PHOTOGRAPH: where PHOTOelectrochemical hydrogen production meets GRAPHene-based interfaces

PHOTOGRAPH: donde la producción fotoelectroquímica de hidrógeno se encuentra con las interfaces basadas en grafeno

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Abstract

PHOTOGRAPH is subproject (Ref. PID2019-104272RB-C51) of a coordinated national project entitled NEXT-ENER, associated at the 2019 national R&D program *"Proyectos de I+D+i – Retos"* and led by the Group of Carbon Nanostructures and Nanotechnology (G-CNN) at the Instituto de Carboquímica (ICB-CSIC). Within the overall frame of the coordinated project, devoted to the integration of new energy conversion and storage technologies and, being developed by five Spanish research groups, PHOTOGRAPH focuses on the photoelectrochemical hydrogen production using optimized graphene-based interfaces. The main motivation of PHOTOGRAPH is to improve the photoelectrochemical device performance while reducing costs and the ecological footprint, directly tackling several problems that humankind is facing nowadays. In this communication, a journey throughout past, present and future perspectives of PHOTOGRAPH is presented, especially emphasizing ongoing activities.

Resumen

PHOTOGRAPH es un subproyecto (Ref. PID2019-104272RB-C51) del proyecto coordinado a nivel nacional titulado NEXT-ENER, asociado al programa nacional de I+D "*Proyectos de I+D+i – Retos*" de 2019, liderado por el Grupo de Nanoestructuras de Carbono y Nanotecnología. Dentro del marco general del proyecto coordinado, dedicado a la integración de nuevas tecnologías de conversión y almacenamiento de energía y, estando desarrollado por cinco grupos de investigación españoles, PHOTOGRAPH se encarga de la producción fotoelectroquímica de hidrógeno mediante interfaces optimizadas basadas en grafeno. La principal motivación de PHOTOGRAPH es la de mejorar la respuesta de los dispositivos fotoelectroquímicos a la vez que se reduce el coste y la huella ecológica de los mismos, afrontando directamente algunos de los problemas a los que la humanidad se está enfrentando actualmente. En esta comunicación, se hará un recorrido a lo largo del pasado, presente y perspectivas futuras de PHOTOGRAPH, haciendo especial énfasis en las actividades se están llevando a cabo.

1. Introduction

Generation of storable fuels from sunlight and water is one of the greatest challenges of the modern age. Humankind is facing fossil fuels depletion and global warming, which will likely lead to a climatic and energetic crisis if no action is taken. In this context, solar energy is one of the most relevant technologies that can be potentially applied to alleviate the dependence on fossil fuels. Nevertheless, the relatively low power densities and its fluctuating nature are some issues that are hindering the rapid adoption of such solar technologies [1].

Regarding the storage of green energy sources, molecular hydrogen (H_2) strikes as a promising and sustainable alternative to fossil fuels only if produced from renewable resources. However, fossil fuels still stand as the main source of hydrogen over the last few years (**Figure 1**) [2]. It remains clear that novel and efficient technologies should be sought to fully exploit the potential of hydrogen. Under this scenario, photoelectrochemical water splitting (PEC-WS) is an emerging technology that combines both solar energy and electricity to produce hydrogen by the photoelectrolysis of water [3]. In other words, as sustainable energy sources are employed for this purpose, no greenhouse gases are emitted. Additionally, the direct conversion of sunlight allows producing hydrogen under milder conditions with respect to typical electrolytic processes.

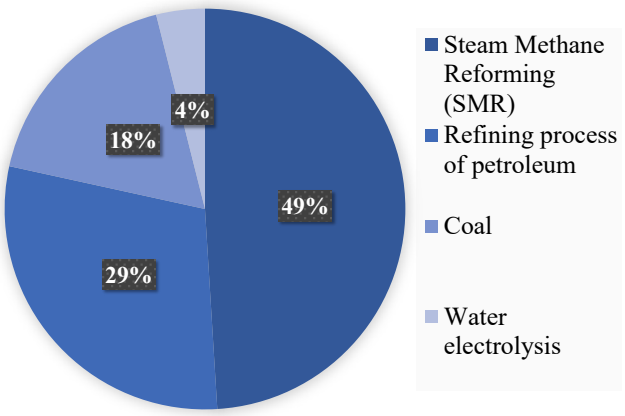

Figure 1. Relative proportions of hydrogen production and their provenance [2].

