1. Introduction

1D carbon nanostructures have attracted major attention since their first discovery in 1991.[1] Typically, 1D carbon nanostructures possess high electric conductivity, improved chemical & physical stability, and ultrahigh mass transfer efficiency. Therefore, in the past several decades, 1D carbon nanostructures have been exploited as robust materials in catalysis,[2] either as active materials or functional matrices to anchor various metal species.[3] To improve the application potential, introduction of heteroatoms into the 1D carbon nanostructure is essential as it allows to effectively engineer the electronic structure.[4] P and N are the popular choices but incorporating these heteroatoms into 1D carbon nanostructures normally needs multiple synthetic steps. It is important to develop simple and controllable method to synthesize heteroatom-doped 1D carbon nanostructures with superior abilities in cutting-edge applications.

Alkene hydrosilylation is the addition of Si–H to the unsaturated bonds, which is one of the most important chemical reactions to produce the organosilicon compounds. Platinum (Pt) homogeneous catalysts, namely the Speier Pt catalyst and Karstedt Pt catalyst,[5] have been the most popular choice in alkene hydrosilylation[6] and consume nearly 5.6 tons of platinum annually in silicone industry.[7] Unfortunately, the side reactions, including the alkene isomerization and dehydrogenation silylation, normally accompany with the main reaction, and expensive purification is needed.[8] Moreover, the additional side reactions occur due to the formation of colloidal Pt species,[9] and the recycling of Pt homogeneous catalyist is a well-known challenge. This not only increases the production cost but also introduces impurities to the final product.[10] In this context, single-atom catalysts, which contains atomic dispersion of active metallic species on a support, have been recently developed to overcome these challenges. It exhibits an unexpected catalytic performance, while it also owns great convenience in recovery. The synthesis of the atom support is the key step to obtain this interesting material.

More recently, based on P2O5 chemistry, we successfully synthesized metal-free C–O–P functionalized carbon-nanofiber assemblies.[11] This unique carbon nanostructure was proven to possess exceptional adsorption properties, a useful pre-requisition for catalysis. The outcome further inspired us to upgrade this in situ P2O5 chemistry to introduce novel functional groups to 1D carbon nanostructure. Unfortunately, the previously
2. Results and Discussion

2.1. Synthesis of Carbon Nanofibers

In a typical synthesis, the \( \text{P}_2\text{O}_5 \) powder was added into NMP solution, and the mixture was heat-treated in tube furnace in \( \text{N}_2 \) atmosphere following a set program (Figure 1a,b). After washing and drying, a black carbon powder with N and P doping was obtained. The products were named as \( \text{C}_{\text{NMP}-\text{x}} \), where \( x \) represents the carbonization temperature (°C). Scanning electron microscopy (SEM) was taken to see the morphology, and the temperature obviously affected the final morphology of the carbon nanofibers. As shown in Figure 1c–e, the majority of \( \text{C}_{\text{NMP}-500} \) and \( \text{C}_{\text{NMP}-600} \) are carbon nanofibers assemblies. As indicated from the cross-section image of \( \text{C}_{\text{NMP}-500} \) (Figure 1d) and \( \text{C}_{\text{NMP}-600} \) (Figure 1f), the fibers are assembled together in a relatively loose manner. The carbon nanofibers assemblies are in addition covered with a secondary structure – carbon nanosheets forming a sheath. For \( \text{C}_{\text{NMP}-700} \) (Figure 1g,h), the original carbon nanofibers seem to further fuse together to form much bigger fiber bundles standing on thick carbon sheets.

2.2. Possible Reaction Process

To understand the reaction process, the intermediates were synthesized by selecting different temperatures at 200, 300, and 400 °C. The intermediates are denoted as intermediate-\( x \), where \( x \) represents the reaction temperature (°C). As shown in Figure S1 (Supporting Information), the intermediate-200 is a hard, red solid, while the intermediate-300 becomes black, porous, and brittle. The intermediate-400 is very similar to the final carbon product. The intermediate-200 is completely soluble in water. With the increase of temperature, the solubility of the intermediate in water decreases. This is quite different from the intermediates prepared by \( \text{P}_2\text{O}_5 \)-plant oil reaction at 200 °C, which is nearly insoluble to any solvents. This interesting phenomenon possibly indicates that the oligomerization occurs at relatively low temperature, while the oligomer gradually polymerizes by increasing the reaction temperature.

