

www.advenergymat.de

Carbon Nanoforms for Photovoltaics

Vladimir Dyakonov* and Juan Luis Delgado*

Dedicated to Prof. Nazario Martín on the occasion of his 60th anniversary

Sustainable energy supply represents nowadays one of the most important challenges also for scientific research. The massive usage of fossil fuels has undoubtedly produced environmental issues, which jeopardize the sustainable development of mankind. Thus, clean energy sources are necessary to maintain our progress, avoiding pollution and climate damages to our planet. In this scenario, solar energy is called to play a key role, as we receive enough sunlight daily to power the earth for a whole year. Therefore, a suitable sunlight harvesting, properly combined with an efficient conversion of this energy into electricity would ensure the route towards satisfying the global energy demand.

Carbon has been a highly influential element for the development of life on Earth. On one hand, carbon combustion is the origin of carbon dioxide production. On the other hand, carbon is an essential component of all known life on Earth, and may also become the key element to find a solution in the generation of clean energy.

In this regard, the advent of carbon nanoforms has produced a significant improvement in a variety of photovoltaic devices, such as all-organic, dye sensitized solar cells and more recently, even perovskite-based solar cells. Owing to their outstanding electronic and optical properties, carbon nanoforms have been used as sunlight harvesters, charge transport materials, electrodes and sensors, illustrating their high impact in photovoltaics as well as optoelectronics (Figure 1).

The aim of this special issue of Advanced Energy Materials is to bring to the attention of the scientific community the most recent and significant advances of the use of fullerenes, carbon

Prof. V. Dyakonov Experimental Physics VI Julius Maximilian University of Würzburg Am Hubland, 97074 Würzburg, Germany E-mail: dyakonov@physik.uni-wuerzburg.de Prof. V. Dyakonov Bavarian Centre for Applied Energy Research (ZAE Bayern) 97074 Würzburg, Germany Prof. J. L. Delgado POLYMAT & Faculty of Chemistry University of the Basque Country UPV/EHU Avenida de Tolosa 72 & P. Manuel Lardizabal 3 20018 Donostia-San Sebastián, Spain E-mail: juanluis.delgado@polymat.eu Prof. J. L. Delgado **Ikerbasque** Basque Foundation for Science 48011 Bilbao, Spain

DOI: 10.1002/aenm.201700252



Vladimir Dyakonov holds the Chair of Experimental Physics (Energy research) on the Faculty of Physics and Astronomy of Julius-Maximilian University of Würzburg, Germany since 2004 and he is the Scientific Director of the Bavarian Centre of Applied Energy Research (ZAE Bayern) since 2005. He studied physics at

the University of St. Petersburg and received his doctorate at the A. F. Ioffe Physico-Technical Institute in 1996. Since 1990, he has been a visiting researcher at the universities of Bayreuth (Germany), Antwerp (Belgium) and Linz (Austria). Dyakonov's main research interests are in the fields of thin-film photovoltaics, semiconductor spectroscopy and functional energy materials.



Juan Luis Delgado obtained his Ph.D. in 2004 from the University of Castilla-la Mancha (Spain) under the supervision of Prof. Fernando Langa and Prof. Pilar de la Cruz. Afterwards he joined the group of Prof. Jean-François Nierengarten, at the ECPM-CNRS (Strasbourg, France) where he worked as a postdoctoral fellow (2005–2006). He

then joined the group of Prof. Nazario Martín at University Complutense of Madrid in 2006 as a "Juan de la Cierva" post-doctoral fellow. From 2008–2014 he was a Senior "Ramón y Cajal" Researcher at IMDEA-Nanoscience (Madrid, Spain). Since 2014 he leads the Hybrid Materials for Photovoltaics group at POLYMAT (Donostia-San Sebastián, Spain).

nanotubes, carbon nanohorns, and graphene in the field of photovoltaics.

