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Diazonium functionalized fullerenes: a new class of efficient molecular catalysts for the hydrogen evolution reaction†

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Considerable efforts are being made to find cheaper and more efficient alternatives to the currently commercially available catalysts based on precious metals for the Hydrogen Evolution Reaction (HER). In this context, fullerenes have started to gain attention due to their suitable electronic properties and relatively easy functionalization. We found that the covalent functionalization of C₆₀, C₇₀ and Sc₃N@I_hC₈₀ with diazonium salts endows the fullerene cages with ultra-active charge polarization centers, which are located near the carbon-diazonium bond and improve the efficiency towards the molecular generation of hydrogen. To support our findings, Electrochemical Impedance Spectroscopy (EIS), double layer capacitance (C_{dl}) and Mott–Schottky approximation were performed. Among all the functionalized fullerenes, DPySc₃N@I_hC₈₀ exhibited a very low onset potential (−0.025 V vs. RHE) value, which is due to the influence of the inner cluster on the extra improvement of the electronic density states of the catalytic sites. For the first time, the covalent assembly of fullerenes and diazonium groups was used as an electron polarization strategy to build superior molecular HER catalytic systems.

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Introduction

Since the discovery of C₆₀ in 1985,¹ the chemical and physical properties of fullerenes have been extensively studied.^{2–7} Their diverse functionalization protocols allow the tuning of their structural features and their interesting electronic and physicochemical properties for multiple applications.^{7–9} On the other hand, based on the growing fears about the use of fossil fuels as traditional energy sources and their associated environmental issues, alternative renewable energy sources are being investigated to replace them.^{10,11} One of the most explored alternatives is the production of hydrogen *via* water splitting. The HER continues to receive considerable attention from the

scientific community¹² due to its potential impact in the development of renewable energy systems for the clean production of hydrogen using sustainable and clean catalysts.^{12–15} As a result of the high cost and scarcity of platinum (Pt), the best existing catalyst for this purpose, cheaper and equally efficient catalysts are being searched. In the past years, researchers have been studying electrocatalysts with high electronic conductivities, large surface areas and low overpotentials that could someday replace Pt. Reported studies range from the development of metal–organic frameworks such as ultra-small Fe₃S₄ nanosheets attached to 3D MIL-53(Fe) hybrid catalysts¹⁶ to metal-free materials as hybrid electrocatalysts comprising fullerene quantum dots (FQD)-decorated CoNi layered double hydroxide (CoNi-LDH) nanosheet arrays, anchored on porous Ni foam (NF).¹⁷

Recent articles have shown the potential that fullerenes have for electrocatalysis and the influence of structural and electronic factors on the catalytic properties due to their unique physicochemical characteristics.^{18–20} For example, a hybrid photocatalyst containing C₆₀ [WO₃/fullerene@1.5% Ni₃B/Ni(OH)₂] significantly improved the rate of formation of hydrogen which was 9.6 times higher than for the pure WO₃ photocatalyst.²¹ C₆₀ nanotubes have also shown efficient catalytic performance with a small onset potential of −0.13 V vs. RHE and ultrahigh electrochemical stability properties towards

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† Electronic supplementary information (ESI) available: Experimental details of the synthetic procedures used as well as the characterization techniques performed are presented. ¹H, ¹³C-NMR and mass spectrometry spectra are shown for the fulleropyrrolidine amine derivatives, fulleropyrrolidine diazonium derivatives and fulleropyrrolidine derivatives used as controls. Additionally, FTIR of fulleropyrrolidine amine derivatives and their respective diazonium salts are shown. EIS measurements for the synthesized compounds are presented. See DOI: 10.1039/d1nr05498h

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the generation of molecular hydrogen.¹⁹ More recently, Echegoyen *et al.* synthesized 1T-MoS₂/C₆₀ nanohybrids in which the C₆₀ molecules templated the formation of the MoS₂ nanosheets, and the resulting heterostructures exhibited an excellent catalytic activity for HER.²²

