Review

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Advancements in Plasma-Enhanced Chemical Vapor Deposition for Producing Vertical Graphene Nanowalls

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Posted Date: 10 August 2023

doi: 10.20944/preprints202308.0866.v1

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Review

Advancements in Plasma-Enhanced Chemical Vapor Deposition for Producing Vertical Graphene Nanowalls

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Abstract: Vertical graphene nanowalls (VGNWs) have emerged as a highly promising material in recent years due to their exceptional properties, such as a high specific surface area, excellent electrical conductivity, scalability, and compatibility with transition metal compounds. These attributes make VGNWs a compelling candidate for various applications, including energy storage, catalysis, and sensing, fostering great interest in their use in next future commercial graphene-based sensors like optoelectronic and plasmonic devices, energy storage electrodes, and catalytic systems. Among the diverse graphene synthesis methods, plasma-enhanced chemical vapor deposition (PECVD) has proven to be a robust technique for producing large-scale graphene films and creating VGNWs on diverse substrates. However, despite substantial progress in optimizing growth conditions to achieve micrometer-sized graphene nanowalls, the outcomes are often obtained through empirical approaches, and a comprehensive understanding of the underlying physicochemical mechanisms governing nanostructure formation remains elusive. In particular, a deeper exploration of atomic-level phenomena, such as nucleation, carbon precursor adsorption, and surface diffusion of adatoms, is imperative to exert precise control over the growth process. Concerning the synthesis of VGNWs, hydrogen plays a dual role in the graphene growth process, acting as both a co-catalyst and an etchant for the nanowalls. Nevertheless, a thorough comprehension of the intricate growth process is still required. To address these knowledge gaps, this review paper aims to investigate the nucleation and growth of VGNWs using PECVD, with a specific focus on exploring the temperature effect on the graphene growth ratio and nucleation density across a wide range of temperatures. By providing valuable insights into the PECVD process, our objective is to enable the optimization of growth conditions for tailoring VGNWs' properties, thereby facilitating their application in energy storage, catalysis, and sensing fields.

Keywords: graphene; carbon nanowalls (CNWs); vertical graphene nanowalls (VGNWs); plasma-enhanced chemical vapor deposition (PECVD); structural and morphological characteristics

Introduction

Carbon nanowalls (CNWs) have attracted considerable interest in recent years owing to their exceptional properties, including high surface area and excellent conductivity, making them promising candidates for diverse applications. Significant progress in the field has been driven by numerous studies investigating different synthesis methods, growth conditions, and substrate materials to optimize CNWs' properties. Among these, plasma-enhanced chemical vapor deposition (PECVD) has emerged as a prominent technique for producing large-scale graphene films and creating vertically oriented carbon nanowalls (VOCNWs) on various substrates. Overall, the methodologies employed for graphene growth and analysis have shown remarkable diversity. Different techniques, with varying parameters, have contributed to the understanding of graphene

 doi:10.20944/preprints202308.0866.v1

growth and the synthesis of unique carbon nanostructures like carbon nanowalls. This diversity has opened exciting opportunities for tailoring VGNWs' properties for specific applications in energy storage, catalysis, and sensing.

As the field of Plasma-Enhanced Chemical Vapor Deposition for producing Vertical Graphene Nanowalls continues to evolve, a comprehensive review of the latest advancements is essential. By shedding light on the underlying physicochemical mechanisms that govern VGNWs' formation and growth, this review aims to pave the way for further breakthroughs in this promising area of research and accelerate the practical utilization of VGNWs in cutting-edge technologies. The insights gained from this review will serve as a valuable resource for researchers and engineers seeking to optimize growth conditions and harness the full potential of VGNWs for a wide range of applications.

Background

Earlier reviews by Vesel et al.(Vesel et al., 2019) and Hiramatsu and Hori(Hiramatsu and Hori, 2010) provided comprehensive overviews of the achievements in CNWs deposition, establishing a foundation for subsequent research endeavors. Wu et al.(Wu et al., 2002) presented the first report on CNWs synthesis using a methane and hydrogen gas mixture, highlighting the role of substrate temperature and catalyst in the growth process. Since then, various studies have explored alternative methods like capacitive coupled plasma chemical vapor deposition (CCP-PECVD) and microwave plasma-enhanced chemical vapor deposition (MWCVD), resulting in high growth rates and morphological variations. Crucial investigations emphasized the significance of hydrogen in gas mixtures, the competition between growth and etching, and the role of Ar in CNWs growth.

