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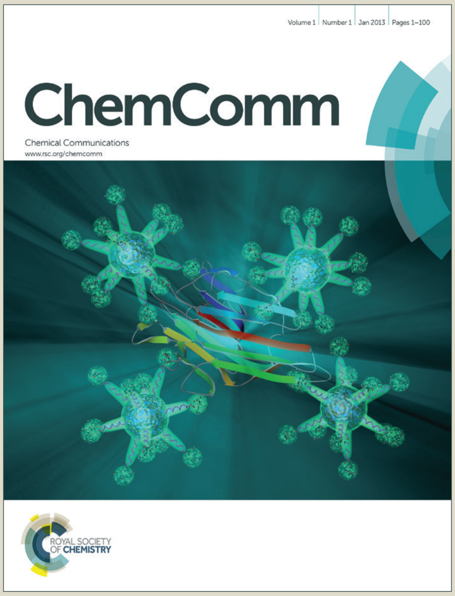

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Residual metal presents in “metal-free” N-doped carbons

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To date, “metal-free” catalysts originated from graphene and CNT were unraveled containing metal impurities. There were significant types of such “metal-free” carbons synthesized with metal-involved methods, and it was urgent to confirm the origin of the catalytic performance. Herein, we verified that the residual metals were inevitably present in those metal-involved synthetic N-doped carbons and the catalytic properties of hydrogen evolution reaction (HER) were dominated by the remaining metals though with a ppm level.

Metal-free carbon (MFC) materials, a rising star of carbon family, have attracted numerous attentions from both scientific and practical worlds.[1-3] Various types of MFCs have been fabricated based on doped carbon materials (DCM), widely spanning their applications in energy-related fields, especially in electrocatalysis of the reduction/evolution of oxygen and hydrogen.[1, 4-9] The characteristics of low cost and high efficiency of DCM have been demonstrated equally effective as their precious metal counterparts such as Pt, driving more sights into this specific area.[2] For instance, the N-doped graphene/carbon nanotube complex, reported by Dai group, showed superior activity towards oxygen reduction reaction (ORR) in both acid and base electrolytes, resembling the precious Pt catalyst.[10] Also the highly comparable performance of water splitting was found with the N-doped DCM electrode relative to a precious IrO_2 electrode.[4]

Considering the overwhelming utilization of metals in the synthetic carbon catalysts, in this study, we aimed at identifying the responsible sites of MFCs for electrochemical reactions whether they are related to the residual metals or not. The DCM fabrication was developed from our reported method.[11] Transition metal elements Fe, Co, and Ni were engaged to influence the carbonization/graphitization process of carbon materials, respectively. The resultant complexes were thoroughly washed with acid to hopefully remove all the introduced transition metals (the final Fe/Co/Ni involved products after purification were nominated to be PU-0.5Fe-DCM, PU-0.5Co-DCM and PU-0.5Ni-DCM, respectively). However, using inductively coupled plasma (ICP) technique, we managed to find some residual metals presenting in the final products no matter how harsh we treated them. Afterwards, the hydrogen evolution reaction (HER) was applied to probe the catalytic property difference of these metal-involved synthetic DCM and then remarkable variation were found with the different types of incorporated metals. Finally, comprehensive experiments were designed and carried out, indicating that the residual metals in these metal-involved synthetic DCM were the decisive for high HER activity.

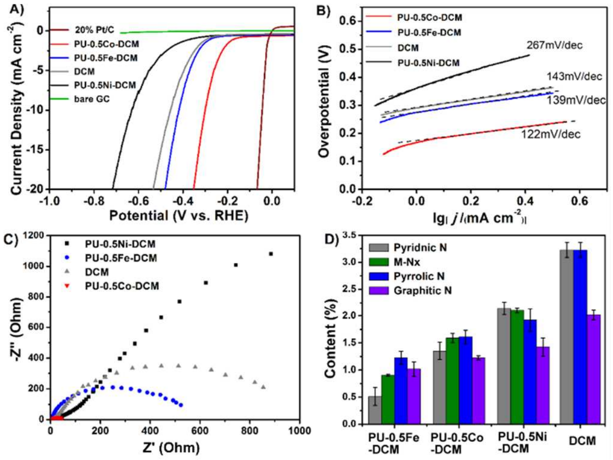

Fig. 1 (A) Polarization curves resulting from hydrogen evolution at glassy carbon modified with DCM (gray line), PU-0.5Fe-DCM (blue line), PU-0.5Co-DCM (red line), PU-0.5Ni-DCM (black line), Pt/C (20 wt%, brown line) and at bare glassy carbon (green line) at the scan rate of 5 mV s^{-1} in 0.5 mol L^{-1} H_2SO_4 electrolyte; (B) Tafel plots of DCM and purified Fe/Co/Ni involved DCM; (C) Nyquist plots of DCM and purified Fe/Co/Ni involved DCM at -0.3 V versus RHE; (D) Contents of various N species of DCM and purified Fe/Co/Ni involved DCM.