In this article, we report the application of diazonium functionalized fullerene derivatives as carbon-based molecular electrocatalysts for the HER. The compounds were obtained by synthetic modification of C₆₀, C₇₀ and Sc₃N@I_hC₈₀ with diazonium groups following a strategy reported by Hirsch *et al.*²³ After the resulting structures were characterized by ¹H and ¹³C-NMR, FT-IR spectroscopy and MALDI-TOF spectrometry, they were tested as electrocatalysts, resulting in improved catalytic activities compared to the corresponding starting materials. Experimental techniques were used to unveil the structure/catalytic function relationships of the diazonium functionalized fullerenes, showing that the functionalization is a key factor for the improved catalytic activity.

Results and discussion

In an attempt to find new, more affordable, precious metal-free catalysts for the HER, fullerene derivatives that could act as potential catalysts were synthesized. Diazonium salts are organic molecules that have proven to have high affinity for carbon surfaces.²⁴ Many reports have shown that diazonium salts can be electroreductively attached to graphene and carbon nanotubes,²⁵ and their electron transfer processes have been studied.²⁶ These reports have shown the potential that these compounds have as biosensors in catalysis applications. However, to the best of our knowledge, there are no reports of functionalized diazonium fullerene derivatives used as catalysts for the HER. In this work, we decided to covalently link diazonium salts to fullerenes to evaluate their performance as catalysts for the HER. The main objective of this work was to explore the impact that the diazonium moiety has on the electronic properties of the different fullerene cages as well as its influence in their overall catalytic performance.

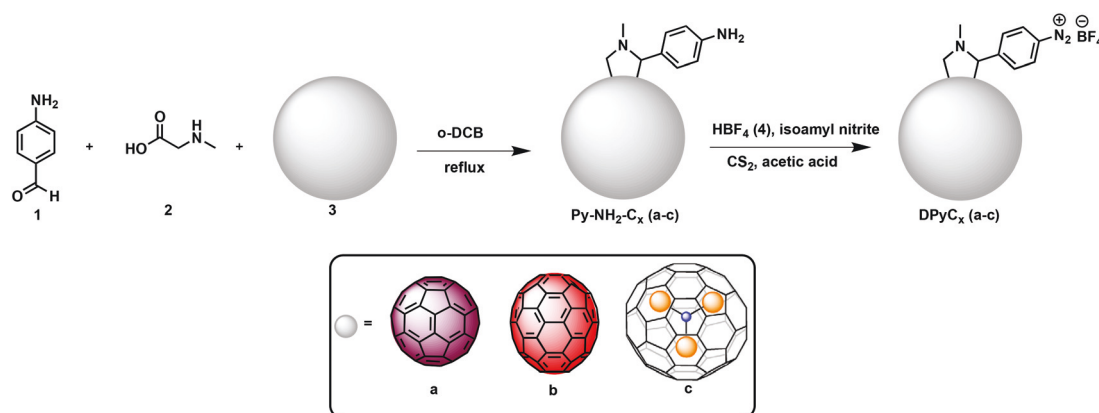
As shown in Scheme 1, the synthesis was carried out using a 1,3-dipolar cycloaddition reaction with 4-aminobenzaldehyde (1), sarcosine (2) and the fullerene cages (3) dissolved in *ortho*-dichlorobenzene (*o*-DCB) to obtain Py-NH₂-C₆₀ (a), Py-NH₂-C₇₀ (b) and Py-NH₂-Sc₃N@I_hC₈₀ (c). The fullerene derivatives (Py-NH₂-C_x, a-c) were then reacted with tetrafluoroboric acid (4) and isoamyl nitrite in carbon disulfide (CS₂) in the presence of acetic acid to yield the fullerene diazonium salt derivatives (DPyC_x, a-c). The compounds were purified by column chromatography and characterized by MALDI-TOF spectrometry, FTIR, ¹H and ¹³C-NMR spectroscopy (ESI Fig. S1–8†). As evidenced by NMR characterization, Py-NH₂-C₆₀ and Py-NH₂-Sc₃N@I_hC₈₀ were obtained as pure isomers, having the addend bonded to the fullerene cage on [6,6] bonds of C₆₀ and a [5,6] bond of Sc₃N@I_hC₈₀ respectively, while Py-NH₂-C₇₀ was obtained as a mixture of isomers (α, β and γ) as previously described.²⁷

