



Cutting-edge research for a greener sustainable future

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Liu, S. Chen, A. Yu, Y. Hu, B. Yu, H. Wang, P. Peng and F. Li, Green Chem., 2020, DOI: 10.1039/D0GC02040K.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/greenchem

## ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

# Confined pyrolysis of a dye pollutant for two-dimensional F,N,S tri-doped nanocarbon as a high performance oxidative coupling reaction catalyst<sup>†</sup>

Sijie Liu,<sup>a</sup> Sian Chen,<sup>b</sup> Ao Yu,<sup>a</sup> Yajing Hu,<sup>a</sup> Bingzhe Yu,<sup>a</sup> Haining Wang,<sup>b</sup> Ping Peng,<sup>\*a</sup> and Fang-Fang Li<sup>\*a</sup>

Nanocarbon materials as metal-free catalysts for the oxidative coupling of primary amines to imines suffer from high catalyst loading, low reaction rate and high oxygen demand. Doping heteroatom in nanocarbons is realized as an effective strategy to improve the catalytic activity, however, the doping of fluorine has been rarely studied. Here we synthesized a F,N,S tri-doped hierarchical nanocarbon (FNSHC) by pyrolyzing a fluorine-containing azo-sulphonate dye (acid red-337, a pollutant in wastewater) confined in layered double hydroxides (LDH). LDH-confined synthetic method is beneficial to the formation of a two-dimensional porous structure with large specific surface area (~1432 m<sup>2</sup> g<sup>-1</sup>) and high fluorine contents, enabling remarkable catalytic performance (98% yield in 4 h at 2 wt% catalyst loading under open-air conditions) and high recyclability, outcompeting current metal-free carbocatalysts. Conversion of environmental pollutants into heteroatom-doped carbon materials provides a new green strategy for the design and synthesis of functinal carbon catalysts.

#### 1. Introduction

Published on 25 September 2020. Downloaded by California Institute of Technology on 9/27/2020 10:42:04 AM.

Imines are critically important organic intermediates containing C=N bond for the production of various biomolecules and fine chemicals.<sup>1-3</sup> For imine synthesis, the oxidative coupling of amines offers a great alternative to the traditional condensation methods which usually require activated aldehydes, dehydrating agents and Lewis acid catalysts.<sup>4-6</sup> Most of the oxidative coupling reactions from amines to imines were catalysed by metal-based catalysts.<sup>7-11</sup> However, the cost issue, poor reusability and metal contamination in the final products have limited their practical applications. In recent years, metalfree carbon nanomaterials, such as the defect-rich graphene oxides,<sup>12,13</sup> B,N-codoped graphene monoliths,<sup>14,15</sup> mesoporous carbons with high surface area and sufficient pore volume,16-18 N-doped hierarchical carbons,<sup>19-23</sup> O-rich carbon quantum dot.<sup>24</sup> B,O-doped carbon,<sup>25</sup> N,O-doped carbon,<sup>26</sup> and P-doped graphene<sup>27</sup> have attracted considerable attention as costeffective and sustainable catalysts for the selective oxidation of amine.28 Studies have shown that heteroatom doping can greatly improve the activity of carbocatalysts, however, challenges still remain because of the high catalyst loading (28110 wt%),<sup>12,14,15,21,26</sup> long reaction time (12-24 h),<sup>13,20-22,25</sup> and high oxygen demand (1-5 atm  $O_2$ )<sup>12,14,16,18,26</sup> in the reaction.

As mentioned above, N-doped carbons have been used as effective catalysts for the oxidative coupling of amines.<sup>19-23,26</sup> On the other hand, S-doped carbons have exhibited excellent properties in various catalytic reactions.<sup>29-30</sup> Compared to the N and S heteroatoms, fluorine (F) possesses the largest electronegativity and has great potential to modify the surface properties of graphitic carbon frameworks. F-doping on carbon not only creates structural defects but also induces the adjacent carbon atoms to have substantial positive charges, which enable the materials with unique electronic configurations and more active sites. The F single-doped, F,N co-doped and F,N,P tridoped carbon materials have exhibited enhanced performance in electrocatalysis<sup>31-33</sup> and energy applications.<sup>35-37</sup> However, to the best of our knowledge, the application of F-doped carbocatalysts in liquid-phase organic reactions remains largely unexplored and far from well known. A critical bottleneck to the extensive studies of F-doped carbocatalysts lies in the synthetic methods. The synthesis of F-doped carbons usually requires highly toxic and corrosive F<sub>2</sub>, HF, or trifluorotoluene as F sources.<sup>32,37-39</sup> And high-temperature pyrolysis of the costly F-containing precursors results in the inevitable loss of F atoms and thus very low F content (0.13-1.14 at%) in the final carbon materials.<sup>31,33,36,37,40,41</sup> Therefore, the development of an eco-friendly synthetic strategy to achieve carbocatalyst with a high F dopant is highly desirable.

In the present work, we develop a facile, cost-effective and environmentally friendly approach to construct F,N,S tri-doped hierarchical carbon nanomaterials (FNSHC) through LDHconfined pyrolysis of an F-containing azo-sulphonate dye (acid

<sup>&</sup>lt;sup>a.</sup> State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China. E-mail: ppeng@hust.edu.cn; ffli@hust.edu.cn

<sup>&</sup>lt;sup>b.</sup> Beijing Key Laboratory of Bio-inspired Energy Materials and Devices, School of Space and Environment, Beihang University, Beijing 100191, China.

