Bionatura Journal
Ibero-American Journal of Biotechnology and Life Sciences

Editorial

Zero-Dimensional Carbon Nanomaterials: Building Blocks for Efficient Energy Conversion

Alain R. Puente Santiago [1,*]

[1] *[Florida International University (FIU)](), Department of Chemistry and Biochemistry, Miami, FL, USA. alpuente@fiue.edu .*
* *Correspondence: alpuente@fiu.edu*

ABSTRACT

Low-dimensional carbon-based materials, including 0D fullerene, 1D carbon nanotube, and 2D graphene, have been widely used as electroactive building blocks for sustainable energy conversion heterostructure nanosystems. These materials have unique physical and chemical properties at the nanoscale, such as high conductivity, high specific surface area, and tunable electronics, making them the focus of new renewable energy technologies. In this context, 0D carbon-based nanomaterials, like fullerenes and fullertubes, have garnered substantial attention as rising star energy materials. This editorial spotlight article outlines the current advancements in the utilization of 0D-fullerene and fullertube-based nanoelectrocatalysts for energy conversion.

Keywords: 0D-nanocarbons, low-dimensional heterostructures, energy conversion

INTRODUCTION

Nanomaterials with dimensions less than 1 nm are called zero-dimensional (0D) nanomaterials. Examples of materials in this category include carbon quantum dots (CQDs), single atoms, nanoclusters, fullerenes, and fullertubes.[1] These 0D materials often exhibit excellent electronic properties, such as electrical and optical properties and high quantum yield. As a result, they can be utilized in various energy conversion applications. In recent years, fullerenes and fulleretubes, have been incorporated into the fascinating field of energy catalysis, demonstrating a new range of tunable electrocatalytic features and opening new horizons.[1]

In this editorial spotlight article, a clear, concise, and authoritative status report on the use of fullerene and fullertube-based nanomaterials for energy catalysis is elegantly presented, thus emphasizing the new opportunities of these 0D nanostructures as rising star energy materials.

0D NANOCARBON-BASED ELECTROCATALYSTS

Buckminsterfullerenes (C_{60}) are excellent candidates for forming low-dimensional catalytic heterointerfaces because they can facilitate intermolecular charge transfer and create highly active interfacial sites.[2] They can be easily coupled to many low-dimensional materials via covalent or non-covalent interactions.

Santiago and colleagues developed a new solvent engineering approach to fabricate vdW 2D-2D 1T-MoS_2/C_{60} nanohydrids for high-performance hydrogen evolution reaction (HER).[3] As shown in **Figure 1A**, the 2D-2D configuration was achieved when the C_{60} weight content was around 20% in solution, thus indicating that the MoS_2-C_{60} interactions are optimized at a narrow range of fullerene concentration to form well-ordered 2D arrays. **Figure 1B** displays the Raman peaks at 380 and 405 cm^{-1}, which correspond to the E^1_{2g} and A_{1g}

vibrational modes of MoS_2, while the peak at 1460 cm^{-1} unequivocally corresponds to the A_{2g} mode or pentagonal pinch mode of the fullerene nanocages. The 2D-2D nanoheterostructure exhibited an ultrasmall onset potential of -0.027 V vs RHE, surpassing the catalytic activity of its counterparts and comparable to Pt/C (**Figure 1C**). This work establishes that the catalytic performance and structure of C_{60}-based heterointerfaces can be precisely tailored by modifying the fullerene weight contents, opening up a new chapter in the rational design of 2D-2D low-dimensional HER catalysts.

Fullertube molecules combine the structural elements of fullerenes (hemispherical end-caps) and tubular belts of single-walled carbon nanotubes (SWCNTs).[4,5] Fulleretubes have been recently introduced in the field of energy conversion as a significant breakthrough[6] as they offer the potential to create different active sites within a single metal-free molecule, thus becoming promising 0D-platforms for various crucial energy conversion reactions. Noufal and coworkers have explored for the first time the electrocatalytic properties of C_{90}, C_{96}, and C_{100} fullertubes **(Figure 1D)** for oxygen reduction reactions (ORR). Noteworthy, C_{96} exhibited exceptional ORR activity, showing an onset potential of 0.85 V and a halfway potential of 0.75 V, which are comparable to the values of the benchmark Pt/C catalyst **(Figure 1E)**. The long-term durability properties of C_{96} and Pt/C were also evaluated. Remarkably, after 1000 cycles, the half-wave potential ($E_{1/2}$) for C_{96} showed a 30 mV shift, compared to the 12 mV observed for commercial Pt/C **(Figure 1F)**. This contribution paved the way for the future development of fullertube-based catalysts as outstanding metal-free low-dimensional architectures for energy conversion.