To study the influence of the functional groups on the catalytic performance, the fulleropyrrolidine compounds were used as controls (see details in the ESI†) as well as a commercially available diazonium salt (4-nitrobenzenediazonium tetrafluoroborate) with similar structural features to those of the final compounds (Fig. 1A).

Electrocatalytic HER performance of the fullerene derivatives

To understand the effects of diazonium functionalization on the HER activity of C₆₀, C₇₀ and Sc₃N@I_hC₈₀, linear sweep voltammograms (LSV) of the unfunctionalized fullerenes, the fulleropyrrolidine derivatives and the diazonium functionalized fullerenes, including the commercially available diazonium salt and Pt/C 40%, were obtained using a three-electrode electrochemical configuration in 0.5 M H₂SO₄ at 2 mV s^{−1} (Fig. 1B, C and D). Functionalization of the fullerene cages with diazonium salts increased the catalytic performances of all when compared to those of the unfunctionalized fullerenes and their fulleropyrrolidine analogues, showing the importance of the diazonium group on proton electroreduction.

DPyC₆₀, DPyC₇₀ and DPySc₃N@I_hC₈₀ displayed onset potential values of −0.16, −0.15 and −0.025 V vs. RHE, respectively,



Scheme 1 Synthesis of diazonium fulleropyrrolidine derivatives with C₆₀, C₇₀ and Sc₃N@I_hC₈₀.

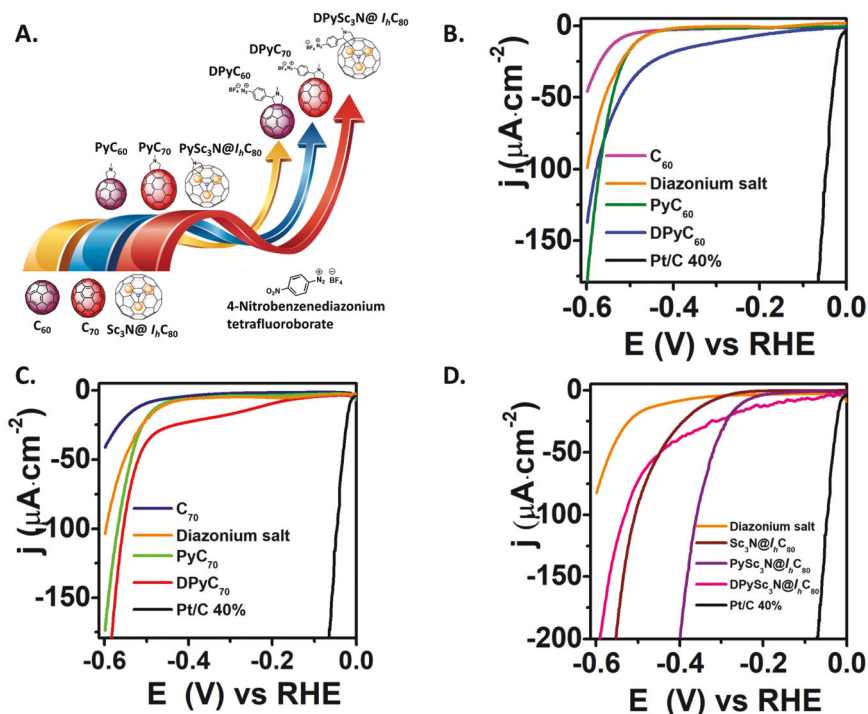


Fig. 1 (A) Summary of the compounds used in this study as controls and catalysts, (B) LSV curves for C₆₀ and C₆₀ derivatives, (C) LSV curves for C₇₀ and C₇₀ derivatives, (D) LSV curves for Sc₃N@I_hC₈₀ and Sc₃N@I_hC₈₀ derivatives.