The structure of the intermediate was investigated by FTIR and NMR techniques to elucidate the morphology evolution. Figure 2a provides the FTIR spectra of the intermediates, which includes the assignment of major functional groups. As seen, the HC=\( \text{C} \)-O and P=\( \text{O} \)-C (800–1000 cm\(^{-1}\)) are found in all intermediates, but the relative content of HC=\( \text{C} \)-O decreases with increasing temperature. Noticeably, it is found that there are C=\( \text{C} \)-C=C and C=N=P=O (overlapped between 1000–1300 cm\(^{-1}\)) in all intermediates,[12] which are absent in \( \text{P}_2\text{O}_5 \)-plant oil intermediates.[13] Moreover, the IR spectrum of intermediate-400 changes obviously after removing the soluble part. As shown in Figure 2a, the insoluble part of intermediate-400 contains relatively high content of P=\( \text{O} \)-C and relatively low content of HC=\( \text{C} \)-O. Moreover, for the insoluble part, the C=\( \text{O} \) disappears, and the two peaks are located in the range of 1000–1300 cm\(^{-1}\) red shift, which might correspond to the decreased content of HC=\( \text{C} \)-O. These data most possibly indicate that the HC=\( \text{C} \)-O and C=\( \text{O} \) mainly existed in the water-soluble fragment of the intermediates (or oligomers part of intermediates). Based on the structural fragments from FTIR analysis, the possible structure of the intermediate is provided in Figure 2c. As illustrated in Figure 2c, the oligomers, typically the trimers, were formed due to the cyclization of ketene, which is also in line with the previous research.[11] The decreased content of HC=\( \text{C} \)-O when increasing the reaction temperature is possibly due to the polymerization through double bond to form the cross-linked structure. This can also explain the declined solubility of intermediate-300 and -400 in water. Figure 2b shows the NMR spectra of intermediate-200. As seen in \(^1\text{H}-\text{NMR} \) spectrum, the HC=\( \text{O} \) (3.6 ppm), O=\( \text{C} \)=\( \text{CH} \) (4.3 ppm), and C=\( \text{CH} \)=\( \text{CH}_3 \) (3.5 ppm) could be found. Moreover, the \(^{13}\text{C}-\text{NMR} \) spectrum demonstrates the O=\( \text{C} \) (178 ppm), C=\( \text{O} \) (63 ppm), and O=\( \text{C} \)=\( \text{CH} \)=\( \text{CH}_3 \) (101 ppm) respectively in intermediate-200. In addition, the phosphoric acid (0 ppm), O=P\( \text{O} \) (11.5 ppm), and O=P=N=N=P=O (20 ppm, P[\( \text{II} \)] can be found in \(^{31}\text{P}-\text{NMR} \) spectrum. Totally speaking, the NMR analysis matches the FTIR analysis very well. Interestingly, based on the NMR analysis, a major part of the P(V) was chemically transformed into P(III), and the phosphoric acid is generated by the reaction between residual \( \text{P}_2\text{O}_5 \) in the intermediate and \( \text{D}_2\text{O} \). The elemental analysis of the final product indicates the formula of \( \text{H}_2\text{C}_4\text{N}_0\text{O}_3\text{P} \). As compared to the formula of NMP (\( \text{H}_5\text{C}_4\text{NO} \)), the elimination products can be accounted as \( \text{H}_2\text{C}_4\text{N}_0\text{O}_3\text{P} \) and \( \text{H}_2\text{C}_4\text{N}_0\text{O}_3\text{P} \). That means abundant reduction products are liberated throughout the reaction NMP, and that \( \text{P}_2\text{O}_5 \) can act under reaction conditions as an oxidation agent, while being itself reduced from P(V)-oxide to P(III)-nitride. The formation of the carbon nanofibers is possibly derived from the “ketene-like polymerization” of the intermediate, followed by carbonization. Additionally, the effect of the structure of diverse starting monomers on the carbon morphology was investigated, including different chain length and functional groups. Results indicated that both the chain length and functional groups heavily affect the morphology of the carbon materials (Figures S2 and S3, Supporting Information).
2.3. Characterizations of the Carbon Nanofibers