<sup>+</sup>Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

#### ARTICLE

Page 2 of 9

**Breen Chemistry Accepted Manusc** 

red-337, designated as AR-337), which is a dye pollutant in wastewater. AR-337 anions were effectively intercalated into the interlayer spaces and also attached on the surface of LDHs. The two-dimensional space and surface of LDH protect the F atoms from escaping during the high-temperature carbonization. The samples obtained by annealing at 600, 700, and 800 °C were named FNSHC-600, FNSHC-700, and FNSHC-800, respectively. Thanks to the LDH-confined synthetic method, the as-prepared FNSHC-700 displays a two-dimensional hierarchical porous structure with a large specific surface area of 1432 m<sup>2</sup>g<sup>-1</sup>, and high content of F dopant, which results in the superior catalytic performance for self-coupling of primary amines to imines. Density functional theory calculations demonstrate that the F-doping promotes the adsorption of benzylamine and creates more active sites.

#### 2. Results and discussion

#### 2.1. Synthesis of catalysts

The synthetic procedure of two-dimensional (2D) FNSHC samples is illustrated in Scheme 1. Mg-Al LDH (Fig. S1, ESI<sup>†</sup>) was synthesized by a urea co-precipitation method.<sup>42</sup> Its structure can be described as the stacking of the positively charged magnesium/aluminum double hydroxide layers neutralized by intercalated carbonate anions (Scheme 1). The interlayer carbonate anions were removed by calcination to form Mg-Al LDO (layered double oxide). Mg-Al LDO (Fig. S1) serves as an efficient adsorbent for AR-337 (see chemical structure in Fig. S2). During the adsorption process in aqueous solution, AR-337 anions were effectively inserted into the interlayers and also adhered to the surface of LDH (AR337-LDH) (Fig. S1). It is worth mentioning that Mg-Al LDO reverted to Mg-Al LDH by rehydration in an aqueous environment. Then AR337-LDH was carbonized at 600, 650 700, 750 and 800 °C, respectively under an argon atmosphere, during which AR-337 was under the two-dimensional space and surface confinement of LDH. After removal of the template by acid washing, 2D F,N,S tri-doped hierarchical porous carbon nanomaterials FNSHC-600/650/700/750/800 were obtained (Fig. S1).

For comparison, AR-337 was directly carbonized at 700 °C to obtain the sample of FNSC-700. N single-doped (NHC-700), S single-doped (SHC-700) and N,S dual-doped hierarchical carbon nanomaterial (NSHC-700) were synthesized via the

same method as described for FNSHC-700 by using  $h_{e}$  containing (methyl red sodium salt, Fig.): \$349,395 containing (sodium *p*-toluenesulfonate, Fig. S3b) and N,S-containing adsorbates (methyl orange, Fig. S3c), respectively.

#### 2.2. Characterizations of catalysts

Scanning electron microscopy (SEM) images of Mg-Al LDH, Mg-Al LDO, AR337-LDH and the target FNSHC samples are shown in Fig. 1 and Fig. S4. Mg-Al LDH exhibits plate-like hexagon with side length about 1.2 µm (Fig. S4a) and this hexagonal structure is maintained in Mg-Al LDO upon calcination (Fig. S4b). Powder X-ray diffraction (PXRD) pattern of Mg-Al LDH displays the peaks that can be wellassigned to Mg<sub>4</sub>Al<sub>2</sub>(OH)<sub>12</sub>CO<sub>3</sub>·3H<sub>2</sub>O (Mg<sub>2</sub>Al-LDH) (PDF # 51-1525) (Fig. S5a). The intercalation of carbonate anions was verified by the basal space of  $d_{003} = 7.7$  Å.<sup>43,44</sup> PXRD of Mg-Al LDO shows only the diffraction peaks of MgO (PDF # 65-0476) (Fig. S5b) owing to the low crystallinity of Al<sub>2</sub>O<sub>3</sub> in LDO. After the adsorption of AR-337, AR337-LDH composite was formed (Fig. S4c). The PXRD pattern of the AR337-LDH corresponds to the hydrotalcite-like compounds, confirming the structural reconstruction (Fig. S6). The increase of the basal space from 7.7 Å (carbonate-containing LDH) to 8.2 Å was ascribed to the intercalation of AR-337 anions running parallel to the double hydroxide layers.<sup>45</sup> The diffraction peak at 43 degrees was possibly due to the attachment of AR-337 on the surface of LDH. After the carbonization of AR337-LDH and removal of the template, the target products FNSHC-600/700/800 were obtained.

SEM examinations of FNSHCs reveal two-dimensional hierarchical structures with ultra-small and ultrathin (~10 nm) carbon nanosheets well distributing on the hexagonal carbon nanoplates (Fig. 1a, Fig. S4d-h and S7a,b). Moreover, the adjacent carbon nanosheets are interconnected and assembled to a porous network. The transmission electron microscope (TEM) image of FNSHC-700 further verifies the two-dimensional hierarchical architecture (Fig. 1b and Fig. S7c). The energy dispersive X-ray (EDX) elemental mapping of NSFHC-700 indicates that the C, F, N and S elements distribute homogeneously in the carbon matrix (Fig. 1c-f). In contrast, the FNSC-700 synthesized without an LDH template displays an irregular blocky morphology and no specific hierarchical or porous structure was observed (Fig. S8).



Scheme 1 Schematics depiction for the confined synthesis of 2D F,N,S tri-doped hierarchical carbons (FNSHC)

#### Journal Name

#### ARTICLE

**Green Chemistry Accepted Manuscri** 

#### View Article Online



Fig. 1 SEM/TEM characterizations of FNSHC-700. (a) SEM image. (b) TEM image. (c-f) EDX elemental mapping. Scale bar, 500 nm.