which are much lower than those for C₆₀ (−0.51 V), PyC₆₀ (−0.45 V), C₇₀ (−0.50 V), PyC₇₀ (−0.45 V), Sc₃N@I_hC₈₀ (−0.30 V) and PySc₃N@I_hC₈₀ (−0.22 V). The diazonium salt used as a control did not show any additional improvement in the catalytic yields compared to those of the unfunctionalized fullerene cages (Fig. 1B, C and D), implying that the synergistic association of the covalently bonded diazonium groups in the fulleropyrrolidinium derivatives might decrease the adsorption energy states of the intermediate catalytic species, thus favoring HER thermodynamics. Additionally, we compared the catalytic activities with that for bare glassy carbon (Fig. S18†), and the results showed a notable difference, thus eliminating the possibility of the glassy carbon electrode influencing the results. The Tafel plots for the molecular electrocatalysts provided insights on the kinetic properties for the HER reaction (Fig. 2). A significant reduction in the Tafel slopes was observed after diazonium functionalization of both C₆₀ and C₇₀, indicating faster HER electrokinetics. DPyC₆₀ and DPyC₇₀ showed Tafel slope values of 95 and 90 mV dec^{−1}, respectively, which are lower than those for C₆₀ (119 mV dec^{−1}) and C₇₀ (149 mV dec^{−1}). These findings indicate a change in the kinetic mechanism upon diazonium functionalization from a sluggish Volmer mechanism (slopes >120 mV dec^{−1}) to the more efficient Volmer–Heyrovsky mechanism (<120 mV dec^{−1}), which means that the HER catalysis is taking place following a charge–transfer–induced hydronium ion dissociation step on both DPyC₆₀ and DPyC₇₀.²⁸ Nevertheless, although it has a low HER overpotential value, the Tafel slope for DPySc₃N@I_hC₈₀ (115 mV dec^{−1}) was comparable to that for Sc₃N@I_hC₈₀ (94 mV

dec^{−1}), which indicates that the diazonium groups do not have a notable effect on the electrokinetic efficiency of the endohedral metallofullerenes (EMFs).

It has been recently reported that the tip-enhanced local electric field of Pt situated at the sites with more curvature on the surfaces of carbon nano onions can greatly enhanced the HER electrocatalytic activity.²⁹ We believe that the electron transport efficiency, and, in turn, the electrocatalytic yields, of the diazonium functionalized cages are controlled by the charge polarization effects of the diazonium groups on the surface of the fullerenes, which redistributes the overall formal negative charges at the fullerene surfaces, thus favoring electron accumulation over specific spots that can serve as active sites for very efficient HER electrocatalysis. Additional factors should also be considered in the case of the DPySc₃N@I_hC₈₀. The strong electronic coupling between the d orbitals of the Sc²⁺ ions and the carbon atoms of the cage results in an increase of net negative charge on the fullerene surface, which contributes to the formation of an extra-number of high-density electronic sites and, therefore, to the improvement of the catalytic rates. This EMF derivative exhibits an onset potential value of −0.025 V vs. RHE that is comparable with those of the best carbon-nanomaterial electrocatalysts known (Table S1†).