Figura 1. Proporciones relativas en la producción de hidrógeno y sus procedencias [2].

The PHOTOGRAPH project addresses the development of layered photoelectrode device structures for the production of green hydrogen by PEC-WS. Particularly, photoelectrodes composed of a nanoparticulated photoactive phase are tested to carry out that type of light-driven process. Furthermore, its combination with graphene-based interfaces, namely graphene oxide (GO), carbon nanotubes (CNTs) and carbon dots (CDs) (**Figure 2**), renders favorable combinations of photoelectrodes. Such versatility has been previously demonstrated by the Group of Carbon Nanostructures and Nanotechnology (G-CNN). For instance, GO not only acts as a hole-transport layer in nanostructured TiO_2 and ZnO photoanodes [4,5], but also favors photoinduced charge-transfer in nanostructured conjugated polymer-based photocathodes [6]. Moreover, CNTs being processed into films of conductive network structures contribute to achieve impressive charge separation in TiO_2 photoanodes, which additionally improves the efficiency of the process [4,7]. Regarding CDs, their outstanding potential as sensitizers has been demonstrated in TiO_2 hybrid structures within perovskite solar cells and PEC electrodes with an improved photoactivity for cell hydrogen production [8].

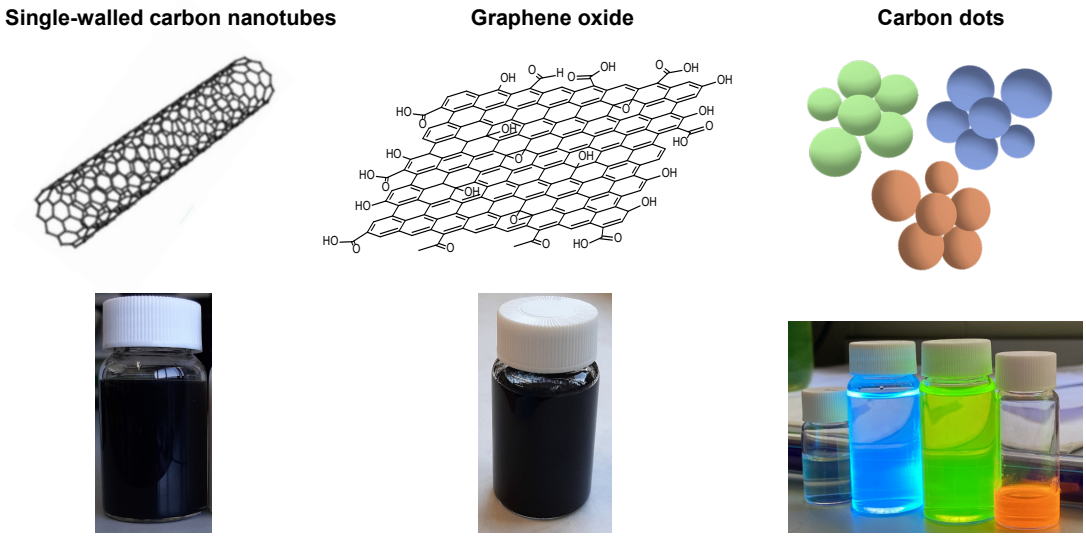

Figure 2. Different carbon nanomaterials selected in PHOTOGRAPH and their water-based inks and dispersions.

Figura 2. Distintos nanomateriales de carbono seleccionados para PHOTOGRAPH y sus respectivas tintas y dispersiones acuosas.