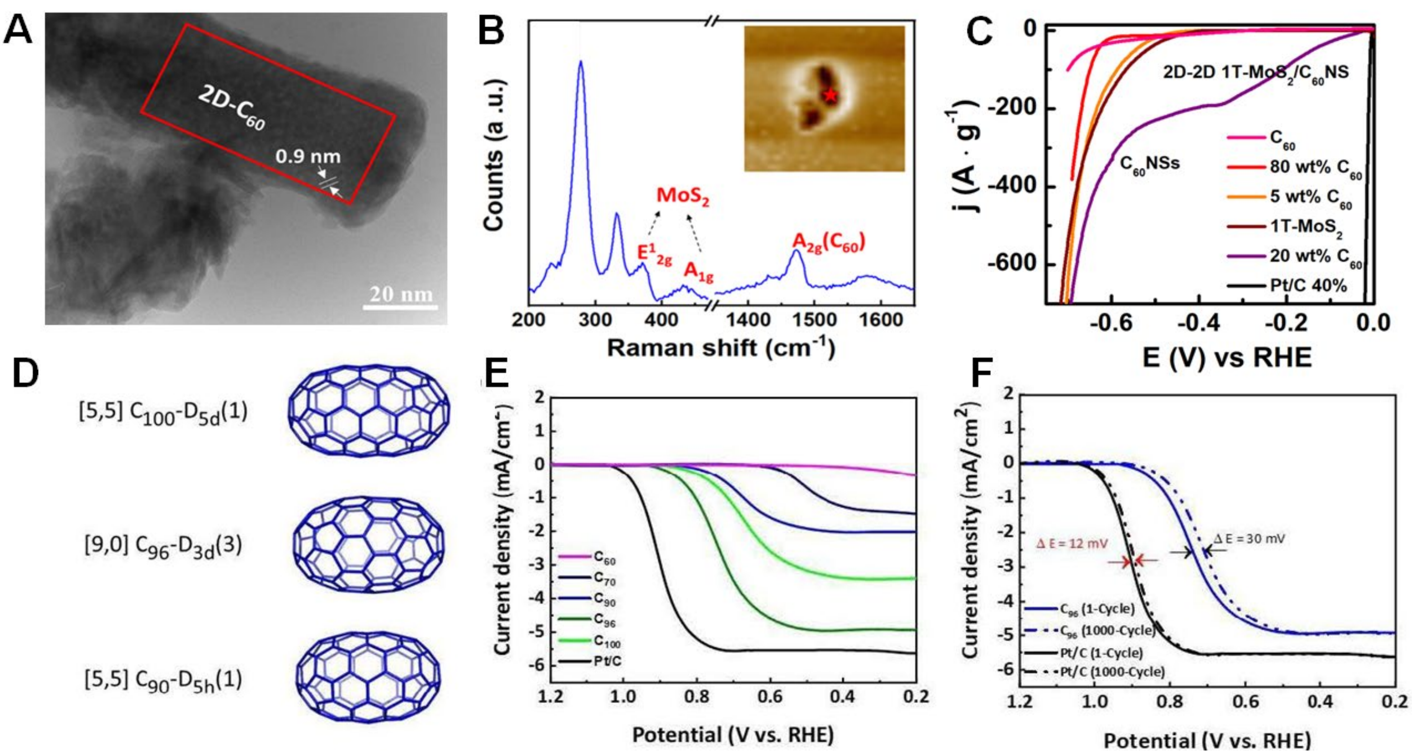

Figure 1. A) HRTEM image of the 2D-2D 1T MoS_2/C_{60} nanoheterostructure. **B)** Representative Raman spectrum of a MoS_2 and C_{60} heterostructure sample. The inset shows the 2D spectrum of the sample region from which the Raman spectrum image is recorded. **C)** Mass-normalized catalytic currents for C_{60}, 1T-MoS_2, commercial Pt/C 40%, and the 1T-MoS_2/C_{60} heterostructures with 5, 20, and 80 wt% of C_{60} at 2 $mV \cdot s^{-1}$ in 0.5 M H_2SO_4. Reproduced from ref 3 with permission of the American Chemical Society. **D)** Illustration of the structures of C_{90}, C_{96} and C_{100} fullertubes. **E)** ORR LSVs of C_{60}, C_{70}, C_{90}, C_{96}, and C_{100} compared to Pt/C at 1600 rpm. **F)** Polarization curves of C_{96} and Pt/C catalysts before (solid) and after (dotted) 1000 ORR. Reproduced from ref 6 with permission of Wiley.