To have a better understanding about the electrocatalytic mechanisms, the double layer capacitance values (*C*_{dl}) of the fullerenes were determined (Fig. S15 and 16†). It is worth noting that all the diazonium functionalized fullerenes exhibited high *C*_{dl}, indicating that diazonium functionalization

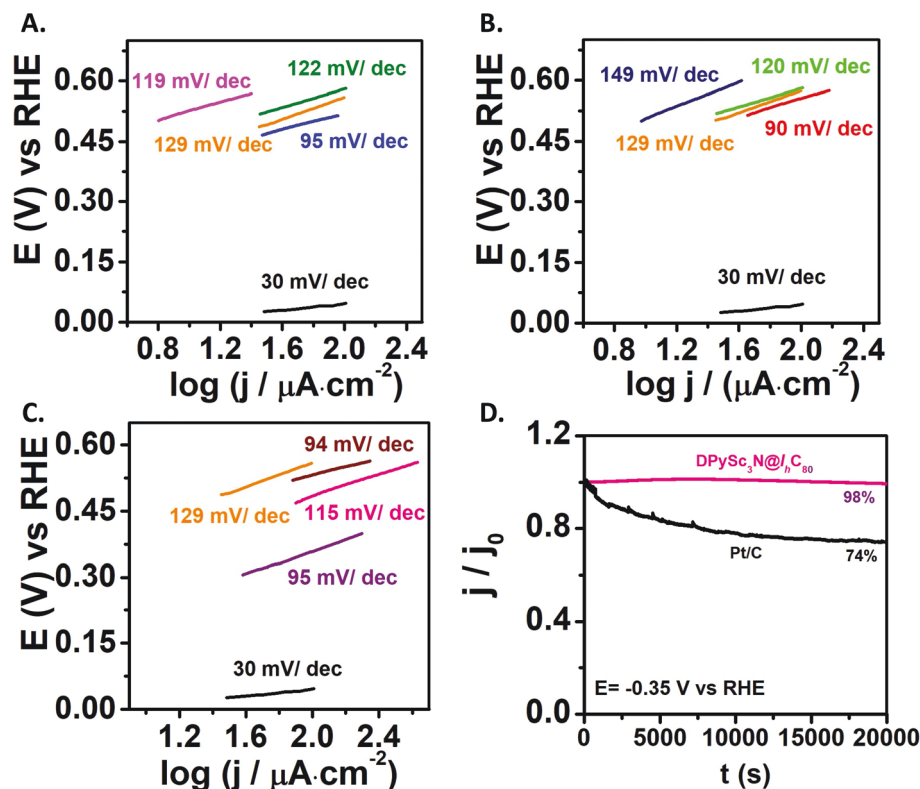


Fig. 2 Tafel plots for (A) C_{60} (magenta), PyC_{60} (green), diazonium salt (orange), DPyC_{60} (blue) and Pt/C 40% (black); (B) C_{70} (navy), PyC_{70} (light green), diazonium salt (orange), DPyC_{70} (red) and Pt/C 40% (black); (C) $\text{Sc}_3\text{N}@I_h\text{C}_{80}$ (brown), $\text{PySc}_3\text{N}@I_h\text{C}_{80}$ (purple), diazonium salt (orange), $\text{DPySc}_3\text{N}@I_h\text{C}_{80}$ (pink) and Pt/C 40% (black); (D) electrochemical stability studies for the best catalyst $\text{DPySc}_3\text{N}@I_h\text{C}_{80}$ (pink) compared to the commercially available Pt/C 40% (black).

increased the intrinsic catalytic activity as well as the surface density of the catalytic active sites,³⁰ most likely due to charge polarization processes. The $\text{DPySc}_3\text{N}@I_h\text{C}_{80}$ shows the largest C_{dl} value (28 mF cm^{-2}), thus demonstrating that this material is the best HER fullerene catalyst when compared to the rest of the diazonium functionalized fullerenes presented in this work.