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The Fe/Co/Ni involved DCM with 0.5 mmol of each metal dosage before purification showed obvious metallic particles with 2 – 6 nm in diameter (Fig. S1A/D/G), and subsequently they were thoroughly treated with dilute sulfuric acid (1 mol L^{-1}) for 7 days using sonication and vigorous stirring to remove metals as much as possible. Effective removals of metals were paid in these graphitized carbon matrix, confirmed by the visual disappearance of metallic particles (Fig. S1, the HRTEM images of purified (B, C) Co, (E, F) Fe, and (H, I) Ni involved DCM). However, the ppm-level metals were still remaining: Co 0.31%, Fe 0.11%, and Ni 0.04%, collected using ICP instrument. These residual metallic species might be in the form of Metal-Nx coordination which is commonly accepted as a stable configuration in DCM,[12] and they also probably formed Metal-Cx coordination which was confirmed by the HRTEM images of the pristine metal-involved DCM before purification (Fig. S1A/D/G).[8, 10, 12-14] All the synthetic carbon materials displayed similar sheet-like morphology at micron scale (Fig. S2). The distinguishable electrochemical performances of Fe/Co/Ni involved DCM (PU-0.5Fe-DCM, PU-0.5Co-DCM, and PU-0.5Ni-DCM) were displayed in Fig.1A/B. Compared to the metal-free DCM, the PU-0.5Co-DCM showed significant enhancement of HER properties with an onset potential of ~90 mV and a Tafel slope of ~122 mV dec^{-1}. The PU-0.5Fe-DCM exhibited a very close onset potential (~160 mV) and Tafel slope (~139 mV dec^{-1}) to the metal-free DCM (~170 mV; ~143 mV dec^{-1}). While the PU-0.5Ni-DCM demonstrated the worst HER properties among four samples, with an onset potential of ~250 mV and a Tafel slope of ~267 mV dec^{-1}. Its sluggish activity was speculated to originate from the nature of Ni in acidic electrolytes.[15-16] The impedance variation in Fig. 1C also confirmed highly different electrochemical capabilities of purified Fe/Co/Ni involved DCM, in which the most active PU-0.5Co-DCM gave the lowest reaction impedance considering the smallest semicircle of Nyquist plot.

What are intrinsic active sites of these metal-involved carbon materials are still ambiguous in previous reports,[1, 7, 17-21] while we could list a few common factors which are closely correlated to HER performance, including N species state, overall N content, defect density, morphology, and residual metals of the catalysts. First, we performed Raman and XPS techniques to investigate the difference in N species state, overall N content and defect density between each DCM sample. The N 1s XPS spectra of the samples (Fig. S3C/D) could be deconvoluted into four different signals of pyridic N (~398.5 eV), Metal-N (~399.4 eV), pyrrolic N (~400.5 eV) and graphitic N (~401.4 eV), respectively, indicating the formation of Metal-Nx configurations.[22-24] The types and contents of N species are summarized and compared in Fig. 1D. The N contents variation of Fe/Co/Ni involved DCM revealed that the involvement of transition metals was capable of promoting the nitrogen elimination from carbon matrix during annealing process, and the overall N contents of three products were more likely determined by the nature of transition metals.[25-26] The PU-0.5Co-DCM with the highest HER activity only maintained an intermediate level of N content among them. Additionally, all the synthetic DCM showed similar defect densities considering the narrow window of varying I_D/I_G (the common indicator for defect density) from 1.04 to 1.08 as shown in Fig. S3B. In the TEM (Fig. S1) and SEM (Fig. S2) images, we found that all the synthetic DCM displayed mesoscopic sheet-like morphology, confirming parallel surface wettability between each other.[27] These above mentioned results clearly pointed out that the HER activity should depend on the remaining criterion: residual metal, and thus the ppm-level metals inevitably remaining in these metal-involved synthetic DCM should be decisive for high HER activity.