ENERGY-RELATED DEVICES

0D carbon nanomaterials have also been explored as part of different electrochemical devices. For instance, a two-electrode configuration water electrolyzer was developed to evaluate the overall water splitting reaction in a 0.5 M NaOH electrolyte, utilizing a 10% C_{60}/boron carbon nitride nanosheets (BCN) nanoheterostructure loaded on carbon cloth to function as both the anode and cathode. According to **Figure 2A**, the 10% C_{60}/BCN||10% C_{60}/BCN only requires a cell potential of 1.61 V to achieve a current density of 10 mA cm^{-2}. Remarkably, the electrocatalytic performance of the 10% C_{60}/BCN||10% C_{60}/BCN electrolyzer is shown to be comparable and competitive with recently reported water-splitting devices, indicating the effectiveness of the assembled overall water-splitting system. Moreover, chronoamperometric measurements at 1.61 V (**Figure 2B**) revealed that the electrochemical stability of the 10% C_{60}/BCN catalyst is excellent, with current densities remaining stable (only 9% of the initial current lost) for 20 hours.

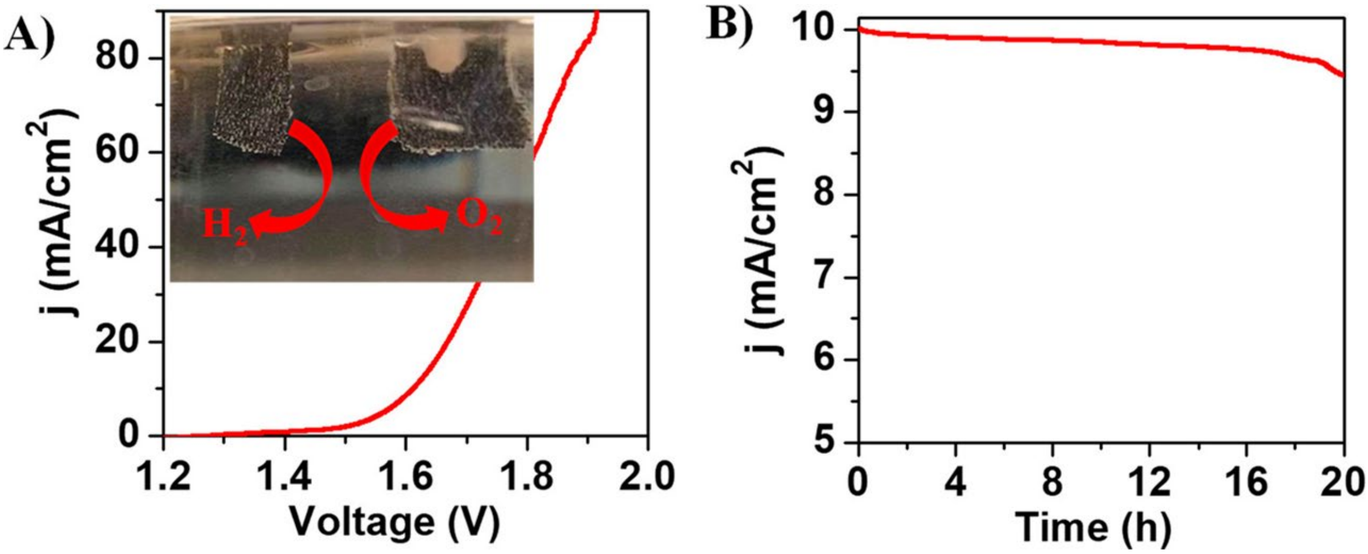

Figure 2. A) LSV curve for the water electrolyzer device using 10% C_{60}/BCN as both cathode and anode in a 0.5 M NaOH solution. The inset in (A) shows the digital photograph for producing O_2 (anode) and H_2 (cathode) bubbles on the fullerene-decorated BCN carbon cloth electrodes. **B)** Chronoamperometric measurements at 1.61 V for 20 h. Reproduced from ref 7 with permission of the American Chemical Society.