When designing a molecule or material as a catalyst, one of the most important aspects to consider is that they have appropriate conduction and valence band edge states for HER. An appropriate bandgap is needed to ensure an efficient electron transfer and conduction. Additionally, electrocatalysts should also exhibit good charge transport properties under different operation conditions, such as in acidic or alkaline electrolytes. Calculation of the band edge positions, and Fermi levels is crucial since these determine electron densities at the surface. Band gap energy and flat-band potentials were calculated for DPyC_{60} , DPyC_{70} and $\text{DPySc}_3\text{N}@I_h\text{C}_{80}$ using Tauc plots and the Mott-Schottky approximation (Fig. 3A and B). The valence band (E_v) and conduction band (E_c) state positions must balance the HER reactions. Fig. 3C shows the bandgap profile and band-edge states of the diazonium fullerene derivatives and their starting materials relative to the standard hydrogen electrode potential. Having a Fermi level above the standard hydrogen evolution potential and closer to zero should drasti-

cally favour the HER. As can be observed, the flat-band potential starts getting closer to zero from C_{60} (0.43 V) to $\text{DPySc}_3\text{N}@I_h\text{C}_{80}$ (0.019 V), a result that matches perfectly with the obtained catalytic performances.

The catalytic properties were further analyzed by Electrochemical Impedance spectroscopy (EIS), which was measured from 100 kHz to 0.1 Hz (ESI, Fig. S17†). Spectra consist of a semicircle assigned to the charge transfer process attributed to the materials' conductivity. The model parameters were extracted by fitting the EIS data with Z-View software. The EIS results are consistent with the excellent HER kinetics of diazonium functionalized fullerenes, where the Nyquist plots show decreasing charge transfer resistances for DPyC_{60} ($R_{CT} = 117 \text{ W}$), DPyC_{70} ($R_{CT} = 84 \text{ W}$) and $\text{DPySc}_3\text{N}@I_h\text{C}_{80}$ ($R_{CT} = 5 \text{ W}$) among the studied catalysts at -0.6 V vs. RHE , confirming the increase of the interfacial charge-transfer kinetics upon diazonium functionalization. Additionally, $\text{DPySc}_3\text{N}@I_h\text{C}_{80}$ showed good long-term electrochemical stability (Fig. 2D) as well as minimal changes in the onset potential during the 10 h $i-t$ test at -0.35 V vs. RHE (Fig. 4), retaining 90% of the initial current density after 20 000 s, thus surpassing the electrochemical stability of commercial Pt/C 40%. This is due to the highly stable structure of the diazonium-decorated EMF as well as to its excellent electrocatalytic performance.

