano-PPy as produced by radiolytic polymerization, induce the observed catalytic activity. In the absence of a clear structural view of the polymerization pattern of the overoxidized pyrrolic units, we inventoried the different proposals in the literature to tentatively propose a putative mechanistic pathway for the oxidation of water. In our case, based on the presence of oxidized pyrrole groups, we reasoned that the nitrogen atoms can be the site for the water activation process. It is noteworthy, that in a recent publication the authors report on the photocatalytic water splitting reaction with a designed polymer based on free base porphyrins in absence of any metal ions.^[28] Although no mechanistic pathway has been provided, it is anticipated that the un-metalated porphyrin macrocycle is the locus for the water activation process. Furthermore, N-oxide containing heterocycles such as pyridine N-oxide moiety is widely reported for its catalytic activity for oxygen atom transfer (OAT) as well as hydrogen atom transfer (HAT) reactions.^[29–31] To test this proposal, we realized the polymerization of the N-methyl pyrrole where the nitrogen atom is blocked with a methyl group. A clear difference is observed between the Infrared spectral features of the gamma irradiation synthesis and those of the chemical oxidized form, which is the presence of the intense signal at around 1680 cm^{-1} that can be attributed to the C=O group (Fig. S16-b, S17-b). However, none of N-methyl polypyrrole (NMPPy) (chemically or radiolytically synthesized) exhibited any photocatalytic O_2 evolution upon irradiation under the same conditions as for Nano-PPy (Fig. S18, S19). These results bring supporting elements that the nitrogen atoms of the oxidized pyrrole in NanoPPy may be at the origin of the water activation and oxidation. A plausible sequence of events leading to the formation of O_2 is given in Scheme 1.

Scheme 1: Proposed photocatalytic cycle for the O_2 evolution and H_2O_2 formation with NanoPPy under visible light irradiation: i) photoaccumulation of positive charges at the nitrogen atoms, ii) water activation, iii) N-oxide



tautomeric form, iv) coupling of two N-oxide under irradiation to form O_2 , v) reduced forms to react with O_2 to form H_2O_2 .

We have described here the synthesis of nanostructured overoxidized polypyrrole particles (Nano-PPy) prepared by radiolysis at 77 kGy of pyrrole monomers in water. Nano-PPy material is devoid of any presence of metallic ions. Electrochemical studies and Tauc plot point to a semiconducting material forged with a band gap of ca. 1.8 eV with the conduction band at ca. -0.5 V and a valence band at around 1.3 V. When suspended in water and under irradiation at $\lambda > 420\text{ nm}$, we discovered that the Nano-PPy lead to O_2 evolution. Concomitantly, we detected the presence of H_2O_2 that originates from O_2 reduction instead of water oxidation. Accordingly, we observed upon intermittent irradiation and dark phases, a consumption of the evolved O_2 from the oxidation of water. Interestingly, we also found that part of the electrons and protons released from water oxidation process could be recovered in the form of reduced quinone. Further work is under way to gain more insights in the functioning of such organic semiconducting materials based on operando techniques and theoretical analyses.

Acknowledgements

This work has been supported by the the French Infrastructure for Integrated Structural Biology (FRISBI) ANR-10-INSB-05-01, and the French National Research Agency (ANR-21- SCOOPE). We thank CNRS, CEA Saclay, ICMMO and University Paris-Saclay for the financial support. A. Aukauloo thanks the Institut Universitaire de France for support.

Keywords: Overoxidized • polypyrrole • organic semiconductors • photocatalytic water splitting • H_2O_2

