Nitrogen Functionalized Carbon Black: A Support for Pt Nanoparticle Catalysts with Narrow Size Dispersion and High Surface Area

Suzanne S. Rich,^a Jonathan J. Burk,^a Chang Sun Kong,^b Cynthia D. Cooper,^a Daniel E. Morse,^{bc} and Steven K. Buratto*^a

^aDepartment of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106-9510, United States. E-mail: buratto@chem.ucsb.edu; Tel: 1-805-893-3393

^bCenter for Energy Efficient Materials, Institute for Collaborative Biotechnologies, California NanoSystems Institute and Materials Research Laboratory, University of California, Santa Barbara, CA 93106-9510, United States

^cDepartment of Molecular Cellular, and Developmental Biology, University of California, Santa Barbara, CA 93106-9510, United States

Abstract

Amorphous carbon is widely used as a support for Pt nanoparticle catalysts. We show here that catalytic performance can be greatly improved by functionalizing the carbon support with a nitrogen-containing molecule, in conjunction with a new method for the *in situ* synthesis of nanocrystalline Pt. Vulcan® carbon black is covalently functionalized with 4-aminomethylpyridine (4AMP) via formation of an acid chloride on the surface followed by amidation. The resulting 4AMP-functionalized Vulcan® (4AMP-VC) was thoroughly characterized and shown to contain N at the surface of the Vulcan® carbon support. Pt nanoparticles grown on the 4AMP-VC have a smaller average size and much narrower size distribution than Pt nanoparticles grown on bare Vulcan® (VC). In addition, the Pt/4AMP-VC catalysts show higher catalytic activity and are more durable than their Pt/VC counterparts. We infer through careful analysis of x-ray photoelectron spectra that the Pt nanoparticles bind preferentially to the pyridinic nitrogen of the 4AMP.

*Corresponding author. Tel: 805 893-3393. E-mail: buratto@chem.ucsb.edu (Steven K. Buratto)

1. Introduction

Supported Pt nanoparticles with high surface area have found application in a number of areas including the automotive industry (catalytic converters), petrochemical processing (reforming catalysts) and alternative energy (electrocatalysts for fuel cells). Despite its wide-spread use, the high cost of Pt has been a major deterrent to the commercialization of polymer electrolyte membrane fuel cells. While the cost per kilowatt has been significantly reduced over the last few years, the cost remains 50% higher than the US Department of Energy target of \$30/kW [1]. Pt nanoparticles are used as catalysts in both the anode and cathode catalyst layers. One approach to reducing this cost is to decrease the size and improve the dispersion of the Pt particles [2]. This can be accomplished, in part, by controlling the Pt adsorption sites on the catalyst support. It has been shown recently that by doping the carbon support with N-containing molecules, it is possible to provide a high density of active sites on the catalyst support, which ultimately leads to a high density of small Pt particles on the support and high catalytic activity with a much smaller amount of Pt [3,4].

Several studies have shown that N-doping increases the catalytic activity of carbon nanostructures [4–6]. Theoretical calculations involving N-doping of carbon nanotubes (CNTs) suggest that pyrrolic and pyridinic N atoms decrease the band gap of the graphite lattice [7]. N-doping adds a delocalized electron, which improves electron donation from graphite to reactant molecules [6,7]. It has also been suggested that N promotes the oxygen reduction reaction (ORR) by polarizing the adjacent carbon and creating a desirable binding site for O₂ [8]. In addition, calculations indicate N-doped CNTs adsorb Pt more strongly than undoped CNTs, which should lead to better stabilization of Pt nanoparticles [9,10]. This is supported by accelerated durability testing (ADT) which has shown that Pt particles supported on N-doped CNTs resulted in a smaller loss of electroactive surface area (ESA) after 4000 voltammetric cycles than for Pt particles supported on bare CNT [11].

Although there have been several studies on N-doping [8,11] and noncovalent attachment [12] of N groups to conductive carbon structures, there have only been a few studies that employ organic synthesis to covalently modify the surface of other carbon nanostructures [13,14]. The covalent approach is expected to be superior to noncovalent attachment, as covalent functionalization results in a larger degree of surface coverage. In addition, covalent bonds are more stable than van der Waals, π - π stacking and/or electrostatic interactions that are exploited in noncovalent attachments [15]. Another advantage of covalent functionalization over doping is the ability to control the desired functional group. While N-functionalization using covalent attachment has been shown for CNTs, to the best of our knowledge, this is the first study where covalent functionalization with N heterocycles has been performed on Vulcan® XC-72R carbon nanoparticles.