Methods and Discussion

Recent advancements, exemplified by Zhang et al.'s work(Zhang et al., 2019), have demonstrated faster growth rates and novel morphological structures, providing new opportunities for CNWs' applications. However, to fully leverage their potential, a deeper understanding of the underlying growth mechanisms is required. In this context, the present review aims to investigate advancements in PECVD for producing vertical graphene nanowalls (VGNWs). The primary objectives are to explore the effect of temperature on the number of atomic layers in VGNWs and to gain insights into the plasma conditions, gas flow, and pressure that are crucial for modulating the growth process. By understanding the physicochemical mechanisms governing VGNWs formation, this review seeks to facilitate optimized growth conditions tailored for specific applications in energy storage, catalysis, and sensing. The diversity of methodologies employed for graphene growth and analysis has significantly contributed to the understanding of CNWs' synthesis and unique carbon nanostructures. Various techniques, including CVD growth, DC arc discharge evaporation, and PECVD, have been utilized with varying parameters, resulting in distinct morphologies and properties. Characterization techniques, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS), have provided crucial insights into structure and properties of all kinds of CNTs.

Given the significant progress in the field and, in particular, the potential of VGNWs for various applications, a comprehensive review of the advancements in PECVD-based synthesis and growth mechanisms is essential. By bridging the gaps in current knowledge and presenting a thorough understanding of the growth process, is convenient to accelerate the development and practical implementation of VGNWs in cutting-edge technologies. Furthermore, the evolution of graphene growth experiments has led to the development of a diverse range of setups and procedures. Chaitoglou et al.(Chaitoglou and Bertran, 2017) investigated graphene nucleation through CVD growth at varying temperatures, estimating an activation energy of 3.01 eV. The synthesis of carbon nanowalls has mainly focused on multi-layered graphene. However, this study aims to investigate the effect of temperature on the number of atomic layers in VGNWs. The authors discuss the use of ICP-CVD with methane as the carbon precursor, providing insights into crucial parameters for modulating the growth process, such as plasma conditions, gas flow, and pressure. The advantages

 doi:10.20944/preprints202308.0866.v1

of ICP-CVD, such as the absence of catalysts and higher electron density of the plasma, are highlighted.

Ando et al.(Ando et al., 1997) employed DC arc-discharge evaporation of graphite in a hydrogen-filled vacuum chamber, resulting in interlaced petal-like sheets and smaller nanometric petal-like structures. Recently, manipulating the electronic structure of graphene through surface defect sites and functional-group modifications has been found to enhance its electrocatalytic activity. In a new study, researchers developed three-dimensional graphene networks with abundant sharp edge sites by depositing vertical graphene sheets on SiO_x nanowire networks(Wang et al., 2018). The resulting 3D graphene networks exhibited excellent electrocatalytic activity for hydrogen evolution reaction (HER), making them highly active and stable metal-free and dopant-free HER electrocatalysts. Also, the study of electrochemical activity of carbon nanowalls (CNWs) was examined through the morphology and nanostructure of CNWs synthesized by PECVD(Lehmann et al., 2018). The height of the CNWs increased with deposition time, and they consisted of interconnected vertically aligned carbon sheets. The nanostructure was also characterized using Raman spectroscopy, which revealed defects in the graphitic lattice. X-ray photoelectron spectroscopy (XPS) confirmed the presence of sp2 hybridized carbon and the absence of heteroatom doping. The electrochemically active surface area of the CNWs increased with film thickness and deposition time. However, the peak potential difference in cyclic voltammetry measurements was larger than expected, possibly due to surface contamination. Overall, the study provides insights into the morphology and electrochemical properties of hierarchical carbon nanowalls (hCNWs) synthesized by PECVD. Lehmann et al. also focused on hCNWs synthesized using radio frequency plasma-enhanced chemical vapor deposition with p-xylene as the carbon precursor(Lehmann et al., 2018). Microwave (MW) reactors operating in TE mode have been widely used for vertical graphene (VG) synthesis. Bo et al.(Bo et al., 2013) utilized a 2.45 GHz MW source coupled to a cylindrical quartz tube to create a standing wave with the strongest electric field in the growth region. To overcome the limitations of transverse electric microwave (TE-MW) reactors, the transverse magnetic microwave (TM-MW) reactor was introduced, allowing better control of substrate temperature and enabling higher operating power and pressure. Hiramatsu et al.(Hiramatsu et al., 2013) grew carbon nanowalls (CNWs) through inductively coupled plasma-enhanced chemical vapor deposition (ICP-CVD) employing a CH_4/Ar mixture. They explored the role of n-type Si(100) and SiO_2-coated Si(100) substrates with a 50 nm oxide layer, along with Ti-catalyzed SiO_2-coated Si substrates for nucleation enhancement. Yu et al.(Yu et al., 2011) employed a plasma reactor operating at atmospheric pressure, utilizing argon as the plasma gas and various substrates, including silicon wafers and stainless steel plates.