These were some examples of how versatile the interaction between graphene-based interfaces and photoactive nanostructured materials could be, leading to enhanced and/or new properties that can be easily tuned, stemming from the wide expertise of the G-CNN. However, the journey has just started, thus opening space for developing new ways of processing of nanomaterials and rendering its integration into suitable device structures to achieve enhanced optoelectronic/photoelectrochemical/ photoelectrocatalytic properties and efficient photoelectrode combinations. In the following, we provide further insights on the current status of PHOTOGRAPH along with its future perspectives.

2. Objectives

PHOTOGRAPH focuses on the photoelectrochemical production of hydrogen by optimized graphene-based interface components. One of the PEC-WS strengths is that it allows reducing the electrical input, thus rendering a more affordable process. With this aim, a straightforward bottom-up approach in which three objectives are identified will be followed:

- Development and optimization of well-defined functional graphene-based materials

  This refers to a broad set of carbon-based nanostructures such as GO, CNTs and CDs, as well as related functional hybrid materials with photoactive compunds (e.g. TiO2, ZnO, conductive poymers), while not excluding other promising nanomaterials.

- Macroscopic assembly into optimized interface architectures and electrode materials

  Dispersion and solution processing of nanomaterials into layered films is another key aspect being tackled. The emphasis lies on the control of surface chemistry, water-based dispersions, highly conductive and environmentally friendly functional inks and pastes, and optimized photoelectrochemically active interface architectures.

- Photoelectrochemical hydrogen production through water splitting in a photoelectrochemical cell

  This alludes to the use of the developed interface structures as photoelectrodes in a photoelectrochemical cell, the understanding of solid-liquid interface processes, the optimization of hydrogen production and the evaluation of the overall performance and technological feasibility of the photoelectrocatalytic hydrogen production technology with respect to efficiency and environmental impact.

Summarizing, the aim of PHOTOGRAPH is not only devoted to hydrogen generation employing graphene-based interfaces, but also to the development of environmentally friendly formulations of the selected nanomaterials. Furthermore, such mixtures could be processed by using potentially scalable techniques (e.g. screen-printing, spray-coating). Thus, the as-prepared electrodes would be free of critical elements, demonstrating that new alternatives based on abundant and inexpensive nanomaterials may find their place along with the yet-established technologies for green hydrogen production.

3. Ongoing activities

This section describes promising ongoing activities with respect to the development of layered photoelectrodes based on carbon nanostructures towards enhanced PEC-WS performance. Particularly, it considers the specific aspects referring to the use of low cost abundant photoactive materials, the exploitation of liquid phase processing conditions compatible with aqueous media, as well as the combinations of materials and layer configurations which provide superior light absorption and photoelectrochemical and photoelectrocatalytic properties.

In this context, the chosen photoactive semiconductor should provide a favorable bandgap for efficient solar light absorption, great absorption coefficients, appropriate conduction band and valence band edges and lastly, enough carrier lifetime and mobility to assure that the photogenerated entities effectively reach the interface [9]. Considering all of the previously mentioned requirements, TiO_2 stands as one of the best photoactive semiconductors as it exhibits a combination of desirable properties including low price, non-toxicity, good chemical stability and a suitable band structure that makes water splitting possible from a thermodynamic point of view [10].

One of the established objectives is to develop dispersions or inks of the desired nanomaterials, and given that TiO_2 is insoluble in water, stable colloids must be achieved to process them into photoactive films. Typically, TiO_2 is mixed with organic solvents and additives (e.g. ethanol, acetonitrile, terpineol, ethylcellulose) yielding highly viscous pastes in a non-environmentally friendly process [11]. Here, we have developed stable waterborne TiO_2 dispersions that can be easily processed into films (**Figure 3a**) by a highly-reproducible spray coating technique. Additionally, the porosity of the as-prepared photoanodes can be easily tuned, which will lead to a better PEC-WS performance presumably caused by a higher specific surface area exposed to the electrolyte. Furthermore, mathematical modelling of their photoelectrochemical response is being undertaken, which will allow delving much deeper into the light-based water splitting process.