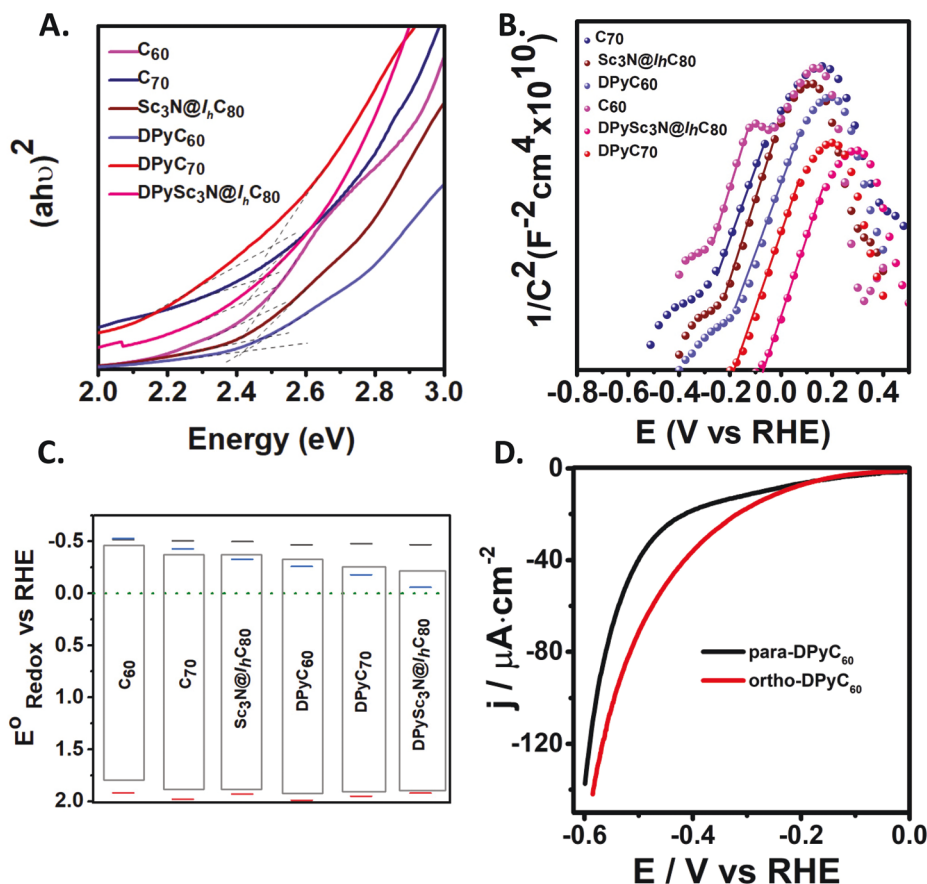


Fig. 3 (A) Tauc plots; (B) Mott-Schottky plots (capacitance values were derived from the electrochemical impedance obtained at each potential with 1 kHz frequency); (C) band gap profile; and D. LSV curves comparing *para*-DPyC₆₀ and *ortho*-DPyC₆₀.

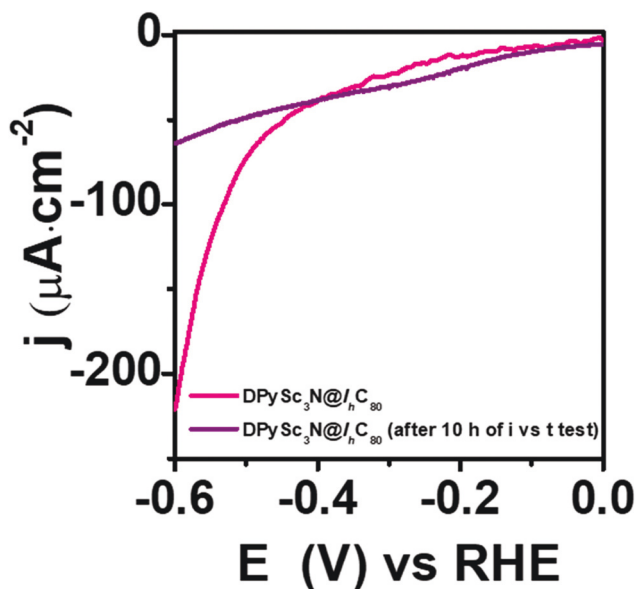


Fig. 4 Final LSV curve of the DPySc₃N@I_hC₈₀ of a 10 h *i-t* experiment.

To explore how the functionalization with the diazonium moiety contributes to the HER reaction, we decided to synthesize the analogue of DPyC₆₀ but with the functional group

closer to the fullerene cage in the *ortho* position (*ortho*-DPyC₆₀, see ESI for structural characterization Fig. S12–14†). The idea was to assess whether the influence of the diazonium group would be stronger if it is closer to the fullerene cage. As shown in Fig. 3D, the diazonium derivative *ortho*-DPyC₆₀ exhibits a lower onset potential (−0.101 V) when compared to the *para*-DPyC₆₀ (−0.160 V), which clearly shows that the electronic effect of the diazonium group is a key factor for their performance as HER catalysts. We believe that the strong electron withdrawing character of the diazonium group generates a polarization of charges which favors the accumulation of net negative charge in spots near the fullerene surface which can serve as active sites for the HER reaction.