Among the most interesting achievements we have 3D graphene networks(He et al., 2013). The fabrication process and properties of 3D graphene networks involves pressing commercially available Ni foam, cleaning it, and coating it with graphene using a chemical vapor deposition method. The resulting 3D graphene network exhibits flexibility, mechanical strength, and high electrical conductivity. The pressed Ni foam prevents the network from collapsing and cracking during bending. The graphene networks are further modified by electrodeposition of MnO2, which results in a uniform coating over the entire surface. The graphene/MnO2 composite demonstrates good capacitance and electrochemical performance, making it suitable for flexible electrode applications.

Research has been carried out on vertical graphene as a nanocarbon thin-film material with unique 3D hierarchical structures(Hang et al., 2019) and reported in the recent review of Zheng et al.(Zheng et al., 2021). Unlike planar growth graphene, vertical graphene has abundant out-exposing edges, high porosity, nano-passages, and a large surface area, making it suitable for applications in electrochemistry, bioelectronics, and flexible electronics. The challenges in studying vertical graphene include standardizing nomenclature, characterizing its complex structure, understanding its growth mechanism, and integrating small-sample processing into mass production. Various techniques are being explored, such as using solid-state carbon sources and applying magnetic fields. Vertical graphene shows promise for commercial applications in areas like flexible electronics,

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 10 August 2023 doi:10.20944/preprints202308.0866.v1

microenergy conversion, electrocatalysis, biosensing, and wearable devices, surpassing conventional graphene and carbon nanotube materials. Water splitting through electrocatalysis is another promising method for producing clean and renewable fuel, *i.e.* molecular hydrogen (H_2).

Recently, VGNWs have been grown on flexible stainless steel substrates suitable for electrochemical systems such as batteries, supercapacitors, and catalysts(Bertran-Serra et al., 2023). Graphene nanowalls growth has mainly focused on multi-layered graphene. This study aims to investigate the effect of temperature on the number of atomic layers in VGNWs. High quality bilayer vertical graphene nanowalls were grown at temperatures around 700ºC. The experimental section details the growth conditions and the methodology employed to analyze the structural and morphological characteristics of the VGNWs. The authors discuss the use of ICP-CVD with methane as the carbon precursor. They provide insights into the plasma conditions, gas flow, and pressure, which are crucial parameters for modulating the growth process. The advantages of ICP-CVD over other techniques, such as the absence of catalysts and the higher electron density of the plasma, are highlighted. In this fundamental study the effect of growth temperature through Raman spectroscopy and electron microscopy was investigated. Carbon nanostructures were grown on SS310 substrates at different temperatures using a remote plasma process. The results show that the growth temperature influences the structure and morphology of the carbon nanostructures. Capacitively-coupled plasma (CCP) promotes the growth of carbon nanotubes (CNT), while inductively coupled plasma (ICP) favors the growth of vertical graphene nanowalls (VGNWs). The mass deposition rate and Raman spectroscopy were used to analyze the carbon nanostructures, confirming the presence of graphene nanowalls and carbon nanotubes at different growth temperatures. The study provided valuable insights into the growth mechanisms of carbon nanostructures (Figure 1). They conclude that the temperature in which graphene nanowalls grow by ICP-CVD on SS310 substrates from pure methane and without catalyst ranges between 675ºC and 775ºC, and the characteristics resulting from the analysis with Raman spectroscopy of the graphene nanowalls show that their thickness is at least two monatomic layers, because of the growth mechanism of the graphene nanowalls in 3D formations. Also, the defects in the graphene nanowalls in the above temperature range mentioned reside mainly on the nanowalls' edges—and not on their faces, which upgrades their electric transport characteristics, and affects and facilitates the growth — in a prominent place—of nanoparticles of metallic oxides and carbides for the energy storage and catalysts applications.