Although the ultimate goal of the design of the carbon-based materials for solar cells remains the highest energy conversion efficiency, the reviews presented in this special issue will also





Figure 1. Artistic representation, illustrating the strong impact of carbon nanoforms on the development of photovoltaics.

address a great variety of potentially interesting carbon-based materials.

Nazario Martín has extensively contributed to the development of a wide variety of the aforementioned carbon nanoforms. Since his research stay in the laboratory of Prof. Fred Wudl in California (UCSB, USA) he has been engaged in the synthesis of a great number of fullerene as well as endohedral fullerene derivatives. Under his supervision, a variety of new reactions on the fullerene sphere has been discovered and reported such as the thermal [2+2] intramolecular cycloaddition of fuller-1,6-enines"^[1a] or the important thermal retro-cycloaddition reaction of pyrrolidinofullerenes.^[1b]

His pioneering paper entitled: "An efficient approach to chiral fullerene derivatives by catalytic enantioselective 1,3-dipolar cycloadditions" [2a] paved the way to the synthesis of enantiomerically pure fullerenes for application in bio-medical but also in materials sciences. The further extension to the synthesis of chiral fullerenes by means of asymmetric organocatalysis in fullerenes science has also been reported in his group, thus opening a highly versatile and powerful procedure for preparing enantiomerically pure fullerenes. [2b]

Recently, Prof. Martín has also contributed to the synthesis of hexakisadducts of glycofullerenes and to the first tridecafullerenes where 13 fullerenes endowed with 120 mannoses resulted to be highly efficient inhibitors for the Ebola virus infection.^[3]

The most outstanding aspect recently developed in his group has been the use of π -extended tetrathiafulvalene (exTTF) derivatives as suitable concave receptors for fullerenes, based on the principle of concave-convex complementarity through van der Waals and π - π interactions. The novelty of this new tweezer is the combination of supramolecular and electronic reciprocity between exTTF and C_{60} and, therefore, an excellent candidate for the self-organization of electroactive materials. [4]

The reaction mechanisms involving electron transfer in nature are highly important for the understanding and further design of active photovoltaic materials. In Martin's research group, a wide variety of D-A systems endowed with tetrathiafulvalenes, porphyrins and other π -conjugated compounds as electron donor moieties, and fullerenes, carbon nanotubes

and graphene as the electron accepting moiety, have been synthesized. In these compounds they have carried out, a pioneering work, studying the donor-acceptor interactions in covalently connected systems, publishing an impressive number of papers.^[5]

Prof. Martín has been engaged, from the first EU project in the field of organic photovoltaics (Joule III, 1997), in different EU projects directed to the understanding and preparation of photovoltaic devices and artificial photosynthetic systems. In his group, molecules showing a photovoltaic behavior with remarkable energy conversion values have been synthesized.^[6a] In addition to different modified fullerenes^[6b,c] his group has also been engaged in other type of solar cells such as molecular BHJ solar cells^[6d] and Dye Sensitized Solar Cells, in collaboration with Prof. Michael Grätzel group.^[6e]

Nazario Martín group has also contributed to the development of perovskite-based solar cells, reporting outstanding power conversion efficiencies, thorough the use of innovative hole transporting materials.^[7]

Editing this Special Issue of *Advanced Energy Materials* has been an honor and a pleasure for us. Evidently, the broad field of carbon nanoforms for photovoltaics cannot be comprehensively covered in a single journal issue; therefore, we apologize to those who might feel their works have been omitted. We would like to thank our colleagues for their excellent contributions and the editorial team of *Advanced Energy Materials* for valuable support.

Acknowledgements

This work was supported by Basque Government, MINECO (Ministerio de Economía y Competitividad, Spain) and Gipuzkoa Council under projects PC2015-1-03 (16-79), CTQ2015-70921-P and MSFP (Macromolecules for Single Fission Photovoltaics). J.L.D. acknowledges Ikerbasque, the Basque Foundation for Science, for an "Ikerbasque Research Fellow" contract, Polymat Foundation, MINECO of Spain for IEDI-2015-00666 grant and Iberdrola Foundation for financial support.