High-resolution transmission electron microscopy (HRTEM) was used to investigate the carbon nanofibers assemblies. As shown in Figure 3a,b, the carbon nanofibers (C_{NP-500} and C_{NP-600}) assembled with relatively loose contact. However, when the carbonization temperature increased to 700 °C, the carbon nanofibers completely fused into much bigger sub-microfibers (Figure S4, Supporting Information). This is in consistence with the above SEM results that increasing the temperature would be conducive to triggering the fusion of carbon nanofibers. Based on the elemental mapping (Figure 3c,d; Figure S4, Supporting Information), the C, N, P, and O could be clearly seen on the carbon materials, which demonstrates the N and P co-doping on the carbon nanofibers. Typically, the N and P account for ≈4 and ≈6 at% of the total element, respectively.

Furthermore, X-ray photoelectron spectroscopy (XPS) was used to see the heteroatoms doping in carbon nanofibers by taking C_{NP-600} as a typical example (Figure 3e-h). As seen in the survey spectrum in Figure 3e, the carbon materials contain

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**Figure 1.** a,b) Illustration of the synthesis of N, P-doping carbon nanofibers. c–h) SEM images of the carbon materials: c,d) C_{NP-500}, e,f) C_{NP-600}, and g,h) C_{NP-700}.
C, N, O, and P, which confirms the P,N co-doping in the final materials. The atomic content of N and P is 4.85 and 7.54 at%, respectively. The deconvolution of N, O, and P provides more information on these heteroatoms. Figure 3f presents the N1s spectrum of C\text{NP}-600. The well-known components like pyridinic-N (≈398.8 eV), pyrrolic-N (≈400.5 eV), and graphitic-N (≈401.9 eV) are all found here.\[14\] However, the peak center in Figure 3f is at ≈399.9 eV, which is different from most of the previous reported spectra. Based on previous empirical research,\[15\] the P=N units with P connecting to electrophiles such as O-based groups exhibit the peak at ≈399.8 eV, which could explain the XPS N1s spectrum. To the best of our knowledge, this interesting P=N=P doping is rare in carbon materials. This kind of doping could be further proved with the deconvolution of O1s (Figure 3g) and P2p (Figure 3h) spectra. Noticeably, another P doping is in the form of P\text{C}=C bond in carbon structure. Differing from the carbon nanofibers synthesized by P2O5-plant oil, the C\text{NP}-600 absorbed a certain amount of adsorbed oxygen, which might be due to the different, very oxyphilic structures in this material. The effect of temperature (500 and 700 °C, in Figures S5 and S6, Supporting Information respectively) on the doping conditions was investigated by XPS, too, which shows no significant difference to C\text{NP}-600.

To further confirm the formation of −N=P− doping, electron energy loss spectroscopy (EELS) was applied to detect the electronic structure of C\text{NP}-600. As given in Figure 3i, C\text{K} edge shows the characteristic maximum at 285 eV induced by the transitions of the electrons to \(\pi^*\) molecular orbital, and the second broad peak with onset at 290 eV corresponds to transitions to \(\sigma^*\) orbitals.\[16\] Three peaks at 397, 407, and 419 eV at N−K edge (Figure 3j) correspond to the \(\pi^*\) and the two \(\sigma^*\) peaks, similar to the spectra of pyridine-like nitrogen.\[16,17\] Moreover, as referred to the previous study, the P-L2,3 edge at 137 and 145 eV (Figure 3k) suggests the presence of −N=P−O in the carbon materials;\[18\] while the P-L2,3 edge at 183 eV (Figure 3k) is related to the presence of P=N coordination.\[19\] Another two different positions were selected to get the EELS spectra to confirm the uniform distribution of the chemical

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**Figure 2.** Characterization of the P2O5-NMP intermediates: a) FTIR spectra, b) liquid-state NMR spectra of intermediate-200, c) possible reaction pathways.
structures (Figure S7, Supporting Information). In summary, the EELS analysis is in good agreement with the XPS analysis. In addition, the C–K edge gives us a relative indication of electron delocalization in the carbon structure, and aromatization seems to be restricted, as typical for such low synthetic temperatures. This is confirmed by solid-state NMR on the main product. As seen in Figure S1m, the carbon material is mainly made up of all C–C sp² C, so-called graphitic carbon.