Powder X-ray diffraction (PXRD) and Raman spectra were measured to analyse the graphitic features and structural defects of the FNSHC samples. As shown in Fig. S9, the broad peaks around 25.0 and 43.0 degrees correspond to the (002) and (100) characteristic reflections of the hexagonal graphite. The peak intensities increase with the carbonization temperatures. Raman spectra of the samples (Fig. 2a) display the G band at ~1586 cm<sup>-1</sup> originated from the band stretching of graphitic carbon and the D band at ~1345 cm<sup>-1</sup> associated with the defect carbon. As an index of the graphitic degree of the samples,  $I_{\rm G}/I_{\rm D}$  of FNSC-700, FNSHC-600, FNSHC-700 and FNSHC-800 are 1.07, 1.12, 1.15 and 1.17, respectively, which are consistent with the PXRD results. The higher graphitic degree of FNSHC-700 than FNSC-700 is due to the benefit of the LDH-confined synthetic method. Nitrogen adsorption/desorption experiments were carried out to calculate the specific surface area (SSA) and pore size distribution of the samples. All the isotherms exhibited a typical type IV, indicating the presence of mesopores (Fig. S10-13). The dominant pore sizes distribution of FNSHC-600, FNSHC-700 and FNSHC-800 are calculated to be about 3.7, 3.7 and 2.8 nm, respectively. The Brunauer-Emmett-Teller (BET) SSA of FNSC-700, FNSHC-600, FNSHC-700 and FNSHC-800 are determined to be 367, 943, 1432 and 1070 m<sup>2</sup> g<sup>-1</sup>, respectively (Fig. 2b). LDH confinement strategy facilitates the formation of large-area hierarchical nanocarbon architectures.

X-ray photoelectron spectroscopy (XPS) measurements were performed to probe the compositions and chemical states of the elements in the samples. The corresponding atomic ratio of C, F, N and S are shown in Fig. 2c and Table S1. Ascribing to the LDH-confined synthesis, FNSHC-700 possesses a much higher content of F (2.43 at%) than FNSC-700 (0.12 at%). As shown in Fig. 2d, the high-resolution spectra of N 1s for all the samples can be fitted into three peaks of pyridinic N (398.3 eV), pyrrolic N (400.1 eV) and graphitic N (401.0 eV).46-48 It is noteworthy that FNSHC-700 has the highest atomic ratio of graphitic N, which can significantly improve the activity of carbocatalyst for liquid-phase organic reactions.<sup>49-51</sup> The highresolution spectra of S 2p (Fig. 2e) in FNSHC-700 can be

deconvoluted to two peaks at 163.99: 10atrate,9/DP65.92040 corresponding to the S2p<sub>3/2</sub> and S2p<sub>1/2</sub> of thiophene,<sup>52-54</sup> which can endow the carbon nanomaterials with enhanced catalytic activity for organic transformations.29,30,55 Interestingly, the chemical states of the F element are different in each sample. As displayed in Fig. 2f, the high-resolution spectrum of F 1s for FNSC-700 was deconvoluted to a single peak of the covalent CF<sub>2</sub> group (688.9 eV) located at the defects and edges of the carbon nanosheets.<sup>40,41</sup> The spectrum of F 1s in FNSHC-600 can be divided into two peaks assigning to covalent C-F (687.4 eV) and semi-ionic C-F (683.8 eV).34,40,41 While the spectrum of F 1s for FNSHC-700 was deconvoluted to only a single peak corresponding to the CF<sub>2</sub> group. For FNSHC-800, F 1s was divided into two peaks of the CF<sub>2</sub> group (688.9 eV) and the CF<sub>3</sub> group (691.3 eV), respectively.<sup>40,41,56</sup> The high-resolution spectra of C 1s for all the samples in Fig. S14 further confirm the various chemical states of F. The different chemical states of F element in the samples possibly lead to the different catalytic properties. For example, the semi-ionic C-F bond is more active than covalent C-F bond in the electrocatalysis of oxygen reduction reactions.<sup>31</sup> And the introduction of CF<sub>2</sub> groups into the graphene framework is more beneficial for the cycling stabilities and rate capabilities of graphene-based anodes than CF groups in lithium-ion batteries.39

#### 2.3. Catalytic properties of catalysts

The catalytic properties of the synthesized FNSHC samples for the oxidation of primary amines to imines were investigated (Reaction conditions: amines (0.5 g), catalyst (2 wt% loading



Fig. 2 Raman, SSA and XPS results of FNSC-700 and FNSHC-600/700/800. (a) Raman spectra. (b) SSA. (c) Heteroatoms percentage. (d-f) High-resolution XPS spectra of N 1s, S 2p and F 1s.

Published on 25 September 2020. Downloaded by California Institute of Technology on 9/27/2020 10:42:04 AM

based on substrate, 10 mg), CH<sub>3</sub>CN (1 mL), 85 °C, open air, 4 h). Control experiments without catalyst and with graphite as a catalyst produce less than 2% imine yield (Fig. 3a and Table 1, entries 1 and 2). In comparison, when the reaction was performed in the presence of FNSHC-700 (in open air or pure  $O_2$ ), the yield can approach to 98% (Fig. 3a and Table 1, entries 9 and 15). The catalytic activity of FNSHC-700 was superior to that of NHC-700, SHC-700 and NSHC-700 (Table 1, entries 3-5) indicating the significance of F doping. Moreover, FNSHC-700 demonstrates better performance than FNSHC-600, FNSHC-650, FNSHC-750 and FNSHC-800, which is attributed to its large SSA, high content of CF<sub>2</sub> and graphitic N (Fig. 3b, and Table 1, entries 7-11). While in the presence of bulky FNSC-700 with small SSA (Fig. 2b) and low content of F (Fig. 2c), the yield of imine is merely 53% (Table 1, entry 6).