CONCLUSIONS AND FUTURE PERSPECTIVES

Undoubtedly, fullerene and fullertubes are emerging as promising 0D-nanostructures for renewable energy. Despite the recent experimental progress in developing catalysts based on fullerene and fullertubes, certain key drawbacks have remained unresolved. Identifying the active sites and the structure-catalytic function of these nanomaterials is still in an early stage. New characterization methods need to be developed to better understand the dynamic interactions between the active sites and catalytic intermediates, providing deeper insight into relevant electrocatalytic reactions. Additionally, to bridge these gaps, the rapid development of machine-learning methods, and the synergy of theory and experiment will be useful tools to accelerate the development of the next generation of 0D carbon-based nanocatalysts.

Conflicts of Interest: "The author declares no conflict of interest."

REFERENCES

1. He, T.; Chen, M.; Sun, H.; Mei, J.; Noufal, M.; Liu, Q.; Puente Santiago, A. R. Chemical insights into the interfacial phenomena of low-dimensional heterointerfaces. *Chem* **2024**, *10*, 19874-1993.
2. Gao, R.; Dai, Q,; Du, F.; Yan, D.; Dai, L. C_{60}-Adsorbed Single-Walled Carbon Nanotubes as Metal-Free, pH-Universal, and Multifunctional Catalysts for Oxygen Reduction, Oxygen Evolution, and Hydrogen Evolution. *J. AM. Chem. Soc.* **2019**, *141*, 11658-16666.
3. Puente Santiago, A. R.; He, T.; Eraso, O.; Ahsan, M. A.; Nair, A. N.; Chava, V. S. N.; Zheng, T.; Pilla, S.; Fernandez-Delgado, O.; Du, A.; Sreenivasan, S. T.; Echegoyen, L. Tailoring the Interfacial Interactions of van der Waals 1T-MoS_2/C_{60} Heterostructures for High-Performance Hydrogen Evolution Reaction Electrocatalysis. *J. Am. Chem. Soc.* **2020**, *142*, 17923– 17927,
4. Stevenson, S.; Dorn, H.C. Fullertubes: A 30-Year Story of Prediction, Experimental Validation, and Applications for a Long-Missing Family of Soluble Carbon Molecules. *Acc. Chem. Res.* **2024**, *57*, 2154-2165.
5. Stevenson, S.; Liu, X.; Sublett, D. M.; Koenig, R. M.; Seeler, T. L.; Tepper, K. R.; Franklin, H. M.; Wang, X.; Huang, R.; Feng, X. Semiconducting and Metallic [5,5] Fullertube Nanowires: Characterization of Pristine D_{5h}(1)-C_{90} and D_{5d}(1)-C_{100}. *J. Am. Chem. Soc.* **2021**, *143*, 4593– 4599.
6. Sanad, M. F.; Franklin, H. M.; Ali, B. A.; Puente Santiago, A. R.; Nair, A. N.; Chava, V. S. N.; Fernandez-Delgado, O.; Allam, N. K.; Stevenson, S.; Sreenivasan, S. T.; Echegoyen, L. Cylindrical C_{96} Fullertubes: A Highly Active Metal-Free O2-Reduction Electrocatalyst. *Angew. Chem., Int. Ed.* **2022**, *61*, 20211672.
7. Ahsan, M. A.; He, T.; Eid, K.; Abdullah, A. M.; Curry, M. L.; Du, A.; Puente Santiago, A. R.; Echegoyen, L.; Noveron, J. C. Tuning the Intermolecular Electron Transfer of Low-Dimensional and Metal-Free BCN/C_{60} Electrocatalysts via Interfacial Defects for Efficient Hydrogen and Oxygen Electrochemistry. *J. Am. Chem. Soc.* **2021**, *143*, 1203– 1215.

Received: 21 August, 2024 / **Accepted**: 1 September, 2024 / **Published:** 15 September 2024

Citation: Puente Santiago A R. Zero-Dimensional Carbon Nanomaterials: Building Blocks for Efficient Energy Conversion. Bionatura journal. 2024;1(3):1. doi: 10.70099/BJ/2024.01.03.1

Additional information Correspondence should be addressed to *alpuente@fiu.edu*

Peer review information. Bionatura thanks anonymous reviewer(s) for their contribution to the peer review of this work using https://reviewerlocator.webofscience.com/

ISSN.3020-7886