Conclusions

In this work, we have successfully synthesized and characterized diazonium fullerene derivatives of C₆₀, C₇₀, Sc₃N@I_hC₈₀ and analyzed their electrocatalytic properties for HER. The results revealed improved electrocatalytic activities for the functionalized compounds, better than those for the compounds used as controls. Additional measurements such as EIS, double layer capacitance, and Mott-Schottky approxi-

mation provided additional insights about the nature of the electrochemically active sites. The results suggest that the presence of the diazonium group induces polarization of the fullerene derivatives, which concentrates the net negative charge on the carbons closer to the functionalization site on the fullerene surface, allowing a more efficient H^* adsorption. The best catalyst tested was $DPySc_3N@I_hC_{80}$, with an onset potential of -25 mV, which is very close to the value (-13 mV) for the standard Pt/C (40%). This work shows that electron polarization for functionalized fullerenes is an effective strategy in developing efficient catalysts for high-performance HER electrocatalysis.

Experimental section

General procedures

All chemicals were reagent grade, purchased from Sigma Aldrich. Silica gel (Redisep silica, 40–60 μ , 60 Å) was used to separate the products. MALDI-TOF mass spectrometric measurements were obtained on a Bruker Microflex LRF mass spectrometer on reflector positive mode. The UV/Vis-NIR spectra were recorded using a Cary 5000 UV/Vis-NIR spectrophotometer using toluene or chloroform solutions. The NMR spectra were recorded using a JEOL 600 MHz spectrometer. FTIR spectra were recorded for solid samples in a Bruker Tensor 27 spectrometer in transmittance mode.

Electrochemical measurements

The HER performances for the diazonium fullerene derivatives and the fulleropyrrolidine derivatives as well as for pure C_{60} , C_{70} and $Sc_3N@I_hC_{80}$, were obtained using an electrochemical workstation (CHI 660D) with a three-electrode system. Glassy carbon, Ag/AgCl (3 M KCl) and graphite rod electrodes were used as the working, reference and counter electrodes, respectively, for the HER reactions. 0.5 M H_2SO_4 was used as electrolyte for the HER reaction, which was purged with Argon for 30 min before recording the measurements. To prepare the working electrode, 1 mg of the catalysts were dispersed in 1 mL of toluene and, subsequently, 10 μ L of the solution were deposited on the surface of the glassy carbon electrode. Linear sweep voltammetry (LSV) was recorded in 0.5 M H_2SO_4 solutions at 2 mV s^{-1} . The EIS measurements were performed at -0.7 V vs. RHE from 10^{-1} to 10^5 Hz.

General synthesis of fulleropyrrolidine derivatives

In a round bottom flask, the fullerene, paraformaldehyde and sarcosine were added and dissolved in *o*-dichlorobenzene (*o*-DCB). The reaction was stirred under reflux for 30–50 min. After this time, the mixture was chromatographed using silica gel with toluene.

General synthesis of fulleropyrrolidine amine derivatives

In a round bottom flask, the fullerene, pulverized 4-aminobenzaldehyde and sarcosine were added and dissolved in *o*-dichlorobenzene (*o*-DCB). The reaction was stirred under reflux for 30–40 min. After this time, the mixture was chro-

matographed using silica gel with the following eluents: carbon disulfide, carbon disulfide/chloroform (1 : 1) and hexanes/chloroform (1 : 2).

General synthesis of fulleropyrrolidine diazonium derivatives

In a round bottom flask, the obtained fulleropyrrolidine derivatives and $HBFe_4$ 48 wt% in H_2O were added and dissolved in acetic acid/carbon disulfide (2 : 1). Isoamyl nitrite (21 μ L, 0.14 mmol) was added dropwise and the reaction left at room temperature for 30 min. After this time, diethyl ether was added, and the reaction was stirred at about -20 °C for 16 h. Finally, the sample was washed with cooled ether.

Conflicts of interest

No conflicts of interest to declare.

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