In this paper, we chose 4-aminomethylpyridine (4AMP) as the nitrogen-containing molecule to investigate the influence of covalent N-functionalization of Vulcan® XC-72R on the electrochemical activity of Pt catalysts. 4AMP was selected because it contains a pyridine and forms a thermally stable amide bond. Calculations and doping studies suggest that pyridine is a secondary nitrogen structure that leads to better Pt distribution and increased performance [6,7]. Thus, 4AMP should provide the requisite nitrogen functionality for stabilizing Pt nanoparticles.

Fourier-transformed infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) were used to confirm the amidation. X-ray photoelectron spectroscopy (XPS) was used to investigate the interactions between Pt and surface functional groups on the Vulcan® support. Transmission electron microscopy (TEM) was used to compare the size and dispersion of Pt nanoparticles on N-functionalized Vulcan® to clean and oxidized Vulcan®. Finally, cyclic voltammetry (CV) was used to determine the specific current and the oxygen reduction reaction was cycled 800 times to evaluate the durability. From these data we concluded that covalent attachment of 4AMP to Vulcan® was successful and upon *in situ* catalytic growth of the Pt nanoparticles [23], the Pt binds to these N-groups. In addition, the N-functionalized support exhibited a small average Pt nanoparticle size and had a narrow size distribution, which resulted in an electrode with a high catalytic surface area and high catalytic activity.

2. Experimental

Vulcan® XC-72R (Cabot Inc.), AvCarb Grade 1071HCB carbon fiber paper, and Nafion® solution (10 wt%) were purchased from the FuelCellStore.com. Teflon tape, copper tape, and TEM grids were from Ted Pella (Redding, CA). Oxalyl chloride (98%) and potassium bromide (99+%) were supplied by Acros Organics (Fair Lawn, NJ). 4-aminomethylpyridine (Sigma-Aldrich, 98%), ethanol (Gold Shield Chemical Company, 200 proof). 3Å molecular sieves, nitric acid, and tetrahydrofuran (THF) were from EMD (Gibbstown, NJ). Dichloromethane (DCM) was purchased from Fischer Scientific (Fair Lawn, NJ) and isopropanol was from VWR (West Chester, PA). All solvents were ACS grade. DCM and THF were dried on molecular sieves (20 wt %) at least 48 h before use. Sulfuric acid was degassed with argon for at least 15 min before use in electrochemical measurements.

Nanoparticles of Pt were grown *in situ* on both the functionalized and non-functionalized Vulcan® matrices using a recently described method employing the diffusion of ammonia vapor as catalyst, after which the resulting nanocomposites were thoroughly washed [23].

For hydrogen adsorption/desorption measurements, the Pt/C ink was prepared following the procedure reported by Geng and Lu [16] in order to disperse the electrocatalyst onto a FTO working electrode. Approximately 5 mg of Pt/C was ultrasonicated for 30 min in 1.0 mL of ethanol and 20 µL of 5 wt% Nafion solution. The ink was sonicated for 30 min prior to use. The Pt/C/FTO working electrode was prepared by dropcasting 20 µL of the ink onto a 0.5 cm² template using Teflon tape (McMaster) that was adhered to FTO. The Pt/C/FTO sample was dried in a vacuum oven at 80 °C for 30 min. The Teflon tape was removed prior to electrochemical measurements.

For oxygen reduction reaction measurements, the Pt/C ink was prepared by ultrasonication approximately 5 mg of Pt/C for 45 min in 1.0 mL of isopropanol. A carbon cloth electrode was employed as the working electrode to improve adhesion between the electrocatalyst and the electrode for long durability measurements. The Pt/C/carbon cloth working electrode was prepared by dropcasting 100 µL of the ink onto the carbon cloth electrode, which was screwed into a 1 cm² Teflon block template. The Pt/C/carbon cloth sample was dried in a vacuum oven at 80 °C for 2 h. The Teflon block

was removed and the Pt/C/carbon cloth electrode was weighed prior to electrochemical measurements.