- [1] A. Fujishima, X. Zhang, *Comptes Rendus Chimie* **2006**, *9*, 750–760.
- [2] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nature Mater* **2009**, *8*, 76–80.
- [3] J. Liu, Y. Liu, N. Liu, Y. Han, X. Zhang, H. Huang, Y. Lifshitz, S.-T. Lee, J. Zhong, Z. Kang, *Science* **2015**, *347*, 970–974.
- [4] R. S. Sprick, J.-X. Jiang, B. Bonillo, S. Ren, T. Ratvijitvech, P. Guiglion, M. A. Zwiijnenburg, D. J. Adams, A. I. Cooper, *J. Am. Chem. Soc.* **2015**, *137*, 3265–3270.
- [5] L. Wang, Y. Wan, Y. Ding, S. Wu, Y. Zhang, X. Zhang, G. Zhang, Y. Xiong, X. Wu, J. Yang, H. Xu, *Advanced Materials* **2017**, *29*, 1702428.
- [6] Z.-A. Lan, Y. Fang, Y. Zhang, X. Wang, *Angewandte Chemie International Edition* **2018**, *57*, 470–474.
- [7] J. Yu, J. Lee, Y. Kim, J. Song, O. Jiyeon, S. Lee, M. Jeong, Y. Kim, J. Kwak, S. Cho, C. Yang, J.-W. Jang, *Nature Communications* **2020**, *11*, DOI 10.1038/s41467-020-19329-0.
- [8] D. Zhang, H.-H. Cho, J.-H. Yum, M. Mensi, K. Sivula, *Advanced Energy Materials* **2022**, *12*, 2202363.
- [9] B. Burger, P. M. Maffettone, V. V. Gusev, C. M. Aitchison, Y. Bai, X. Wang, X. Li, B. M. Alston, B. Li, R. Clowes, N. Rankin, B. Harris, R. S. Sprick, A. I. Cooper, *Nature* **2020**, *583*, 237–241.
- [10] S. Vijaykrishnan, J. W. Ward, A. I. Cooper, *ACS Catal.* **2022**, *12*, 10057–10064.
- [11] A. L. Pang, A. Arsad, M. Ahmadipour, *Polymers for Advanced Technologies* **2021**, *32*, 1428–1454.
- [12] Z. Cui, C. Coletta, A. Dazzi, P. Lefrançois, M. Gervais, S. Néron, S. Remita, *Langmuir* **2014**, *30*, 14086–14094.
- [13] X. Yuan, D. Floresyona, P.-H. Aubert, T.-T. Bui, S. Remita, S. Ghosh, F. Brisset, F. Goubard, H. Remita, *Applied Catalysis B: Environmental* **2019**, *242*, 284–292.
- [14] Y. Chouli, F. Belkhadem-Mokhtari, S. Abou-Zeid, D. Dragoe, R. Saint-Martin, F. Brisset, H. Remita, S. Remita, *Radiation Physics and Chemistry* **2022**, *195*, 110079.
- [15] T. Bahry, B. Khurshid, Y. Chouli, S. A. Zeid, C. Sollogoub, M. Gervais, T.-T. Bui, F. Goubard, S. Remita, *New J. Chem.* **2021**, *45*, 13142–13157.
- [16] C. Malitesta, I. Losito, L. Sabbatini, P. G. Zamboni, *Journal of Electron Spectroscopy and Related Phenomena* **1995**, *76*, 629–634.
- [17] H. Ge, G. Qi, E.-T. Kang, K. G. Neoh, *Polymer* **1994**, *35*, 504–508.

COMMUNICATION

- [18] J. E. Guillet, *Pure and Applied Chemistry* **1991**, 63, 917–924.
 - [19] M. Bouvet, B. Malézieux, P. Herson, *Chem. Commun.* **2006**, 1751–1753.
 - [20] J. Regeimbal, S. Gleiter, B. L. Trumpower, C.-A. Yu, M. Diwakar, D. P. Ballou, J. C. A. Bardwell, *Proc. Natl. Acad. Sci. U.S.A.* **2003**, 100, 13779–13784.
 - [21] J. N. Schrauben, R. Hayoun, C. N. Valdez, M. Braten, L. Fridley, J. M. Mayer, *Science* **2012**, 336, 1298–1301.
 - [22] T. Wilke, M. Schneider, K. Kleineremanns, *OJPC* **2013**, 03, 97–102.
 - [23] M. D. Symes, L. Cronin, *Nature Chem* **2013**, 5, 403–409.
 - [24] B. Rausch, M. D. Symes, L. Cronin, *J. Am. Chem. Soc.* **2013**, 135, 13656–13659.
 - [25] N. V. Klassen, David. Marchington, H. C. E. McGowan, *Anal. Chem.* **1994**, 66, 2921–2925.
 - [26] S. Lamprakopoulos, D. Yfantis, A. Yfantis, D. Schmeisser, J. Anastassopoulou, T. Theophanides, *Synthetic Metals* **2004**, 144, 229–234.
 - [27] H. Belhadj, A. Hakki, P. K. J. Robertson, D. W. Bahnemann, *Phys. Chem. Chem. Phys.*, **2015**, 17, 22940–22946
 - [28] Y. Ge, Z. Lyu, M. Marcos-Hernández, D. Villagrán, *Chem. Sci.* **2022**, 13, 8597–8604.
 - [29] H. Li, F. Xie, M.-T. Zhang, *ACS Catal.* **2021**, 11, 68–73.
 - [30] V. S. Basistyi, J. H. Frederich, *Org. Lett.* **2022**, 24, 1907–1912.
 - [31] M. Z. Ertem, J. J. Concepcion, *Inorg. Chem.* **2020**, 59, 5966–5974.
-

Entry for the Table of Contents

COMMUNICATION

We report here, that when pyrrole dissolved distilled water is exposed to high energy radiation, this leads to the formation of nanostructured spherical polypyrrole (Nano-PPy) particles that were characterized as overoxidized polypyrrole. Electrochemical studies and Tauc plots highlight the production of a semiconducting material with a band gap of ca. 1.8 eV with the conduction band at ca. -0.5 V and a valence band at around +1.3 V vs NHE. When suspended in water and under irradiation at wavelengths higher than 420 nm, Nano-PPy materials lead to O₂ evolution, while electrons and protons can be recovered in the form of reduced quinone. Interestingly, we observe upon intermittent visible irradiation and dark phases, a consumption of the evolved O₂ from oxidation of water. This concomitant O₂ reduction is found to produce H₂O₂.

*Xiaojiao Yuan,^[a] Girlie Eunice Lopez,^[a]
Viet-Dung Duong,^[a] Samy Remita,^[a]
Diana Dragoie,^[b] Dris Ihiawakrim,^[c]
Ovidiu Ersen,^[c] Yannick Dappe,^[d]
Winfried Leibl,*^[e] Hynd Remita,*^[a], Ally
Aukauloo*^{[b][e]}*

Page No. – Page No.