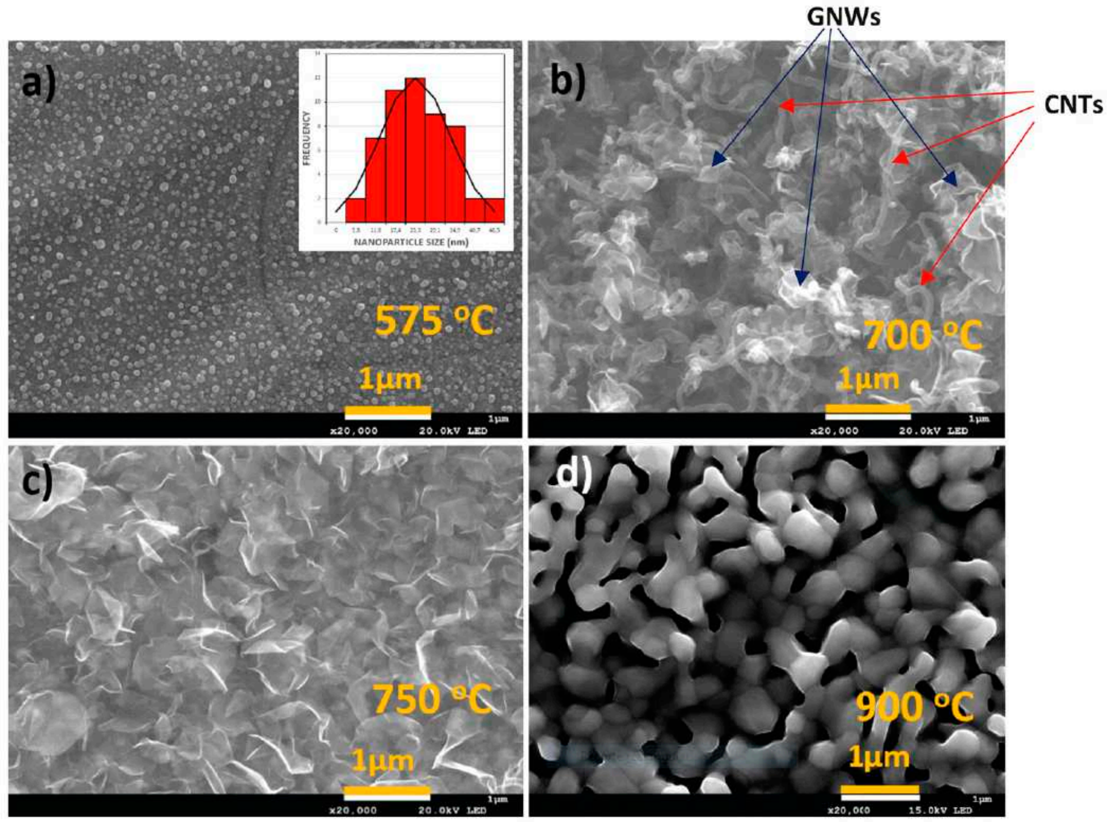

Figure 1. FE-SEM images of carbon nanostructures grown on stainless-steel (SS310) substrate by ICP-CVD from CH_4, corresponding to different processing temperatures: (a) Nucleation of carbon nanostructures on iron domains from the substrate at 575ºC. (b) Growth of a mixture of carbon nanotubes (CNTs) and graphene nanowalls (GNWs) at 700ºC. (c) Growth of GNWs of dimensions around 1 µm at 750ºC. (d) Formation of Cr particles segregated from the stainless-steel substrate (SS310) and their coalescence. Carbon nanostructures are not formed at 900ºC. (Reproduced with permission).

