Size control of nanographene supported iron oxide nanoparticles enhances their electrocatalytic performance for the oxygen reduction and oxygen evolution reactions

Ferdinand Hof,^{a,b,} Meng Liu,^c Giovanni Valenti,^{c*} Emmanuel Picheau^{a,b} Francesco Paolucci,^c Alain Pénicaud^{a,b}*

- a. CNRS, Centre de Recherche Paul Pascal (CRPP), UMR 5031, F-33600 Pessac, France.
- b. Université Bordeaux, CRPP, UMR 5031, F-33600 Pessac, France
- c. University of Bologna, Department of Chemistry “G. Ciamician”, via Selmi 2, 40126, Bologna, Italy

KEYWORDS Synthesis, carbon composite materials, iron oxide nanoparticles, electrocatalysis, OER, ORR

Reduced carbon layers, differing in lateral dimension, are exploited as reduction agent for iron(II) salts, resulting in the decoration of the carbon framework by iron oxide nanoparticles. Depending on the choice of the carbon starting material, the average size of the formed nanoparticles is situated between 3-50 nm. Those composite materials, free of stabilization or

capping agents, show remarkable catalytic activity in the oxygen reduction reaction (ORR) and in the oxygen evolution reaction (OER). The electrochemical performance, the activity and the selectivity depends dramatically on the respective size of the nanoparticles generated.

The synthesis of novel catalysts is crucial for achieving the shift from fossil based energy vectors to renewable and sustainable alternatives such as hydrogen technology.^{1,2,3} Currently, price, stability, and activity are major issues for existing catalysts, hampering widespread mass market application. The oxygen reduction reaction (ORR) is crucial not only for fuel cells but also for metal-air batteries.⁴ Nano catalysts based on earth abundant metals are considered to be capable of replacing established noble metal catalysts, due to economic and ecological considerations such as abundance, and environmental impact.^{5,6} A major hurdle is the catalytic activities of first row transition metal catalysts which are typically lower than that of their noble metal counterparts.⁷ One general trend to tackle this issue is to increase the specific surface area of earth abundant catalysts which typically translates into a higher reactivity and improved selectivity.⁸ Not surprisingly, this is also a promising pathway to improve the activity and selectivity of the ORR.^{9,10,11,12} For platinum based electrocatalysts, the optimal size for the activity is in the range of about 2nm.¹³ It can be expected that the optimal size of nano catalysts from earth abundant metal might differ from that value. Additionally, leaching is a much more pronounced issue in earth abundant nano catalysts, and consequently needs to be limited. To reduce the effect of leaching, nanoparticles are conventionally grafted on substrates. Graphene metal oxide nanoparticle composite materials have been shown to exhibit a high catalytic reactivity, related to the synergy between the nanoparticle and the carbon framework.^{14,15} The synthesis of those composite materials relies mainly on the reduction of metal salts in the presence of graphene oxide or surfactant stabilized few layer graphene, in wet chemical approaches. However, the

specific reaction conditions need to be carefully adjusted for each type of nanoparticles that are grafted to either graphene oxide, reduced graphene oxide, or few layer graphene. Furthermore, synthetic protocols yielding specific distribution of sizes attached to those substrates are rare. Additionally, side reaction of the reduction agent with graphene oxide needs to be considered, hampering significantly the fine tuning of reaction parameters.

We recently reported on the synthesis of iron oxide nanoparticle nano carbon composite materials using a synthetic, sustainable, almost defect free graphitic nano carbon,^{16,17} as carbon starting material. The nanoparticle synthesis is based on the reaction between a graphenide solution, containing negatively charged 15-30 nm sized carbon layers, and stoichiometric amounts of anhydrous iron metal salts. The reaction yields a composite material composed of carbon layers decorated with iron oxide/hydroxide nanoparticles in the range between 2-5nm. The isolated composite material exhibits high bifunctional activity as electrocatalyst in the oxygen reduction (ORR) and oxygen evolution reaction (OER).¹⁸ The synthesis is a generic way to metal nanoparticle carbon composite material as the graphenide can be consequently reacted with other types of metal salts.¹⁹ Here, we generalize the concept by exploiting different carbon starting sources, e.g. flake and powder graphite, and demonstrate that in each case iron oxide nanoparticle carbon composite materials can be generated. The choice of the carbon material is a crucial parameter, determining not only the size of the carbon flakes but also simultaneously tailoring the size of the generated iron oxide nanoparticles. This is a novel concept to alter particle size distributions. The final size distribution in the composite material has a major impact on the performance in the ORR and the OER.