Raman was taken to analyze the samples. As shown in Figure S8 (Supporting Information), the G peak (≈1601 cm⁻¹) and D peak (≈1372 cm⁻¹) could be found in all three samples. The I_D/I_G is ≈0.99 for these samples, usually related to a relatively good graphitization degree, but we also point to the fact that both P- and N doping also bring vibrational dissymmetry and thereby apparent disorder. On the other hand, the thermal stability of the carbon materials was studied by thermogravimetric analysis (TGA). As seen in Figure S9 (Supporting Information), an obvious thermal decomposition occurred when the temperature reached 500 °C, which is in line with the previous research, but also the tendency towards nanotube fusion may result from the electron transfer between the C–C and unsaturated O (C=O). For example, when compared with carbon nanotubes (Figure S9, Supporting Information).[31] In the X-ray diffraction (XRD) pattern (Figure S10, Supporting Information), the samples behave as typical carbons with low long-range translational order, but as compared with activated carbon, the carbon nanofibers possess smaller interlayer distance.

The texture properties of the carbon materials were investigated with N2 adsorption-desorption isotherm. As seen in Figure S11 (Supporting Information), an obvious hysteresis loop could be found in the isotherm of C NP-500 and C NP-600, which strongly suggests the mesoporous nature of the carbon materials. The specific surface area of these two materials is ≈50 m² g⁻¹, the relatively low area might be caused by a relatively compact contact between the nanofibers. For example, the specific surface area of the single-walled carbon nanotubes could drop from 1315 to 151 m² g⁻¹ when 217 nanotubes form a bundle, and the surface area would further be smaller by increasing the number of nanotube units in the bundle.[20] Moreover, for C NP-700, the isotherm completely changed to type II, which is corresponding to the non-porous texture, and the corresponding specific surface area severely declines to ≈7 m² g⁻¹. In sum, the texture properties match with the results of SEM and TEM characterizations very well.

2.4. Pt1@C NP-600 Catalyst Synthesis and Characterization

With rich heteroatom doping/functional groups, C NP-600 has great potential as a carbon support for catching and stabilizing single atoms. The C NP-600 was grafted with Pt atoms: H2PtCl6 precursor used. Meanwhile, XPS spectra of Cl2p (Figure S12c, Supporting Information) show that some Cl⁻ was grafted with Pt atoms: H2PtCl6 precursor used. As far as we know, for the coordination of Cl⁻ and unsaturated O (C=O), it is a little shorter than that for PtO2 (≈1.65 Å, R space), which may result from the higher coordination between Pt and O (P=O/N=O) for Pt–O–P coordination. Therefore, the coordination O is from P=O/N=O=OH.

To gain more information of the electronic and coordination structures of Pt1 atoms in Pt1@C NP-600, X-ray absorption near-edge structure (XANES) and Fourier transform-extended X-ray absorption fine structure (FT-EXAFS) spectra were measured. The white-line intensity in sample Pt1@C NP-600 is between those of Pt foil and PtO2 (Figure 4i), indicating the Pt single atoms in Pt1@C NP-600 is electron deficient, which is consistent with the XPS results (Figure 4g). There are two prominent peaks at 1.58 and 1.9 Å in the FT-EXAFS results (R space, Figure 4j), which are corresponding to the Pt–O and Pt–Cl bonds, respectively.[23] For the peak at 1.58 Å (Pt–O), it is a little shorter than that for PtO2 (≈1.65 Å, R space), which may result from the stronger coordination between Pt and O (P=O/N=O=OH).