The effectiveness and stability of FNSHC-700 were evaluated *via* a large-scale reaction (50 mmol) under solvent-free conditions. The catalyst can be easily recovered by filtration and reused at least 10 times without loss of activity (Fig. 3c).<sup>13,16,27</sup> To understand the good stability of FNSHC-700, XPS analysis of the catalyst after 10 cycling tests (FNSHC-700-R) was conducted and it was found that the compositions and chemical states of the elements remain no change (see Table S1 and Fig. S15). Additionally, acetonitrile (CH<sub>3</sub>CN) seems to be a better solvent than *n*-propanol in the catalytic reaction system. Even under the neat (solvent-free) or trace



**Fig. 3** Catalytic performance of FNSHC-700 for oxidative self-coupling of benzylamine to imines. (a) Control experiments without and with selected catalysts. Reaction conditions: benzylamine (0.5 g), catalyst (2 wt% loading, 10 mg), CH<sub>3</sub>CN (1 mL), 85 °C, open air, 4 h. (b) The content of CF<sub>2</sub>, graphitic N, thiophenic S and reaction yield over FNSC-700 and FNSHC-600/700/800. (c) Large-scale recyclability test. Reaction conditions: benzylamine (50 mmol), FNSHC-700 (5 wt% loading), solvent-free, 85 °C, open air, 16 h. (d) The effects of solvents on the product yield. (e) Comparison of catalytic activities between FNSHC-700 and other carbocatalysts. (f) Comparison of catalytic activities between FNSHC-700 and metal-based catalysts.

Table 1 Oxidative self-coupling of various amines over FNSH	HC-700 catalyst <sup>a</sup>
---	------------------------------

		DOI 10 1039/D0GC02040K
Entry	Catalyst	Yield (%)
1	None	< 2
2	Graphite	< 2
3	NHC-700	63
4	SHC-700	55
5	NSHC-700	74
6	FNSC-700	53
7	FNSHC-600	67
8	FNSHC-650	83
9	FNSHC-700	98
10	FNSHC-750	91
11	FNSHC-800	81
12 <sup>b</sup>	FNSHC-700	75
13 <sup>c</sup>	FNSHC-700	86
14 <sup>d</sup>	FNSHC-700	97
15 <sup>e</sup>	FNSHC-700	98
16 <sup>f</sup>	FNSHC-700	< 2
17 <sup>g</sup>	FNSHC-700	79

<sup>a</sup>Reaction conditions: benzylamine (0.5 g), catalyst (2 wt% catalyst loading, 10 mg), CH<sub>3</sub>CN (1 mL), 85 °C, open air, 4 h. <sup>b</sup>Solvent-free. <sup>c</sup>Solvent-free with 1 mmol H<sub>2</sub>O. <sup>d</sup>benzylamine (50 mmol), FNSHC-700 (5 wt% loading), solvent-free, 16 h. <sup>e</sup>O<sub>2</sub> atmosphere. <sup>f</sup>N<sub>2</sub> atmosphere. <sup>g</sup>The quenching reaction, 5 mmol benzoquinone was added.

water condition, the catalytic activity of FNSHC-700 was retained (Fig. 3d). The catalytic activity of FNSHC-700 was further evaluated by turnover frequency (TOF), which is defined as moles of the benzylamine converted into imine by per mole of catalyst per hour (TOF =  $n_1/(n_2*t)$ ,  $n_1$  represents the amount of benzylamine converted into imine,  $n_2$  represents the amount of catalyst, t represents the reaction time), $^{9,10}$  and a high TOF value of 1.38 h<sup>-1</sup> was achieved, which is one to two orders of magnitude larger than those of previously reported carbocatalysts (Fig. 3e and Table S2).12-27 Moreover, the catalytic performance of the metal-free FNSHC-700 is superior or comparable to that of some metal-based catalysts (Fig. 3f and Table S3).7-11 The remarkable catalytic performance of FNSHC-700 can be attributed to the synergistic effects of the followings: (1) the two-dimensional hierarchical architecture with interconnected porous network enabled the fast mass and electron transfer;<sup>16,57</sup> (2) the high specific surface area afforded more exposed active sites;<sup>14,26</sup> (3) the doping of heteroatoms, especially F, modified the electronic structures of the carbon framework and created abundant active sites, thus enhanced the chemical reactivity toward adsorbates.25,34

Benzylamine oxidation in the presence of benzoquinone was performed to explore if the radical intermediates are involved during the oxidation reaction.<sup>27</sup> It was found that benzoquinone failed to block the reaction, suggesting a nonradical reaction pathway (Table 1, entry 17). Thus, two possible reaction pathways were proposed (Fig. 4) based on previous studies.<sup>12,14,16</sup> In path I, amine (RCH<sub>2</sub>-NH<sub>2</sub>) and O<sub>2</sub> from the air were activated by active sites of FNSHC-700 to form RCH=NH intermediate, which then reacts with another amine (RCH<sub>2</sub>-NH<sub>2</sub>) to form product imine after losing NH<sub>3</sub>. In path II, the FNSHC-700 was accessed by both O<sub>2</sub> (from the air) and amine to form H<sub>2</sub>O and RCH=NH intermediates.

Published on 25 September 2020. Downloaded by California Institute of Technology on 9/27/2020 10:42:04 AM.