Scheme 1 Reaction scheme for the synthesis of different iron oxide nanoparticle carbon composite materials (Fe(NP)/nC) exploiting the reaction between graphenide solutions and anhydrous iron (II) tetrafluoroborate. The different graphenide solutions containing charged graphene layers with varying size distributions, result in composite materials which are composed of carbon layers covered by a distribution of different iron nanoparticle sizes, increasing in the order s-(Fe(NP)/nC), over m-(Fe(NP)/nC) to l-(Fe(NP)/nC)

The synthesis relies on the reaction of graphenide solution obtained from different graphite starting materials with iron(II) tetrafluoroborate (Scheme 1 (for more detail see supporting information, ESI)). The synthesized composite materials exhibit different size distributions of iron oxide nanoparticles, increasing in the order s-Fe(nP)/nC, over m-Fe(nP)/nC to l-Fe(nP)/nC, with a variation of size distribution of over one order of magnitude. This observation highlights the remarkable degree of control that negatively charged graphene layers in solution provide over the redox process and the nanoparticle growth. Typically, the growth of nanoparticles is controlled by the diffusion of the reactants and the surface reaction rate.²⁰ Consequently, to generate particles of different sizes, these two parameters need to be carefully fine-tuned. In contrast, in the case of the reaction between a charged carbon layer and metal salts the situation is different: there is only a finite number of total electrons available on each sheet, originating

from the intercalation step. Consequently, the larger the carbon sheet, the higher the number of available electrons is (see Scheme 1). Assuming that the diffusion rate of the metal salts to the carbon is comparable, the reaction is mainly driven by the surface reaction rate. As the electron mobility on the carbon lattice is astonishingly high,²¹ and the electron transfer energy is low,²² the particle size is based on the available amount of electrons present on the individual sheets and consequently larger carbon lattices lead to larger particles.

The graphenide solutions are obtained upon dissolving the respective intercalation compound of stoichiometry KC_8 (Fig. S1, Table ST2) for 3 days in anhydrous THF under inert gas atmosphere by stirring. Each graphenide solution (Fig. S2), differing in carbon lattice size, was reacted with equimolar amounts of recrystallized iron(II)tetrafluoroborate salts in the glove box. The final composite material has been obtained after quenching the reaction mixture outside the box with water and isolation/purification of the material by filtration. The iron content in the samples is between 1.6 and 2.0 atomic %, determined by TGA (15.4 wt % to 21.4 wt %) experiments (Fig. S3). Fe 2p XPS spectra of the three different composite materials are depicted in Figure 1.

Figure 1 Fe_{2p} XPS spectra of the 3 composite materials varying in carbon lattice size (small, medium and large) grafted with iron oxide nanoparticles. Fits in the $2p_{3/2}$ region show the presence of predominantly iron(III) oxide/hydroxide (Fig. S4).

From the performed fits (Fig. S4), predominantly iron (III) oxide/hydroxide species are present in each of the three composite materials. The shape of the peaks is very similar and thus the ratio between iron(III) oxide and iron(III) hydroxide does not significantly differ between samples. This observation is corroborated by XPS O_{1s} spectra (Figure S5c) as also those peak profiles are very similar. One should note that XPS spectra indicate the presence of iron(III)hydroxides, which can be either ferri(oxyhydroxides) or ferrihydrite and are known to be polycrystalline.^{23,24} XRD measurements reveal that the iron(III) oxides are mainly $\gamma\text{-Fe}_2\text{O}_3$ (Fig. S6). By applying the Scherrer equation, a particle size of sub 10 nm, about 15 nm, and 20 nm for the small, medium and large particle composite material respectively could be determined. In the course of the reaction, upon dissolving the GICs in THF, the carbon layers are separated and are stabilized in solution. Once, the metal salt is added, electron transfer occurs from the carbon lattice to the metal cation and the composite material starts to precipitate, under random stacking of the

carbon layers, explaining the broadening of the carbon (002) peak in the respective composite materials compared to the starting materials (see Figure S7).