- a) N. Martín, M. Altabe, S. Filippone, A. Martín-Domenech, M. Güell, M. Solà, Angew. Chem. Int. Ed. 2006, 45, 1439;
 b) N. Martín, M. Altable, S. Filippone, A. Martín-Domenech, L. Echegoyen, C. M. Cardona, Angew. Chem. Int. Ed. 2006, 45, 110.
- [2] a) S. Filippone, E. E. Maroto, A. Martín-Domenech, M. Suarez, N. Martín, Nat. Chem. 2009, 1, 578; b) J. Marco-Martínez, V. Marcos, S. Reboredo, S. Filippone, N. Martín, Angew. Chem. Int. Ed. 2013, 52, 5115.
- [3] A. Muñoz, D. Sigwalt, B. M. Illescas, J. Luczkowiak, L. Rodríguez-Pérez, I. Nierengarten, M. Holler, J.-S. Remy, K. Buffet, S.P. Vincent, J. Rojo, R. Delgado, J.-F. Nierengarten, N. Martín, Nat. Chem. 2016, 8, 50.
- [4] a) H. Isla, E. M. Porez, N. Martín, Angew. Chem. Int. Ed. 2014, 53, 5629; b) J. López-Andarias, J. L. López, C. Atienza, F. G. Brunetti, C. Romero-Nieto, D. M. Guldi, N. Martín, Nat. Commun. 2014, 5, 3763.
- [5] a) L. Sánchez, M. Sierra, N. Martín, A. J. Myles, T. J. Dale, J. Rebek Jr.,
 W. Seitz, D. M. Guldi, Angew. Chem. Int. Ed. 2006, 45, 4637;
 b) S. S. Gayathri, M. Wielopolski, E. M. Pérez, G. Fernández,



www.advancedsciencenews.com

ENERGY MATERIALS

www.advenergymat.de

- L. Sánchez, R. Viruela, E. Ortí, D. M. Guldi, N. Martín, Angew. Chem. Int. Ed. 2009, 48, 815.
- [6] a) I. Riedel, E. von Hauff, J. Parisi, N. Martín, F. Giacalone, V. Dyakonov, Adv. Funct. Mater. 2005, 15, 1979; b) J. L. Delgado, E. Espíldora, M. Liedtke, A. Sperlich, D. Rauh, A. Baumann, C. Deibel, V. Dyakonov, N. Martín, Chem. Eur. J. 2009, 15, 13474; c) O. G. Poluektov, J. Niklas, K. L. Mardis, S. Beaupré, M. Leclerc, C. Villegas, S. Erten-Ela, J. L. Delgado, N. Martín, A. Sperlich, V. Dyakonov, Adv. Energy Mater. 2014, 4, 1301517; d) P.-A. Bouit,

D. Rauh, S. Neugebauer, J. L. Delgado, E. Di Piazza, S. Rigaut,

- O. Maury, C. Andraud, V. Dyakonov, N. Martin, *Org. Lett.* **2009**, *11*, 4806; e) S. Wenger, P.-A. Bouit, Q. Chen, J. Teuscher, D. Di Censo, R. H.-Baker, J.-E. Moser, J. L. Delgado, N. Martín, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **2010**, *132*, 5164.
- [7] a) A. Molina-Ontoria, I. Zimmermann, I. Garcia-Benito, P. Gratia, C. Roldán-Carmona, S. Aghazada, M. Grätzel, M. K. Nazeeruddin, N. Martín, Angew. Chem. Int. Ed. 2016, 55, 6270; b) I. Zimmermann, J. Urieta-Mora, P. Gratia, J. Aragó, G. Grancini, A. Molina-Ontoria, E. Ortí, N. Martín, M. K. Nazeeruddin, Adv. Energy Mater. 2016, 6, 1601674.