Fig. 4 Possible reaction paths for oxidative self-coupling of primary amines catalyzed by FNSHC-700.

Subsequently, the RCH=NH and  $H_2O$  (trace amounts from the solvent) lose NH<sub>3</sub> to form aldehyde (RCH=O), which is supported by the fact that the introduction of 1 mmol H<sub>2</sub>O into the neat reaction can significantly increase the yield of imine (Table 1, entries 12 and 13), indicating that the oxidation reaction on FNSHC is mainly proceeded via path II.<sup>12</sup> Finally, the obtained RCH=O reacts with RCH<sub>2</sub>-NH<sub>2</sub> to give the product of imine by releasing water.

The catalytic universality of FNSHC-700 toward various primary amines was investigated by large-scale reactions (Table 2). In general, benzylamines substituted with electrondonating groups (methyl-, methoxy-) or electron-withdrawing groups (F-, Cl-, -COOR) are suitable substrates for the catalytic reaction and are converted into the corresponding imines in high yields (Table 2, entries 2-9). Moreover, ortho-, meta- and para-methylbenzylamines produce comparable yields of the corresponding imines, revealing the less effect of steric hindrance of the aryl ring on the efficiency of the self-coupling process (Table 2, entries 2-4). FNSHC-700 is also effective in the oxidation of the bicyclic 1-naphthalenemethylamine to the corresponding imine with a 91% yield (Table 2, entry 10). It is noteworthy that the heterocyclic amines, such as 2thiophenemethylamine and 2-picolylamine which poison the metal catalysts due to the coordination with metal active sites, were successfully transformed to the desired imines by FNSHC-700 in good yields (Table 2, entries 11-12). Besides, catalytic oxidation of the aliphatic amines was attempted. However, the yield of the products was only <10 % (Table 2, entries 14 and 15), which is attributed to the inactive  $\alpha$ hydrogen of the amine.<sup>13,16,17,27</sup> Under the same reaction conditions, the oxidation reaction of aniline, which lacks a hydrogen atom at the  $\alpha$ -carbon position, did not occur (Table 2, entry 16). In addition, the oxidation cross-coupling of two different benzylic amines over FNSHC-700 catalyst was investigated. Due to the dominated self-coupling reactions of benzylamine and 4-fluorobenzylamine, the low selectivity of

#### 2.4 DFT calculations

Density functional theory (DFT) calculations were employed to understand the high catalytic activity of FNSHC-700. Based on XPS results, FNSHC-700 is doped predominantly with graphitic N, thiophenic S and CF2 groups. Thus, the model of FNSHC-700 was simplified as graphitic C, graphitic N, thiophenic S and CF<sub>2</sub> groups (Fig. 5d, FNSC). For comparison, calculations on S-doped (SC), N-doped (NC) and N,S dualdoped (NSC) graphene models were carried out as well (Fig. 5a-c). According to the calculations, the carbon atoms bonded to the heteroatoms possess higher charge densities (Fig. 5), in particular the carbon (charge density: 0.891) bonded with two F atoms (Fig. 5d). These positively charged carbon atoms serve as active sites and exhibit better adsorption toward benzylamine. The adsorption energy  $(E_{ad})$  of benzylamine on various graphene models was chosen as a criterion to evaluate the catalytic activity.<sup>25,27</sup> Parallel adsorption of benzylamine on the graphene models shows AB stacking structures (Fig. 4e). The negative  $E_{ad}$  on various substrates suggests the stable adsorption



**Fig. 5** DFT calculations for the synergetic effect of F, N and S tri-doping on the catalytic activities. (a-d) DFT models and Bader effective charges. (e)  $E_{ad}$  of benzylamine on various graphene models. Black atoms: C, blue atom: N, green atom: S, red atom: F, pink atoms: carbon that calculated as active sites.

ARTICLE

**Green Chemistry Accepted Manuscript** 

#### Journal Name

View Article Online DOI: 10.1039/D0GC02040K

Entry	Reagent	Product	Time (h)	Yield (%)
1	NH <sub>2</sub>		4	98
2	NH <sub>2</sub>	N N	6	96
3	NH <sub>2</sub>	N	5	98
4	NH <sub>2</sub>	N	6	94
5	NH <sub>2</sub>		12	92
6	F NH2	F N F	4	98
7	CI NH2		4	97
8			6	98
9	O NH2		5	78
10	H <sub>2</sub> N		18	91
11	NH <sub>2</sub>	S N S	16	92
12	NH <sub>2</sub>	O N O	24	79
13	N NH2		24	68
14	NH <sub>2</sub>		24	<10
15	NH2 NH2	∧ ∧ N ∧ ∧ ∧ ∧ ∧ ∧ ∧ ∧ ∧ ∧ ∧ ∧ ∧ ∧ ∧ ∧ ∧	24	<10
16			24	No reaction

<sup>a</sup>Reaction conditions: amines (0.5 g), FNSHC-700 (2 wt% catalyst loading, 10 mg), CH<sub>3</sub>CN (1 mL), 85 °C, open air.

Table 2 Oxidative self-coupling of various amines over FNSHC-700 catalyst<sup>a</sup>

of benzylamine molecules on carbocatalysts. When F atoms were presented, FNSC demonstrates the strongest adsorption towards benzylamine with the lowest adsorption energy of - 0.512 eV. F doping is crucial to the catalytic aerobic oxidative coupling of benzylamine, which is in good agreement with the experimental results.