By Raman spectroscopy, the properties of the carbon lattice such as defect density, crystalline size, stress and strain can be probed. The intensity (I) or area (A) of the D-mode ($\approx 1350 \text{ cm}^{-1}$) to the G-mode ($\approx 1582 \text{ cm}^{-1}$) is a measure of the defect density of the carbon lattice.²⁵⁻²⁷ By plotting the A_D/A_G values vs the width of the G-mode it is possible to disentangle the contribution of line (L_a) and point (L_p) defects in carbon samples.¹⁷ Point defects are for instance vacancy defects or attached functional groups. Line defects are grain boundaries within the carbon lattice of edges. In Fig. 2, the statistical Raman analysis of the three starting graphite materials and the 3 composite materials is depicted

Figure 2 Statistical Raman spectroscopic measurements at $\lambda_{\text{exc}} = 532 \text{ nm}$ of the 3 starting graphite materials and the 3 composite materials. a) mean Raman spectra of the composite materials normalized to the G-mode intensity (starting materials S9). b) plot of the A_D/A_G values vs the width of the G-mode based on the fit and analysis of 1681 individual spectra. The solid and the dashed curves are adapted from ref⁷ and are theoretical calculation for the limiting cases for pure line(L_D) and point defects(L_P), respectively.

The Raman data presented are based on the measurement of 1681 individual Raman spectra and the statistical analysis of the fitted spectra histograms width of the G-mode and A_D/A_G values

(Fig. S8). The Gaussian fits of these histograms provide the mean values and the standard deviation used in Fig. 2b. The results of the starting materials, of both the flake and the micrographite, show that the L_a value is close to the limit of the published model and thus the carbon flake size is much larger than 500 nm. For the graphitic nano carbon on the other hand, L_a values of about 25 nm are observed. The L_b values indicate that the starting graphites are predominantly defect free. In the final products, the L_a value is slightly decreased whereas the L_b value is increased. In overall the values of the composite materials are very close to the values obtained for the starting materials. The slight decreased of the lattice size (L_a values) and an increase of the defect density (L_b) may be explained by the reaction. In the first step, the GIC is dissolved upon stirring, which could lead to a slight decrease in lattice size due the stirring process either by preferentially dissolving smaller sized carbon materials or by mechanically breaking larger crystals. Upon oxidation of the graphenide solution by the iron metal salt, or in the course of the work up, where the oxidation of the iron metal nanoparticle to the final iron oxide/hydroxide nanoparticle occurs, some point defect in the lattice may be introduced. It may be noted that sizeable graphene-like domains are still present in the composite samples, comparable with the starting materials, which is a prerequisite for good conductivity and for a performing electrocatalyst. By EDX/STEM analysis, the morphology and the size of the carbon flakes as well as those of the iron nanoparticles can be studied (Fig 3). In Figure 3a, the TEM images of the three composite materials are depicted. The carbon flakes and the iron oxide nanoparticles can clearly be identified. The chemical nature have been studied in more detail by STEM/EDX from both the iron and the carbon edge (Figure 3b,c) respectively.

Figure 3 HR-STEM images of the different composite materials a) s-Fe(nP)/nC, d) m-Fe(nP)/nC g) l-Fe(nP)/nP b), e), h), EDX maps of the carbon edge and c,f,i) EDX maps of the iron edge.

In all three composite materials the nanoparticles are found to be attached to the carbon flakes, which is crucial to prevent leaching in the electrocatalytic study (composite image Figure S10). The graphitic nano carbon is of synthetic origin, and the average size of the carbon domains is 50 nm. The two other carbons used are of natural origin, micro graphite and flake graphite, and not surprisingly both the average lateral size but also the distribution of size is much larger (Fig S11). For the former, flakes up to about 3 μm have been observed, centred at about 0.7 μm , and flakes up to about 10 μm , centred at about 2 μm , for the latter case (see Figure 4a). For liquid based processing the obtained values for the size are large and demonstrate the superior value of

graphenide solutions not only as synthetic pathway to obtain few layer graphene in solution but moreover as platform for the synthesis of nanocomposites. The distribution of sizes for the large and medium composite material is rather broad, which is related to the size distribution in the graphenide solution that depends likely on experimental parameters such as stirring duration, stirring speed, amongst others. The iron nanoparticle size is not equal for all three samples under study and there is a trend (clearly visible also in Figure 4d) towards larger particle size for the sample with larger carbon lattice size. This behaviour was further studied by correlating the surface area of the carbon size vs the average nanoparticle size (Fig 4d) based on more than 100 counts each.