Based on the XPS and FT-EXAFS results, a schematic model of Pt1 coordination environment in 1 wt.% Pt1@C NP-600 was given in Figure 4k, and the best curve fitting indicates that Pt1 atoms are coordinated by two O and two Cl⁻ (Figure 4j; Table S1, Supporting Information).

Figure 3. Characterization of the carbon nanofibers assemblies. a,b) TEM images of the C NP-500 (a) and C NP-600 (b). c,d) TEM mapping of C NP-500 (c) and C NP-600 (d), respectively. e–h) XPS characterizations of the C NP-600: e) survey, f) N1s spectrum, g) O1s spectrum, and h) P2p spectrum. i–k) EELS characterizations of the C NP-600: i) C, j) N and k) P. l,m) Solid-state NMR characterizations of the C NP-600: l) 13C and m) 1H.
Figure 4. Characterization of 1 wt% Pt\textsubscript{1}@C\textsubscript{NP}-600. a–d) High-angle annular dark-field (a,c) and bright-field (b,d) STEM images and e) EDX mapping of 1 wt% Pt\textsubscript{1}@C\textsubscript{NP}-600. f) XRD patterns of C\textsubscript{NP}-600, 1 wt% Pt\textsubscript{1}@C\textsubscript{NP}-600 and the catalyst after reaction. g,h) XPS spectra: g) Pt 4f spectrum and h) O 1s spectrum of 1 wt% Pt\textsubscript{1}@C\textsubscript{NP}-600; i) Pt L\textsubscript{3}-edge XANES of 1 wt% Pt\textsubscript{1}@C\textsubscript{NP}-600; and j) FT-EXAFS spectra of 1 wt% Pt\textsubscript{1}@C\textsubscript{NP}-600, Pt foil, and PtO\textsubscript{2}. k) Schematic model of Pt coordination environment in 1 wt% Pt\textsubscript{1}@C\textsubscript{NP}-600. The red, blue, bright blue, magenta, light green, and gray spheres represent O, Pt, N, P, Cl, and C atoms, respectively.
2.5. Catalytic Properties of Pt\textsubscript{1}@C\textsubscript{NP}-600 for Hydrosilylation

The catalytic ability of Pt\textsubscript{1}@C\textsubscript{NP}-600 was evaluated in hydrosilylation reaction for a wide range for both alkenes and silanes (Table 1). For the benchmark reaction between 1-octene and (Me\textsubscript{3}SiO\textsubscript{2})MeSiH, C\textsubscript{NP}-600 shows no catalytic ability. However, Pt\textsubscript{1}@C\textsubscript{NP}-600 shows an ultrahigh activity with a high selectivity (99%) (Entry 4, Table 1), indicating single Pt atoms immobilized on the C\textsubscript{NP}-600 should be the real catalytic sites. The TOF is as high as 9.2 × 10\textsuperscript{6} h\textsuperscript{-1}, which is almost the same to best performance heterogeneous catalyst Pt\textsubscript{1}@AHA\textsubscript{U}-400 catalyst (9.7 × 10\textsuperscript{6} h\textsuperscript{-1}).\textsuperscript{[22]} Compared to a Karstedt Pt catalyst, no special activation period was needed, and the solution remained colorless and transparent after reaction and separation of the heterogeneous catalyst, indicating high stability of Pt\textsubscript{1}@C\textsubscript{NP}-600 during the hydrosilylation process.\textsuperscript{[7,9,24]} Pt\textsubscript{1}@C\textsubscript{NP}-600 shows no catalytic ability. However, Pt\textsubscript{1}@C\textsubscript{NP}-600 also shows much higher activities than other heterogeneous catalysts when (CH\textsubscript{3}CH\textsubscript{2}O)\textsubscript{2}SiH was used as silane (Entry 6 and 12, Table 1).\textsuperscript{[10,23]}

The high activity and selectivity of Pt\textsubscript{1}@C\textsubscript{NP}-600 shows little change even when the catalyst was recycled for six times (Figure S13, Supporting Information), indicating the high stability of the catalyst. STEM images of the spent catalyst show no aggregation of the Pt single atoms (Figure S14, Supporting Information). To further evaluate the stability of Pt\textsubscript{1}@C\textsubscript{NP}-600 catalyst, a Pt leaching test (Entry 3, Table 1) was performed, and the detected Pt concentration in the crude reaction solution is negligible (0.06 ppm, corresponding to about 0.9% of the initial Pt adding amount). At the same time, no conversion was observed by using the crude reaction solution as catalyst, indicating the atomically dispersed Pt on C\textsubscript{NP}-600 are the real catalytic sites.