#### 3. Experimental

#### 3.1. Preparation of catalysts

#### 3.1.1. Synthesis of Mg-Al LDH and Mg-Al LDO

Mg-Al LDH was prepared via a urea co-precipitation method. 6.41 g Mg(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$ , 4.69 g Al(NO<sub>3</sub>)<sub>2</sub>· $9H_2O$  (Mg/Al molar ratio is 2) and 45.05 g urea were dissolved in 250 mL deionized water. Under reflux condensation, the solution was maintained at 100 °C for 12 h with magnetic stirring. Then the temperature was decreased to 92 °C and the solution was maintained for another 12 h without stirring. After vacuum filtration, the filter cake was washed with deionized water and freeze-dried to obtain Mg-Al LDH. Subsequently, Mg-Al LDO was achieved by calcination of the as-prepared Mg-Al LDH at 500 °C for 3 h under air atmosphere.

#### 3.1.2. Adsorption of AR-337

AR-337 (0.3 g) was dissolved in 150 mL deionized water. After purging with  $N_2$  for 30 min to drive carbon dioxide out, 0.6 g Mg-Al LDO was added into the solution. Magnetic stirring and  $N_2$  protection were maintained during the 48 h adsorption process. Afterward, the solution was vacuum filtrated and the filter cake was washed with deionized water, then the obtained solid AR337-LDH was freeze-dried and ground to a fine powder.

#### 3.1.3.Carbonization of AR337-LDH

The carbonization of AR337-LDH was performed in a tube furnace at 700 °C for 2 h under an N2 atmosphere. To completely remove the Mg-Al LDO phase, the pyrolysis product was washed 3 times with HCl solution (6 M) at 70 °C for 24 h. Then, it was further washed several times with deionized water and then freeze-dried. Thus, the target product FNSHC-700 was obtained. For comparison, 337-LDH was carbonized at 600 °C, 650 °C, 750 °C and 800 °C, respectively and then underwent the same metal etching process to obtain the reference samples FNSHC-600 and FNSHC-800. Besides, AR-337 was directly carbonized and then washed to get FNSC-700. N single-doped hierarchical carbon nanomaterial (NHC-700), S single-doped hierarchical carbon nanomaterial (SHC-700), and N,S dual-doped hierarchical carbon nanomaterial (NSHC-700) were also synthesized via the same method as described for FNSHC-700, by using N-containing, S-containing and N,S-containing organics (methyl red sodium salt, sodium ptoluenesulfonate and methyl orange) respectively.

#### 3.2. Characterization of catalysts

The morphology of the samples was characterized by a field emission scanning electron microscopy (FESEM, FEI Nova NanoSEM 450) and a high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G20) combined with energy dispersive X-ray (EDX) spectroscopy. Powder X-ray diffraction (PXRD) patterns were collected with a step of 0.02 on a Bruker D8 Advance diffractometer with Cu Ka radiation  $(\lambda = 1.54056 \text{ Å})$  and a Lynxeye one-dimensional detector. Raman spectra were recorded on a LabRAM HR800 Raman spectrometer using a 532 nm laser at room temperature. The N<sub>2</sub> adsorption/desorption isotherm was conducted at 77 K using an automated adsorption apparatus (Quantachrome NOVA 4200E). Brunauer-Emmett-Teller (BET) equation was utilized to evaluate the specific surface area (SSA) and density functional theory (DFT) was employed to calculate the pore size distribution. X-ray photoelectron spectroscopy (XPS) measurements were performed on an AXIS-ULTRA DLD-600W spectrometer.

#### 3.3. Oxidative Coupling of Amines

In a typical catalytic reaction, FNSHC-700 (10 mg, 2 wt%) was introduced into a 5 mL two-necked, round-bottom flask equipped with a magnetic stirrer. Then, amines (0.5 g) and 1 mL acetonitrile were added. The mixture was stirred at 85 °C for 4 h under an open-air atmosphere. The thin-layer chromatography (TLC) was used to monitor the reaction process. After the reaction is completed, the mixture was cooled to room temperature. Then, 10 mL methyltetrahydrofuran was added into the reactor to extract the product. The crude product was separated from the catalyst by filtration. The residue concentrated by the organic phase was purified by a column chromatography (petroleum ether/ethyl acetate mixture as eluent with a volume ratio of 20:1) to give the isolated product yield. For those cases in which the benzylic amines were almost quantitative converted into the corresponding imines, the use of column chromatography could be avoided. For the recyclability test, the reactions were conducted under the same conditions as described above, except for using the recovered catalyst. After the reaction, the catalyst was filtered, washed with acetonitrile and ethyl acetate and then separated by centrifuge (3000 rpm, 8 min). Finally, it was dried at 60 °C for use in the next run.

#### 3.4. DFT Calculations

The density functional theory (DFT) calculations are performed with the Vienna Ab Initio Simulation Package (VASP).<sup>58-60</sup> The projector-augmented wave (PAW) formalism implementing the generalized gradient approximation as parameterized by Perdew *et al.* (PBE) was used. The positions of N, S or F atoms in S-doped, N-doped, N,S dual-doped or F, N, S tri-doped graphene were determined from the XPS results. The adsorption energy ( $E_{ad}$ ) of the benzylamine molecule on various graphene is obtained as  $E_{ad} = E_{benzylamine-graphene} - E_{graphene} - E_{benzylamine}$ , where  $E_{benzylamine-graphene}$ , Egraphene, and  $E_{benzylamine}$  are

Vanu

D

the energies of benzylamine-graphene system, graphene and the isolated benzylamine molecule respectively. The adsorption energies were corrected using D3 correction method.