To further prove the influence of residual metals on the HER performance of the DCM, the electrochemical property comparison of a series of Co-involved DCM with varying dosages of Co source before and after acid purification was investigated. After the removal of overwhelming Co substance, the Co characteristic peaks were silent in the XRD patterns (Fig. S4A), but the HER performance of purified Co-involved DCM showed a little variation by comparison with that of the corresponding pristine sample before purification, as shown in Fig. 2A. The slightly decreased activity mainly resulted from Co leaching in washing process, which suggested Co to be active sites towards HER. It was also confirmed by the activity decrease of the PU-0.05Co-DCM with a reduced dosage of Co source. To understand the mechanism of HER process, the Tafel slopes of a series of Co-involved DCM with varying dosages of Co source from 0.05, 0.1, 0.2 to 0.5 mmol were calculated from these recorded linear sweep voltammograms (LSV, Fig. S5A) and plotted in Fig. S5B. The Tafel slopes were in a range of ~110 to ~130 mV dec^{-1}, indicating the same Volmer step to be the rate limiting step.[18]

The added Co dosage against the residual Co content and the overpotential at the given current densities (10, 15 and 20 mA cm^{-2}) were accordingly plotted in Fig. 2B. With the Co dosage increasing, the overpotential quickly faded reaching 0.31 V at a current density of 10 mA cm^{-2} for a Co dosage of 0.2 mmol and then performed a plateau for a further increasing Co dosage of 0.5 mmol. Co species

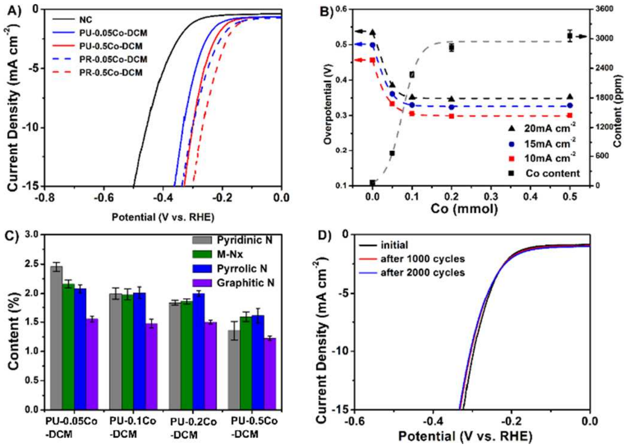

Fig. 2 (A) Polarization curves at glassy carbon modified with DCM, PU-0.05Co-DCM, PU-0.5Co-DCM, pristine Co0.05-DCM without purification (PR-0.05Co-DCM) and pristine Co0.5-DCM without purification (PR-0.5Co-DCM); (B) Overpotentials of purified Co-involved DCM with varying dosages of Co source to reach current densities of 10, 15 and 20 mA cm^{-2}, along with residual Co contents; (C) Contents of various N species of purified Co-involved DCM with varying dosages of Co source; (D) Polarization curves of PU-0.5Co-DCM after 1000 and 2000 potential sweeps between -0.7 V and +0.1 V (vs. RHE).

seemed to be saturated in the DCM with a Co dosage above 0.2 mmol, *i.e.*, the residual Co content was stabilized at a similar level of 3000 ppm, and the HER curves showed hardly variations (Fig. S5A). Subsequently, the high stability of the Co-involved DCM as HER catalysts was revealed by the high activity retention after 2000 cycles (Fig. 2D). We concluded the residual Co to be extremely stable and responsible HER active sites.[28-32] The deconvolution of the Co 2p XPS spectra (Fig. S6) suggested the presence of two chemically distinct species: metallic Co (~778.8 eV) and Co^{2+} in Co-X bond (~781.3 eV; X might be C or N),[33] and the amount of coordinated Co was much more than that of metallic Co. Meanwhile, these Co-involved DCM with varying dosages of Co source gave a very narrow window of I_D/I_G from 1.05 to 1.06 in the Raman spectra (Fig. S4B), suggesting similar defect density. As depicted in Fig. 2C, the N contents of overall and each N specie being extracted from XPS data (Fig. S4C/D) almost showed contrary tendency to the Co content and activity variation in Fig. 2B. The difference in N contents between PU-0.2Co-DCM and PU-0.5Co-DCM was observed, while their residual Co content and HER activity hardly varied. Thus, these involved transition metals in carbon matrix were considered to significantly influence electrocatalytic performances.[34-35] The remaining Co species could possibly be in the form of Co-Nx, as confirmed by the N 1s XPS data.[36-38] Beyond that, Co species could also be coordinated or encapsulated by graphitic C.[39] Thus, chemical stability of such layouts could be enhanced by the surrounding carbon matrix.[28, 34-35]

In conclusion, we gave emphasis on the intrinsic active sites of “metal free” N-doped carbon materials involving metals in their synthesis, *i.e.*, the ppm-level residual metals were responsible for the HER catalytic sites. Furthermore, these remaining metal sites were revealed to be extremely stable and could survive even using strong acid washing for one week. We also hoped to conclude from another perspective that those so-called “metal free” N-doped carbon materials were not truly free of metals once metals were introduced in synthetic procedures. These metal-N/Cx configurations were probably responding as the main electrochemical catalytic species, on one hand, reminding us to be more cautious and scientific to use the item of “metal free”, on the other, driving us to search more stable and active sites by the introduction of such atomic economic configurations.

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