Thermogravimetric analysis (TGA) was performed with a Mettler TGA/sDTA 851e. The temperature was held at 25 °C for 10 min under nitrogen before heating the sample from 25 °C to 900 °C at a ramp rate of 10 °C/min under a flow of nitrogen.

Functional groups on 4AMP-VC were confirmed using fourier transformed infrared (FTIR) spectroscopy. A Nicolet Magna 850 FTIR Spectrometer (Thermo Scientific, Madison, WI) was employed. The 4000-600 cm^{-1} spectral range was scanned 150 times with a resolution of 4 cm^{-1} . Automatic baseline correction was applied through the software to remove the large background of the carbon black absorption.

Quantitative surface composition analysis was executed on high resolution spectra collected with x-ray photoelectron spectroscopy (XPS) on a Kratos Axis Ultra Spectrometer (Manchester, UK) with a monochromatized aluminum x-ray source (Al $K\alpha$). The large C 1s photoemission peak at 284.5 eV corresponding to graphitic sp^2 -hybridized carbon was used for spectral calibration. A Shirley-type background subtraction was performed and the photoemission spectra were fitted with Gaussian peaks using CasaXPS.

The Pt nanoparticle size and distribution was analyzed with a transmission electron microscope, TEM (FEI Company, T20). Pt/Carbon samples were ultrasonicated in ethanol for 20 min then dispersed onto a carbon support grid (Ted Pella, Inc.). ImageJ processing and analysis software was used to determine the average diameter and particle distribution from a sample size of ≥ 200 nanoparticles.

Cyclic voltammetry (CV) was performed in a conventional three-electrode electrochemical cell. The cell consisted of a Pt/C loaded on a fluorine-doped tin oxide, FTO (Pilkington Glass Company, TEC A10), working electrode, platinum mesh counter electrode (Alfa Aesar, 99.9999%), and Ag|AgCl|KCl(sat.) reference electrode (0.197 V vs. SHE). The potential of the working electrode was computer-controlled by a potentiostat (Bio-Logic SAS, VSP model) using EC-Lab software. All potentials are reported in reference to the Ag|AgCl|KCl(sat.) reference electrode unless stated otherwise. For hydrogen adsorption measurements, the electrochemical cell was designed to expose a 0.50 cm^2 geometric area of Pt/C/FTO to deaerated 0.5 M H_2SO_4 . The distance

between the reference electrode and working electrode was fixed to approximately two times the outer diameter of the tip of the Luggin capillary to ensure the solution resistance was minimal. The cyclic voltammograms were recorded from -0.20 V to 1.20 V at a scan-rate of 10 mV s^{-1} in $0.5\text{ M H}_2\text{SO}_4$ electrolyte solution that was deaerated with argon. For oxygen reduction reaction measurements, the carbon cloth working electrode was hung to expose a 1 cm^2 geometric area of Pt/C/carbon cloth to O_2 saturated 0.1 M KOH . The cyclic voltammograms were recorded from -1.2 V to 0.3 V at a scan-rate of 50 mV s^{-1} in 0.1 M KOH electrolyte solution that was saturated with oxygen.

In order to measure the Pt-content of the Pt-coated supports, the Pt nanoparticles were removed from the surface by digestion in $\sim 15\text{ g}$ of $20\text{ v/v } \%$ aqua regia at 60°C for 48 h . The mass of the Pt nanoparticles was then determined by inductively coupled plasma-atomic emission spectroscopy, ICP-AES (Thermo iCAP 6300 model).

3. Results and Discussion

The 4-aminomethylpyridine functionalized Vulcan® (4AMP-VC) was prepared based on a method previously reported for functionalizing CNTs [15]. The synthetic scheme is shown in Fig. 1. Vulcan® XC-72R was refluxed in 6M nitric acid for 16 h . Oxidized Vulcan® (O-VC) was filtered and rinsed with deionized water until pH paper indicated the filtrate was pH 7. O-VC was dried overnight in a vacuum oven at 130°C . O-VC was suspended in dry DCM and purged with dry argon prior to adding oxalyl chloride. The reaction was stirred under a flow of argon for 16 h .

Fig. 1 Synthetic route to functionalize Vulcan® with 4-aminomethylpyridine

Amidation was achieved by resuspending the acylated Vulcan® in dry THF and slowly adding 4-aminomethylpyridine. The reaction was stirred under a flow of argon for 48 h. The reaction mixture was filtered and washed with ethanol until the filtrate was clear. 4AMP-VC was dried in a vacuum oven at 130 °C overnight.