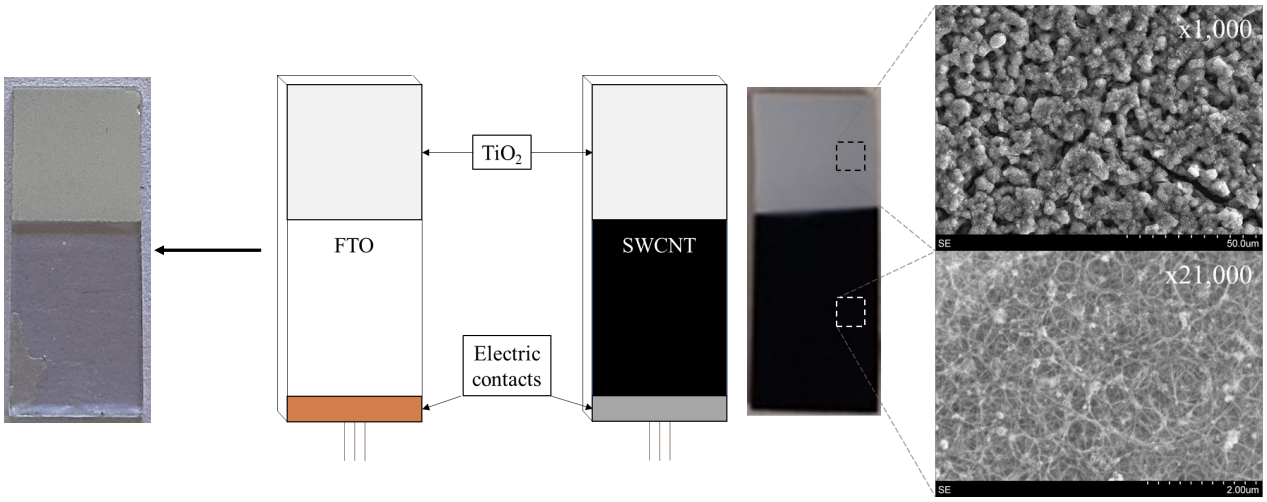

Figure 3. Ideal scheme of the chosen photoanode configuration. **a)** TiO_2/FTO electrode and **b)** TiO_2/SWCNTs electrode combined with scanning electron microscopy images both films. Note that FTO is transparent whereas SWCNTs film is opaque.

Figura 3. Esquema ideal de la configuración elegida para los fotoánodos. **a)** Electrodos TiO_2/FTO y **b)** Electrodos TiO_2/SWCNTs junto a imágenes de microscopía electrónica de barrido de ambas películas. Mientras que el sustrato de FTO es transparente, la película de SWCNTs es opaca.

Following the previous trends of sustainable processing principles, CNTs pose a great challenge in terms of dispersing them in aqueous media. It is well known that the use of surfactants (e.g. anionic, cationic and non-ionic) is widespread when it comes to stabilizing such carbon nanomaterial in water. However, most of the employed surfactants are not environmentally friendly, even detrimental to the applications in which CNTs dispersions are involved, underlining the need to search for alternatives. In that sense, we have demonstrated that single-walled CNTs (SWCNTs) can be readily dispersed in aqueous media by employing nanocrystalline cellulose (NCC) [12]. Given that the resulting films display impressively low electrical resistivities (typically below 50 Ω/□), they should serve as feasible electron collectors for our photoanodes as depicted in **Figure 3b**, thus rendering layered structures of photoactive materials without critical and expensive materials such as fluorinated tin oxide (FTO). Clear is that achieving

a highly homogeneous film and well-interconnected SWCNTs network is key for exploding this particular application of such graphene-based material.