Other very interesting paper on graphene nanowalls formation is the work of Baranov et al.(Baranov et al., 2018), which offers a detailed description of the mechanism of formation of carbon nanostructures using a multi-scale, multi-factor model validated with experimental data. Kondo et al.(Kondo et al., 2009) investigated the initial growth process of CNWs on Si substrates using radical injection PECVD with O_2 gas added to the C_2F_6/H_2 source gas. The addition of O_2 gas effectively controlled CNW nucleation. Giese et al.(Giese et al., 2018) studied the synthesis and characterization of CNWs on various substrates, identifying four distinct morphologies of CNWs and proposing a growth mechanism based on surface diffusion and particle energies.

Recently, Chaitoglou et al.(Chaitoglou et al., 2022) demonstrated that GNWs are the vertical derivatives of 2-dimensional graphene. They successfully grew GNWs on various metallic and non-metallic substrates, providing valuable insights into their morphology and crystalline quality. The inherent electrocatalytic properties of GNWs towards HER in an acidic medium were evaluated for all substrates. When the substrate exhibits lower quality as electrocatalyst compared to GNWs, the electrode's performance resembles that of the GNWs coating. These findings contribute to the development of metal-free electrocatalytic electrodes, potentially replacing rare or noble metals in various practical applications.

The importance of understanding these underlying mechanisms cannot be overstated, as it paves the way for precise control over the growth process, leading to tailored properties of VGNWs for specific applications. By elucidating the role of hydrogen in graphene growth and investigating the dual functionalities of hydrogen as a co-catalyst and etchant for nanowall formation, this review contributes to a deeper comprehension of the intricate growth process of VGNWs.

Moreover, the exploration of various growth methodologies, such as CVD, DC arc discharge evaporation, microwave reactors, and plasma-enhanced chemical vapor deposition, has led to a diverse toolkit for producing carbon nanowalls. This diversity opens exciting possibilities for customizing VGNWs to suit different application requirements.

The potential of VGNWs as a versatile material for energy storage, catalysis, and sensing applications is tremendous. The advancements in growth techniques, morphological variations, and understanding of nucleation processes have propelled this field forward. However, the journey does not end here. Further research is needed to unravel the full potential of VGNWs and optimize their properties for practical applications.

Future challenges

Despite the remarkable progress in the field of PECVD for producing CNWs, there are still several challenges and areas of improvement to address.

a) Catalyst-Free Growth: Tanaka et al.(Tanaka et al., 2005) reported catalyst-free growth of CNWs, which simplifies the fabrication process. However, further investigations are required to optimize this approach and understand the factors influencing catalyst-free growth. Eliminating the need for catalysts can reduce costs and simplify the overall production process.
b) Control of Morphology: While recent studies have explored different morphological forms of CNWs, achieving precise control over their structure remains a challenge. The understanding of how process parameters influence the growth and morphology of CNWs is essential for tailoring their properties for specific applications.
c) Uniformity and Scalability: The uniformity of CNWs over large areas is crucial for their practical applications. As the demand for CNWs in industrial and commercial settings increases, scalability becomes a vital consideration. Developing techniques that can ensure uniform and large-scale CNWs production is necessary for their widespread implementation.
d) Characterization and Standardization: As the field advances, it is essential to establish standardized characterization techniques to evaluate the quality, structure, and properties of CNWs accurately. Standardization will facilitate comparison between studies and accelerate progress in this area.
e) Surface and Interface Engineering: CNWs' surface and interface engineering is crucial to tailor their properties for specific applications. By functionalizing or doping CNWs, their electrical, mechanical, and chemical characteristics can be tuned to meet the requirements of various devices and technologies.
f) Integration with Devices: For practical applications, CNWs need to be integrated with various electronic and optoelectronic devices seamlessly. Research on the compatibility and effective integration of CNWs into existing device architectures is essential for realizing their potential in real-world applications.
g) Cost-Effectiveness: As with any new technology, cost-effectiveness plays a crucial role in determining its commercial viability. Finding more cost-efficient synthesis methods, optimizing precursor gases, and improving deposition rates will be key factors in making CNWs commercially competitive.