Figure 4 Histogram of the size distribution of the carbon flakes in three different composite materials based over 200 individual counts in about 40 TEM images each. The histograms have

been fitted by a Lognormal function and average sizes of about 53, 700 and 2100 nm have been determined for the respective samples a) s-Fe(nP)/nC, b) m-Fe(nP)/nC, and c) l-Fe(nP)/nC. d) Correlation of the area of the carbon flake with the nanoparticle size. The statistics is based on the analysis of 40 TEM images for each sample. The average iron oxide nano particle size distribution has been based on the average of 127, 574, and 653 and counts s-Fe(nP)/nC, m-Fe(nP)/nC, l-Fe(nP)/nC nanocarbon composite material, respectively.

A trend can be seen that connects the carbon size of the flakes with the nanoparticle size for the three samples and the distribution of sizes of the nanoparticles is progressively more disperse the larger the carbon flake is. Arguably, this is related to the synthesis, and the exploitation of the reduced carbon layers for the nanoparticle generation and the existence of a competing mechanism, between initial seed formation and crystal growth. The average size of the iron nanoparticle are about 35 nm for the micrographite starting material and about 50 nm for the flake graphite and the nanoparticles are crystalline (Fig S12). AFM images (Fig. S13) recorded on those samples corroborate those observations.

Electrochemistry The electrocatalytic performance of Fe(np)/nC composites with different size of iron oxide nanoparticles were evaluated towards the ORR and OER. Films of those materials were obtained by drop casting 50 μ L of a THF dispersion (0.5 mg mL⁻¹) onto a glassy carbon rotating disk electrode (RDE) or rotating ring disk electrode (RRDE). Cyclic voltammetry (CV) curves were obtained on RDE in O₂-saturated 0.1 M ultrapure KOH aqueous solution. As shown in Figure 5a the Fe(np)/nC with small size of iron oxide nanoparticles (s-Fe(np)/nC) exhibited an ORR onset potential (+ 0.79 V vs RHE), 40 mV more positive than m-Fe(np)/nC and 60 mV more positive than l-Fe(np)/nC. Notice that the pristine graphitic nanocarbon shows a lower onset potential compared with all composites (see grey signal in Fig. 5a). The ORR limiting current density for s-Fe(np)/nC is also larger compared with the other two

samples (Fig. S14a in ESI). Furthermore, the reaction kinetics of the composites during the ORR process were explored by means of RDE measurements at different rotating speeds (Fig. 5b).

Figure 5 Fe(np)/nC modified electrodes for ORR electrocatalysis. a) Comparison of onset potentials of the pristine graphitic nanocarbon (nC), l-Fe(np)/nC, m-Fe(np)/nC, and s-Fe(np)/nC at a rotation speed of 1600 rpm in O₂-saturated 0.1 M KOH solution (scan rate: 10 mV s⁻¹). The green dashed line corresponds to s-Fe(np)/nC in Ar. b) CV curves of s-Fe(np)/nC at various rotation speeds; inset was the corresponding K-L plots at different potentials. c) Electron transfer numbers of l-Fe(np)/nC, m-Fe(np)/nC, and s-Fe(np)/nC at 0.45 V obtained from RRDE results. d) Current-time chronoamperometric responses of l-Fe(np)/nC, m-Fe(np)/nC, and s-Fe(np)/nC at 0.7 V vs RHE (at 1600 rpm). All potentials were reported versus RHE.