However, due to the limited light absorption range of TiO_2 (**Figure 4a**), the efficiency of the overall process remains below the desired values. To overcome this problem, its interaction with CDs is another feasible combination, as they are well known sensitizers for solar applications. In particular, graphene quantum dots and polymeric dots are being synthesized in our group, whose versatility has been demonstrated by the fact that, when modifying different parameters during their synthesis, several CDs with different light absorption ranges can be obtained. This leads to a wide variety of possible combinations that could cover the entire visible range, as displayed in **Figure 4b**.

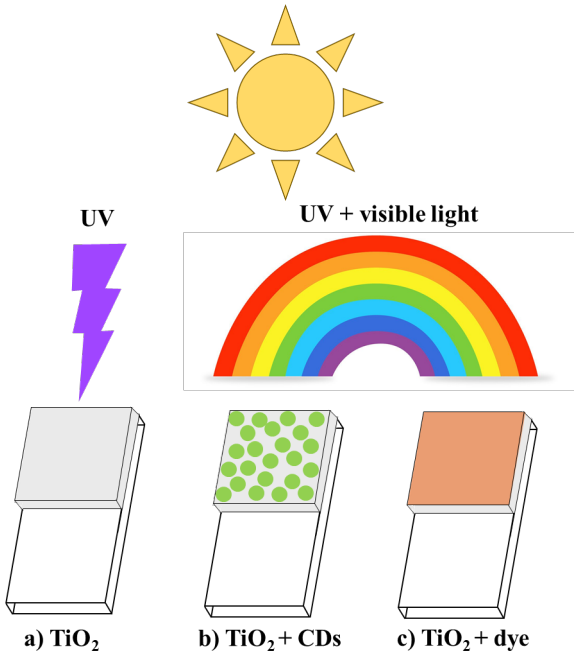

Figure 4. Scheme of different photoanodes along with their corresponding light absorption. **a)** Blank TiO_2 **b)** TiO_2 decorated with CDs and **c)** TiO_2 covered with an organic dye.

Figura 4. Esquema de distintos fotoánodos junto con su correspondiente absorción de luz. **a)** Solo TiO_2 **b)** TiO_2 decorado con puntos cuánticos de carbono y **c)** TiO_2 recubierto con un colorante orgánico.

Regarding sensitization of TiO_2, dyes are other promising materials that must be taken into consideration owing to their impressive performance in terms of light harvesting capability [13]. Nevertheless, most of the common dyes require ruthenium and porphyrins, which do not have a simple synthetic pathway. Particularly, devices containing ruthenium dyes are not environmentally friendly, also being a scarce and expensive metal. In this context, metal-free dyes based on donor and acceptor components are excellent alternatives, mainly due to their more affordable synthesis and tailored light absorption properties [14]. Once both components are linked (**Figure 4c**), an extensive range of visible spectra is covered, thus confirming the great potential of these layered configurations for green hydrogen production.

Not only photoanodes are being studied within this project, but also photocathodes free of critical elements such as platinum are currently under scrutiny. Special focus is given to these photoelectrodes, in which layer-by-layer structures composed of carbon nanostructures and conjugated polymers may be outstanding alternatives to already-established devices. As previously commented, novel combinations could lead to unprecedented properties such as charge transfer and separation processes, highly desired to achieve greater photovoltages that will make PEC-WS more affordable.