#### Conclusions

ARTICLE

In summary, F-doped hierarchical carbon nanomaterials were synthesized by a facile, cost-effective and green synthetic strategy, in which an F-containing dye pollutant was adsorbed by LDH and converted to a high-value carbocatalyst. The twodimensional space and surface confinements of LDH not only create an ultrahigh surface area but also guarantee the high content of F in the samples. For oxidative self-coupling of primary amines to imines, the low catalyst loading, high reaction rate and high activity in the ambient atmosphere were achieved by the as-prepared FNSHC-700. Furthermore, FNSHC-700 shows excellent performance in mass production and recyclability. The origins of the catalytic activity of FNSHC-700 were identified. DFT calculations revealed that CF2-doped FNSHC-700 possesses the optimal active sites and showed the strongest adsorption of benzylamine. This work highlights a promising approach to design and synthesize heteroatomsdoped carbon catalysts for a variety of reactions and energy applications.

#### **Conflicts of interest**

There are no conflicts to declare.

### Acknowledgements

The financial supports from National Natural Science Foundation of China (Grant No. 21672076, 21971077) are gratefully acknowledged. The authors thank the facility support of the Analytical and Testing Center at Huazhong University of Science and Technology for all related measurements.

#### References

- 1 M. Tamura and K. Tomishige, Angew. Chem. Int. Ed., 2015, 54.864.
- S. Chakraborty, G. Leitus and D. Milstein, Angew. Chem. Int. 2 Ed., 2017, 56, 2074.
- H. Zhang, C. Wu, W. Wang, J. Bu, F. Zhou, B. Zhang and Q. 3 Zhang, Appl. Catal. B: Environ., 2018, 227, 209.
- 4 S. Furukawa, A. Suga and T. Komatsu, ACS Catal., 2015, 5, 1214.
- 5 V. R. Battula, H. Singh, S. Kumar, I. Bala, S. K. Pal and K. Kailasam, ACS Catal., 2018, 8, 6751.
- 6 Y. Xiao, G. Tian, W. Li, Y. Xie, B. Jiang, C. Tian, D. Zhao and H. Fu, J. Am. Chem. Soc., 2019, 141, 2508.
- 7 B. Zhu, M. Lazar, B. G. Trewyn and R. J. Angelici, J. Catal., 2008, 260, 1.
- 8 X. Qiu, C. Len, R. Luque and Y. Li, ChemSusChem, 2014, 7, 1684.
- S. Biswas, B. Dutta, K. Mullick, C.-H. Kuo, A. S. Poyraz and S. 9 L. Suib, ACS Catal., 2015, 5, 4394.

- 10 D. Dissanayake, L. A. Achola, P. Kerns, D. Rathnayake, J. He, J. Macharia and S. L. Suib, Appl. Catal. B: Environ, 2019, 249, 32.
- 11 X. Jia, J. Ma, F. Xia, M. Gao, J. Gao and J. Xu, Nat. Commun., 2019. 10. 2338.
- 12 H. Huang, J. Huang, Y.-M. Liu, H.-Y. He, Y. Cao and K.-N. Fan, Green Chem., 2012, 14, 930.
- 13 C. Su, M. Acik, K. Takai, J. Lu, S.-J. Hao, Y. Zheng, P. Wu, Q. Bao, T. Enoki, Y. J. Chabal and K. P. Loh, Nat. Commun., 2012, **3**, 1298.
- 14 X.-H. Li and M. Antonietti, Angew. Chem. Int. Ed., 2013, 52, 4572.
- 15 H. Wang, X. Zheng, H. Chen, K. Yan, Z. Zhu and S. Yang, Chem. Commun., 2014, 50, 7517.
- 16 B. Chen, L. Wang, W. Dai, S. Shang, Y. Lv, and S. Gao, ACS Catal., 2015, 5, 2788.
- 17 B. Chen, S. Shang, L. Wang, Y. Zhang, and S. Gao, Chem. *Commun.*, 2016, **52**, 481.
- 18 X. Wang and Y. Li, J. Mater. Chem. A, 2016, 4, 5247.
- 19 I.-M. Chung and M. Gopiraman, React. Kinet., Mech. Catal., 2017, 122, 205.
- 20 D. Wang and E. Mejía, ChemistrySelect, 2017, 2, 3381.
- 21 L.-B. Lv, S.-Z. Yang, W.-J. Feng, W.-Y. Ke, B. Zhang, Z.-D. Jiang, H.-H. Wang, J. Su, X.-H. Li and J.-S. Chen, ChemCatChem, 2018. 10. 5331.
- 22 P. Yang, J. Zhang, D. Liu, M. Liu, H. Zhang, P. Zhao and C. Zhang, Microporous Mesoporous Mater., 2018, 266, 198.
- 23 K. Wang, P. Jiang, M. Yang, P. Ma, J. Qin, X. Huang, L. Ma and R. Li, Green Chem., 2019, 21, 2448.
- 24 J. Ye, K. Ni, J. Liu, G. Chen, M. Ikram and Y. Zhu, ChemCatChem, 2018, 10, 259.
- 25 Y. Zhai, M. Chu, C. Xie, F. Huang, C. Zhang, Y. Zhang, H. Liu, H. Wang and Y. Gao, ACS Sustainable Chem. Eng., 2018, 6, 17410.
- 26 Y. Li, S. Shang, L. Wang, Y. Lv, J. Niu and S. Gao, Chem. Commun., 2019, 55, 12251.
- F. Yang, X. Fan, C. Wang, W. Yang, L. Hou, X. Xu, A. Feng, S. Dong, K. Chen, Y. Wang and Y. Li, Carbon, 2017, 121, 443.
- 28 B. Chen, L. Wang and S. Gao, ACS Catal., 2015, 5, 5851. 29 F. Wang, S. Song, K. Li, J. Li, J. Pan, S. Yao, X. Ge, J. Feng, X. Wang and H. Zhang, Adv. Mater., 2016, 28, 10679.
- 30 S. Yang, L. Peng, P. Huang, X. Wang, Y. Sun, C. Cao and W. Song, Angew. Chem. Int. Ed., 2016, 55, 4016.
- 31 X. Sun, Y. Zhang, P. Song, J. Pan, L. Zhuang, W. Xu and W. Xing, ACS Catal., 2013, 3, 1726.
- 32 G. Panomsuwan, N. Saito and T. Ishizaki, J. Mater. Chem. A, 2015, 3, 9972.
- 33 J. Zhang and L. Dai, Angew. Chem. Int. Ed., 2016, 55, 13296.
- 34 F. Pan, B. Li, X. Xiang, G. Wang and Y. Li, ACS Catal., 2019, 9, 2124.
- 35 J. Zhou, J. Lian, L. Hou, J. Zhang, H. Gou, M. Xia, Y. Zhao, T. A. Strobel, L. Tao and F. Gao, Nat. Commun., 2015, 6, 8503.
- 36 J. Lu, C. Wang, H. Yu, S. Gong, G. Xia, P. Jiang, P. Xu, K. Yang and Q. Chen, Adv. Funct. Mater., 2019, 29, 1906126.
- 37 Y. Chen, Y. Li, F. Yao, C. Peng, C. Cao, Y. Feng and W. Feng, Sustain. Energy Fuels, 2019, 3, 2237.
- 38 M. Park, I.-Y. Jeon, J. Ryu, H. Jang, J.-B. Back and J. Cho, Nano Energy, 2016, 26, 233.
- 39 H. An, Y. Li, Y. Feng, Y. Cao, C. Cao, P. Long, S. Li and W. Feng, Chem. Commun., 2018, 54, 2727.
- 40 J. Xie, X. Zhao, M. Wu, Q. Li, Y. Wang and J. Yao, Angew. Chem. Int. Ed., 2018, 57, 9640.
- 41 Z. Ju, S. Zhang, Z. Xing, Q. Zhuang, Y. Qiang and Y. Qian, ACS Appl. Mater. Interfaces, 2016, 8, 20682.
- 42 M. Laipan, R. Zhu, Q. Chen, J. Zhu, Y. Xi, G. A. Ayoko and H. He, J. Hazard. Mater., 2015, 300, 572.
- 43 M. José dos Reis, F. Silvério, J. Tronto and J. B. Valim, J. Phys. Chem. Solids, 2004, 65, 487.