The ultrahigh activity of Pt\textsubscript{1}@C\textsubscript{NP}-600 catalyst may be attributed to the atomic dispersion of isolated Pt atoms, the electron

Table 1. Hydrosilylation of terminal alkenes catalyzed by Pt\textsubscript{1}@C\textsubscript{NP}-600.

<table>
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<th>Entry\textsuperscript{a})</th>
<th>Alkene</th>
<th>Silane</th>
<th>Catalyst [mol\textsubscript{%}]\textsuperscript{b)}</th>
<th>t min\textsuperscript{c)}</th>
<th>T Yield [%]</th>
<th>T selectivity [%]</th>
<th>TOF [h\textsuperscript{-1}]\textsuperscript{c)}</th>
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<td>99</td>
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<td>92</td>
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<td>1.1 × 10\textsuperscript{4}</td>
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</table>

\textsuperscript{a}) Experiments were performed at 4 mmol scale: 1 wt.% Pt\textsubscript{1}@C\textsubscript{NP-600} catalyst, silane/olefin = 1.1 (mol mol\textsuperscript{-1}), temperature = 70 °C. The products yield and selectivity were determined by \textsuperscript{1}H NMR analysis using N,N-dimethylaniline as internal standard; \textsuperscript{b}) Based on olefin substrate; \textsuperscript{c}) TOF values were calculated based on T\textsubscript{y}ield, and the calculation method was detailed in Figure S15 (Supporting Information); \textsuperscript{d}) To eliminate the influence of mass transfer, improve solid-liquid contact and easy to weigh the catalyst, 0.5 wt.% Pt\textsubscript{1}@C\textsubscript{NP-600} catalyst was used; \textsuperscript{e}) Temperature = 60 °C.
deficiency of the Pt atoms and the unique coordination of Pt atoms. It is well known that Pt nanoparticles have almost no catalytic ability for hydrosilylation reactions owing to the strong adsorption of silane and olefin reactants on different Pt atoms of Pt nanoparticles. The Pt/N-doped C3P-600 provides great number of anchoring sites for Pt single atoms, while at the same time preventing the aggregation of Pt1 atoms. Meanwhile, strong interactions between the Pt/N-doped C3P-600 (best understood as a heterogeneous P/N-ligand) and the Pt1 atoms may result in the high electron deficiency of Pt1 atom with the electron withdrawn of the support (XPS and XANES results). It has been reported that only moderate coordination strength is beneficial for rapid hydrosilylation, and too strong or too weak interactions both decrease the reactivity. The electron-deficient Pt1 atoms of Pt1@C3P-600 may provide moderate adsorption for reactants or intermediates compared to Pt(0), while the electron deficiency of the Pt1 center may be beneficial for lowering energy barrier by optimizing the electron structure of the transition state. Meanwhile, the Cl ligand can be easily replaced by the reactants (olefin and silane), which may result in the absence of activation period.

3. Conclusion

We have successfully synthesized carbon nanofibers with the −P=N= unit in their chemical structure based on the reaction between P2O5 and NMP. Building on the characterization of the intermediates by FTIR and NMR, the possible reaction mechanism involves the formation of oligomers due to the cyclization of ketene species and subsequently the polymerization at elevating temperature. The −P=N= doped carbon nanofibers were functioned as functional support for Pt atom to build a single-atom catalyst for hydrosilylation. The catalyst displays exceptional performance in the hydrosilylation that the TOF can reach as high as 9.2 × 105 h−1. Moreover, the selectivity of this material is higher than 99%, which promises effective synthesis of targeted product. It is expected that such carbon nanofibers potentially possess superior prospect in other catalysis application, but not limited to hydrosilylation.

4. Experimental Section

The relevant information can be found in Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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