4. Conclusion and future outlook

So far, the current status of PHOTOGRAPH concerning aqueous formulations of target nanomaterials (e.g. TiO_2, SWCNTs, CDs) and their processing into layered architectures for photoelectrodes is given. Photoelectrochemical water splitting has been carried out using the as-prepared devices, demonstrating that the combination of photoactive nanostructured materials with well-defined graphene-based interfaces renders favorable photoelectrodes, suitable for green hydrogen generation (**Figure 5**). Nevertheless, some issues arise from the interaction between the formed interfaces. In particular, charge separation and carrier mobility within the device are key parameters that should be improved if competitive PEC-WS systems are sought. To this end, theoretical simulations of charge transfer processes at the interfaces are currently in progress. Another critical aspect is the electrode/electrolyte interface, which, in the case of sensitized photoelectrodes, leads to non-desirable processes, namely, the leaching of CDs in the electrolytic medium and the relatively low stability of dyes. Thus, a deep understanding of the interfacial processes is mandatory to solve them. For instance, functionalization of carbon nanomaterials, synthesis variations and post-treatments are different options that could help to tailor the previously mentioned interactions. In addition, the implementation of protective thin films is currently being studied to stabilize the employed sensitizers. Indeed, it has been reported that such films improve the photoelectrochemical performance of the device [3,8], as they can act as electron or hole transport layers depending on how and where they are deposited.

To sum up, in PHOTOGRAPH we are demonstrating that functional PEC-WS photoelectrodes can be developed with brand new methodologies, based on environmentally friendly processing of abundant, non-critical nanomaterials and potentially scalable technologies. There is still a long way ahead, in which improved devices, novel nanostructured materials and properties are yet to be discovered. Undoubtedly, we are on the right path and also, very excited and eager to see what kind of discoveries await us!

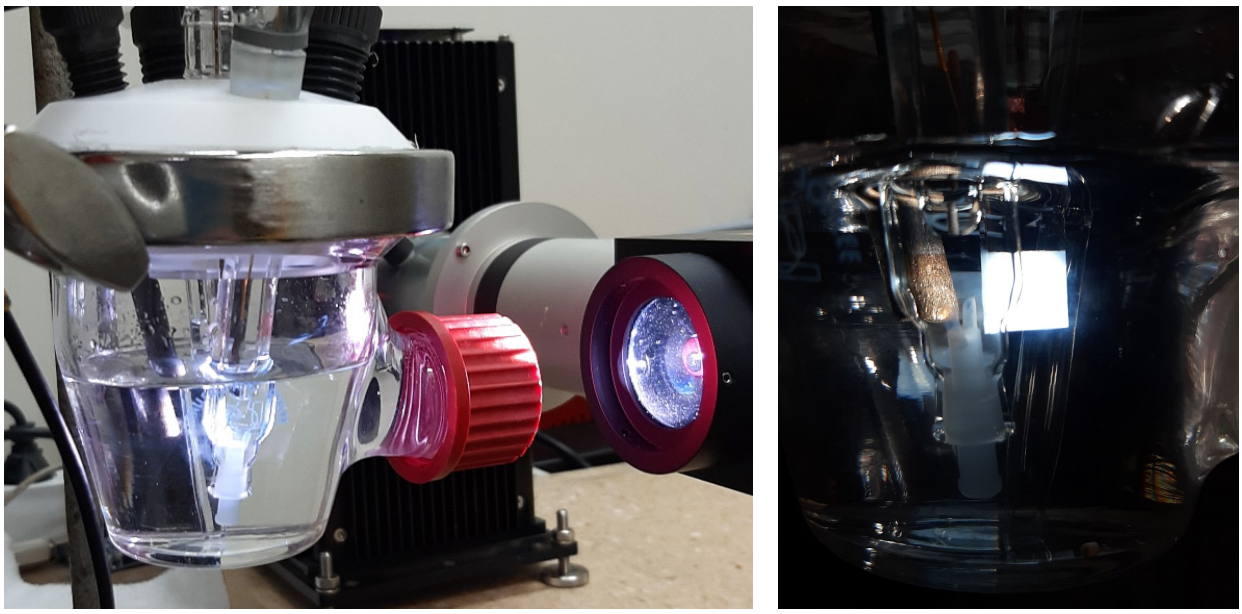

Figure 5. Left: Photoelectrochemical cell in which our electrodes are involved. Right: Photoelectrode under measurement conditions.

Figura 5. Izquierda: Celda fotoelectroquímica en la cual se encuentran involucrados nuestros electrodos. Derecha: Fotoelectrodo bajo condiciones de medida.

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