Published on 25 September 2020. Downloaded by California Institute of Technology on 9/27/2020 10:42:04 AM

View Article Online DOI: 10.1039/D0GC02040K

- Journal Name
- 44 N. D. Setti, N. Jouini and Z. Derriche, *J. Phys. Chem. Solids*, 2010, **71**, 556.
- 45 R. Extremera, I. Pavlovic, M.R. Pérez and C. Barriga, *Chem. Eng. J.*, 2012, **213**, 392.
- 46 X. Duan, H. Sun, Y. Wang, J. Kang and S. Wang, *ACS Catal.*, 2015, **5**, 553.
- 47 R. Lin, S. K. Kaiser, R. Hauert and J. Pérez-Ramírez, ACS Catal., 2018, 8, 1114.
- 48 J. Gao, Y. Wang, H. Wu, X. Liu, L. Wang, Q. Yu, A. Li, H. Wang, C. Song, Z. Gao, M. Peng, M. Zhang, N. Ma, J. Wang, W. Zhou, G. Wang, Z. Yin and D. Ma, *Angew. Chem. Int. Ed.*, 2019, **58**, 15089.
- 49 J. Long, X. Xie, J. Xu, Q. Gu, L. Chen and X. Wang, ACS Catal., 2012, 2, 622.
- 50 H. Watanabe, S. Asano, S.-i. Fujita, H. Yoshida and M. Arai, ACS Catal., 2015, **5**, 2886.
- 51 G. Wen, Q. Gu, Y. Liu, R. Schlögl, C. Wang, Z. Tian and D. S. Su, Angew. Chem. Int. Ed., 2018, 57, 16898.
- 52 S. Yang, L. Zhi, K. Tang, X. Feng, J. Maier and K. Müllen, Adv. Funct. Mater., 2012, 22, 3634.
- 53 Z. Ma, S. Dou, A. Shen, L. Tao, L. Dai and S. Wang, Angew. Chem. Int. Ed., 2015, 54, 1888.
- 54 G. Zhou, E. Paek, G. S. Hwang and A. Manthiram, *Nat. Commun.*, 2015, **6**, 7760.
- 55 X. Duan, K. O'Donnell, H. Sun, Y. Wang and S. Wang, Small, 2015, 11, 3036.
- 56 J.-H. Wang, J.-J. Chen and R. B. Timmons, *Chem. Mater.*, 1996, **8**, 2212.
- 57 Z. Wang, X. Yu, W. He, Y. V. Kaneti, D. Han, Q. Sun, Y.-B. He and B. Xiang, ACS Appl. Mater. Interfaces, 2016, 8, 33399.
- 58 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15.
- 59 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169.
- 60 L. Cui, H. Wang, S. Chen, J. Zhang, Y. Xiang and S. Lu, *Phys. Chem. Chem. Phys.*, 2018, **20**, 26675.