Generally, the diffusion current densities increase with higher rotating speeds due to the shortened diffusion distance. The corresponding Koutecky-Levich (K-L) plots displayed good

linearity with parallelism among the potential range from 0.45 to 0.53 V. From the intercepts of K-L plots, the s-Fe(np)/nC displays a kinetic current density (j_k) of 9.3 mA cm⁻² at 0.45 V, larger than those of the m-Fe(np)/nC (5.4 mA cm⁻²) and l-Fe(np)/nC (1.5 mA cm⁻²) (Fig. S14b in ESI). The electron transfer numbers have been obtained from RRDE voltammograms by comparing the ring current, due to the hyperoxide oxidation, and disk current, due to the ORR (Fig. S15 in ESI). As shown in Figure 5c, the electron transfer number of s-Fe(np)/nC was 3.6 at the potential of 0.45 V, revealing that it proceeds mainly by 4-electron pathway. In comparison, the m-Fe(np)/nC and l-Fe(np)/nC exhibit lower electron transfer numbers of 3.37 and 2.96, respectively, suggesting 2-electron and 4-electron mixed transfer processes. Remarkably, a prolonged electrocatalysis carried out at 0.7 V vs RHE showed excellent stability of the s-Fe(np)/nC electrocatalyst (Fig. 5d). After 2000 seconds of reaction time, the current density of s-Fe(np)/nC catalyst maintained 96.3%, which is better than m-Fe(np)/nC (93.6%) and is far superior to l-Fe(np)/nC, which suffered from a 30.4% decrease. The comparison of CV related to either iron oxide reduction or iron oxidation allowed to estimate the fraction of active nanoparticles electronically connected to the electrode (figure S16 in ESI).

Figure 6 a) Comparison of OER performances of l-Fe(np)/nC, m-Fe(np)/nC, and s-Fe(np)/nC in 0.1 M KOH solution (scan rate: 10 mV s^{-1}). b) Tafel plots of l-Fe(np)/nC, m-Fe(np)/nC, and s-Fe(np)/nC.

Remarkably, as shown in Fig. 6a, s-Fe(np)/nC electrode promoted oxygen evolution reaction with an onset potential (at 1 mA cm^{-2}) of 1.65 V, more positive than those of m-Fe(np)/nC and l-Fe(np)/nC. Comparison with literature and standard catalysts show that s-Fe(np)/nC catalysts is a bifunctional catalysts, comparing well with other iron and manganese based alternatives to the Pt/C reference system for the ORR and as efficient as the IrO_2 catalysts for the OER. (Fig. S18). The Tafel analysis depicted in Figure 6b reveals a slope of 40 mV per decade for s-Fe(np)/nC, indicating a good control over O_2 mass transport.²⁸

Conclusions

The synergy between the extremely good electronic conductivity and low charge transfer energy of carbon nanomaterials and the rich catalytic chemistry of metal oxides composite materials provide access to cheap, renewable, earth abundant and well-performing catalysts. The negatively charged graphene layers in the graphenide solutions are a potent reducing agent controlling and self-limiting the nanoparticle growth, limited by both the number of available electrons and the reducing potential of the graphenide solution. Consequently, the total amount of charges present on the carbon layers is directly related to the size of the formed nanoparticles. Neither any stabilization agents nor any mediators are needed, commonly applied to tailor the particle sizes of a reaction. Simultaneously, the graphenic character of the carbon lattice is preserved, which is crucial for the application of those composite materials as electrocatalysts. Furthermore, the study shows that a narrow and small size distribution iron oxide/hydroxide carbon nanocomposite material is crucial for an efficient electrocatalytic activity for both the OER and ORR.

ASSOCIATED CONTENT

Supporting Information (ESI). The supporting information contain additional details of the synthesis of each graphenide solution, and the respective iron oxide carbon composite materials. Furthermore, additional physiochemical characterization, UV-Vis, Raman, TGA, XPS, TEM and SEM data as well as electrochemical quantification and RRDE measurements are presented.

The file is free of charge

AUTHOR INFORMATION

Corresponding Author

g.valenti@unibo.it and hof@crpp-bordeaux.cnrs.fr

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

FH thanks the Deutsche Forschungsgemeinschaft (DFG) for funding the individual research fellowship HO5903/1-1. This work has been performed within the framework of GDR-I, Graphene and CO, (#3217) of CNRS. EP and AP acknowledge funding from the ANR (Edgefiller project). M.L., G.V. and F.P. thank the University of Bologna, Italian Ministero dell'Istruzione, Università e Ricerca. M.L. thanks Chinese Scholarship Council No. 201709370059 for funding support.