Conclusion

Over the years, the field of PECVD for producing VGNWs has witnessed remarkable progress since its inception in 2002. Researchers have diligently explored a wide array of growth techniques, gas mixtures, growth conditions, and substrate materials, all aimed at optimizing the synthesis and properties of carbon nanowalls. This diverse research landscape has led to the emergence of unique carbon nanostructures with immense promise in energy storage, catalysis, and sensing applications.

The present review paper has focused on the substantial advancements made in PECVD for synthesizing VGNWs. Specifically, it has delved into the nucleation and coalescence stages of the growth process, elucidating the crucial role of hydrogen and the temperature's impact on the graphene growth ratio and nucleation density. By offering a comprehensive overview of the recent developments in the field of VGNWs, with a specific emphasis on their nucleation and growth via PECVD, this review has encompassed a wide range of substrates, growth techniques, and characterization methods, shedding valuable light on the growth mechanisms and properties of VGNWs and other carbon nanostructures. In enhancing our understanding of the PECVD process, researchers can now strive towards developing optimized growth conditions that can precisely tailor the properties of VGNWs for various applications in energy storage, catalysis, and sensing. Moreover, this review has underscored the immense potential of carbon nanostructures and 3D graphene networks, offering prospects for innovative materials and technologies. An especially notable finding discussed in this review pertains to the effect of temperature on the graphene growth ratio and nucleation density, observed across a wide range of temperatures. This study not only provides valuable insights into the growth process but also sheds light on the underlying physicochemical mechanisms governing the formation of VGNWs.

Undoubtedly, this comprehensive review aims to be a valuable resource for researchers and engineers engaged in the exploration of nanomaterials and carbon nanostructures. By providing an extensive overview of recent achievements, methodologies, and challenges, this review significantly contributes to the collective knowledge and understanding of Plasma-Enhanced Chemical Vapor Deposition for producing Vertical Graphene Nanowalls. As we continue to advance our knowledge in this domain, we move closer to harnessing the full potential of VGNWs, thereby addressing some of the most pressing challenges in energy, catalysis, and sensing technologies.

We hope that the search to unlock the innumerable possibilities offered by VGNWS continues, and that this review serves as an incentive to increase the transformative impact on various scientific and industrial applications.

Author Contributions: *Enric Bertran-Serra*: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. *Shahadev Rodriguez-Miguel*: Investigation, Data analysis. *Zhuo Li*: Investigation, Data analysis, Writing – review. *Yang Ma*: Methodology, Investigation, Data analysis. *Ghulam Farid*: Methodology, Investigation, Data analysis. *Stefanos Chaitoglou*: Conceptualization, Methodology, Formal analysis, Investigation, Writing – review & editing. *Roger Amade*: Conceptualization, Methodology, Investigation, Writing – review & editing. *Rogelio Ospina*: Conceptualization, Methodology, Formal analysis, Investigation. *José Luis Andújar-Bella*: Conceptualization, Methodology.

Acknowledgements: The authors acknowledge financial support of the Spanish Ministry of Economy, Industry and Competitiveness (MINECO) under Project PID2020-116612RB-C32, PDC2021-121868-C21,C22, TED2021-132070B-C21, TED2021-131442B-C33 funded by MCIN/AEI/10.13039/501100011033 and, as appropriate, by "ERDF A way of making Europe", by the "European Union" or by the "European Union Next Generation EU/PRTR". The ENPHOCAMAT research group acknowledges support from the AGAUR of Generalitat de Catalunya, Project No. 2021SGR00936. One author (R.O.) acknowledges the financial support from the Requalification of the Spanish University System 2021-23 program funded by the Next Generation EU program through the Ministry of Universities of Spanish Government. Another author (S.C.) acknowledges support from the postdoctoral fellowship program Beatriu de Pinós, funded by the Secretary of Universities and Research (Government of Catalonia) and by the Horizon 2020 program of research and innovation of the European Union under the Marie Sklodowska-Curie grant agreement No H2020-MSCA-COFUND-2017. Another author (Y.M.) acknowledges the support from the predoctoral fellowship funded by the Chinese Scientific Fellowship programme of the Chinese Government. Another author (G.F.) acknowledges the support from the predoctoral fellowship FPU funded by the MICINN of Spanish Government.

Conflict of Interest and other Ethics Statements: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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