ACKNOWLEDGMENT

We thank Ahmed Bentaleb Centre de Research Paul Pascal for XRD measurements.

REFERENCES

- (1) Armaroli, N.; Balzani, V. Solar Electricity and Solar Fuels: Status and Perspectives in the Context of the Energy Transition. *Chem. Eur. J.* **2016**, *22*, 32–57.
- (2) Valenti, G.; Boni, A.; Melchionna, M.; Cargnello, M.; Nasi, L.; Bertoni, G.; Gorte, R. J.; Marcaccio, M.; Rapino, S.; Bonchio, M.; et al. Co-Axial Heterostructures Integrating

- Palladium/Titanium Dioxide with Carbon Nanotubes for Efficient Electrocatalytic Hydrogen Evolution. *Nat. Commun.* **2016**, 7, 13549.
- (3) Lewis, N.; Nocera, D. G. Powering the Planet: Chemical Challenges in Solar Energy Utilization. *Proc. Natl. Acad. Sci. USA* **2006**, 103, 15729–15735.
- (4) Roger, I.; Shipman, M. A.; Symes, M. D. Earth-Abundant Catalysts for Electrochemical and Photoelectrochemical Water Splitting. *Nat. Rev. Chem.* **2017**, 1, 3.
- (5) Kanan, M. W.; Nocera, D. G. In Situ Formation of an Water Containing Phosphate and Co^{2+} . *Science* **2008**, 321, 1072–1075.
- (6) Fominykh, K.; Chernev, P.; Zaharieva, I.; Sicklinger, J.; Stefanic, G.; Döblinger, M.; Müller, A.; Pokharel, A.; Böcklein, S.; Scheu, C.; et al. Iron-Doped Nickel Oxide Nanocrystals as Highly Efficient Electrocatalysts for Alkaline Water Splitting. *ACS Nano* **2015**, 9, 5180–5188.
- (7) Xia, W.; Mahmood, A.; Liang, Z.; Zou, R.; Guo, S. Earth-Abundant Nanomaterials for Oxygen Reduction. *Angew. Chemie. Int. Ed.* **2016**, 55, 2650–2676.
- (8) Wang, D.; Astruc, D. The Recent Development of Efficient Earth-Abundant Transition-Metal Nanocatalysts. *Chem. Soc. Rev.* **2017**, 46, 816–854.
- (9) Guo, S.; Zhang, S.; Sun, S. Tuning Nanoparticle Catalysis for the Oxygen Reduction Reaction. *Angew. Chemie. Int. Ed.* **2013**, 52, 8526–8544.

- (10) Deng, D.; Yu, L.; Chen, X.; Wang, G.; Jin, L.; Pan, X.; Deng, J.; Sun, G.; Bao, X. Iron Encapsulated within Pod-like Carbon Nanotubes for Oxygen Reduction Reaction. *Angew. Chemie. Int. Ed.* **2013**, *52*, 371–375.
- (11) Li, Y.; Wang, H.; Xie, L.; Liang, Y.; Hong, G.; Dai, H. MoS₂ Nanoparticles Grown on Graphene: An Advanced Catalyst for the Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2011**, *133*, 7296–7299.
- (12) Marco, A. B.; Cortizo-Lacalle, D.; Perez-Miqueo, I.; Valenti, G.; Boni, A.; Plas, J.; Strutyński, K.; De Feyter, S.; Paolucci, F.; Montes, M.; et al. Twisted Aromatic Frameworks: Readily Exfoliable and Solution-Processable Two-Dimensional Conjugated Microporous Polymers. *Angew. Chemie. Int. Ed.* **2017**, *56*, 6946–6951.
- (13) Shao, M.; Peles, A.; Shoemaker, K. Electrocatalysis on Platinum Nanoparticles: Particle Size Effect on Oxygen Reduction Reaction Activity. *Nano Lett.* **2011**, *11*, 3714–3719.
- (14) Voiry, D.; Shin, H. S.; Loh, K. P.; Chhowalla, M. Low-Dimensional Catalysts for Hydrogen Evolution and CO₂ Reduction. *Nat. Rev. Chem.* **2018**, *2*, 0105.
- (15) Liang, Y.; Li, Y.; Wang, H.; Zhou, J.; Wang, J.; Regier, T.; Dai, H. Co₃O₄ Nanocrystals on Graphene as a Synergistic Catalyst for Oxygen Reduction Reaction. *Nat. Mater.* **2011**, *10*, 780–786.
- (16) Hof, F.; Kampioti, K.; Huang, K.; Jaillet, C.; Derré, A.; Poulin, P.; Yusof, H.; White, T.; Koziol, K.; Paukner, C.; et al. Conductive Inks of Graphitic Nanoparticles from a Sustainable Carbon Feedstock. *Carbon* **2017**, *111*, 142–149.

- (17) Gustavo Cançado, L.; Gomes da Silva, M.; Martins Ferreira, E. H.; Hof, F.; Kampioti, K.; Huang, K.; Pénicaud, A.; Alberto Achete, C.; Capaz, R. B.; Jorio, A. Disentangling Contributions of Point and Line Defects in the Raman Spectra of Graphene-Related Materials. *2D Mater.* **2017**, *4*, 025039.
- (18) Hof, F.; Boni, A.; Valenti, G.; Huang, K.; Paolucci, F.; Pénicaud, A. From Food Waste to Efficient Bifunctional Nonprecious Electrocatalyst. *Chem. Eur. J.* **2017**, *23*, 15283–15288.
- (19) Hof, F.; Pénicaud, A. Graphenide Solutions: A Chemical Platform for Nanoparticle-Nanocarbon Composites. *Chem. Eur. J.* **2018**, *24*, 16246–16250.
- (20) Thanh, N. T. K.; Maclean, N.; Mahiddine, S. Mechanisms of Nucleation and Growth of Nanoparticles in Solution. *Chem. Rev.* **2014**, *114*, 7610–7630.
- (21) Geim, A. K. Graphene : Status and Prospects. *Science* **2014**, *1530*, 1530–1534.
- (22) Valenti, G.; Zangheri, M.; Sansaloni, S. E.; Mirasoli, M.; Penicaud, A.; Roda, A.; Paolucci, F. Transparent Carbon Nanotube Network for Efficient Electrochemiluminescence Devices. *Chem. Eur. J.* **2015**, *21*, 12640–12645.
- (23) Tüysüz, H.; Salabaş, E. L.; Weidenthaler, C.; Schüth, F. Synthesis and Magnetic Investigation of Ordered Mesoporous Two-Line Ferrihydrite. *J. Am. Chem. Soc.* **2008**, *130*, 280–287.
- (24) Michel, F. M.; Ehm, L.; Antao, S. M.; Lee, P. L.; Chupas, P. J.; Liu, G.; Strongin, D. R.; Schoonen, M. A. A.; Phillips, B. L.; Parise, J. B. The Structure of Ferrihydrite, a Nanocrystalline Material. *Science* **2007**, *316*, 1726–1729.

- (25) Hof, F.; Bosch, S.; Englert, J. M.; Hauke, F.; Hirsch, A. Statistical Raman Spectroscopy: A Method for the Characterization of Covalently Functionalized Single-Walled Carbon Nanotubes. *Angew. Chemie. Int. Ed.* **2012**, *51*, 11727–11730.
- (26) Ferrari, A. C.; Basko, D. M. Raman Spectroscopy as a Versatile Tool for Studying the Properties of Graphene. *Nat. Nanotechnol.* **2013**, *8*, 235–246.
- (27) Cançado, L. G.; Jorio, A.; Pimenta, M. A. Measuring the Absolute Raman Cross Section of Nanographites as a Function of Laser Energy and Crystallite Size. *Phys. Rev. B* **2007**, *76*, 064304.
- (28) Li, G.; Anderson, L.; Chen, Y.; Pan, M.; Abel Chuang, P. Y. New Insights into Evaluating Catalyst Activity and Stability for Oxygen Evolution Reactions in Alkaline Media. *Sustain. Energy Fuels* **2018**, *2*, 237–251.