TGA was employed to investigate the thermal stability of 4AMP-VC compared to its precursors and a physisorbed counterpart. Thermograms of O-VC, physisorbed 4AMP-VC, and functionalized 4AMP-VC are shown in Fig. 2. The thermograms were cropped to start at 125 °C because little change occurred between 25 – 125 °C. Cropping the thermograms highlights the important features of the curves. The red curve in Fig. 2 shows the mass loss of O-VC upon heating. A small mass loss (~2%) occurs between 25 – 100 °C due to the loss of water from this hydrophilic sample. Above 100 °C steady mass loss with no defined step is observed, and is attributed to loss of surface oxide species. The pink curve of Fig. 2 shows the mass loss of physisorbed 4AMP-VC upon heating. The physisorbed 4AMP-VC was prepared by stirring ~ 50 mg of O-VC in 2 mL of 4AMP for 15 min. The product was filtered and washed with ethanol then dried in a vacuum oven at 130 °C overnight. The result was a Vulcan® sample coated with 4AMP, but not functionalized. The physisorbed 4AMP-VC shows an abrupt mass loss at a temperature of 175 °C that corresponds to the mass loss of physisorbed 4AMP. Between 175 – 340 °C the physisorbed 4AMP-VC loses ~ 3% of its mass. Gradual mass loss above 340 °C is observed in the thermogram of physisorbed 4AMP-VC, which is similar to the mass loss observed in the thermogram of O-VC. This suggests that surface oxides are being removed from the oxidized Vulcan used to make the physisorbed product. The blue curve of Fig. 2 shows the mass loss of covalently functionalized 4AMP-VC.

Fig. 2 Thermograms of oxidized VC (red), physisorbed 4AMP-VC (pink), and covalently functionalized 4AMP-VC (blue) in the temperature region where greatest mass loss occurs. The inset highlights the difference in onset temperature between the physisorbed 4AMP-VC and the covalently functionalized 4AMP-VC.

In the thermogram of functionalized 4AMP-VC no mass loss is observed until 200 °C in sharp contrast to the thermogram of physisorbed 4AMP-VC (pink curve). The initial mass loss step of functionalized 4AMP-VC occurs at a temperature 30 °C higher than the corresponding mass loss of physisorbed 4AMP-VC. This shift to higher onset temperature is indicative of the formation of a thermally stable bond between the 4AMP and the Vulcan®, rather than a physisorbed product. The small mass loss (~8%) observed between 205 – 350 °C for functionalized 4AMP-VC is attributed to the decomposition of covalently attached 4AMP. Above 350 °C, a steady mass loss is observed for functionalized 4AMP-VC with a similar slope as the O-VC sample, suggesting surface oxides are also removed from 4AMP-VC at higher temperatures, similar to O-VC. This is expected since the functionalized 4AMP-VC is hydrophilic having been oxidized prior to the 4AMP functionalization. Our TGA results suggest that we were successful in functionalizing Vulcan® carbon with 4AMP.

To confirm the mass loss in the thermogram of 4AMP-VC was due to a covalent functionalization, FTIR was employed to probe the functional groups on VC, O-VC, and 4AMP-VC. The pink spectrum of Fig. 3 shows the FTIR spectrum of bare VC. The small peaks at 2920 cm^{-1} and 2860 cm^{-1} are consistent with the asymmetric and symmetric C-H stretches of sp^3 -hybridized Vulcan® at step edges [17]. The sharp peak at

1380 cm^{-1} corresponds primarily to the C=C ring stretch of Vulcan® but also contains contributions from C-H bending and C-OH bending modes [18,19]. In addition, there is a small peak at 1650 cm^{-1} that corresponds to the aromatic ring stretch. The C-O stretch at 1110 cm^{-1} , the O-H stretch at 3450 cm^{-1} and the weak C=O stretch at 1740 cm^{-1} are attributed to partial oxidation of Vulcan®, which readily occurs when exposed to air [17]. The tiny doublet at 2360 cm^{-1} is attributed to adsorbed CO_2 [20]. All peaks in the VC spectrum are visible in the other spectra as expected.

The red spectrum of Fig. 3 shows the O-VC sample has a stronger carbonyl peak (1738 cm^{-1}) and a stronger O-H stretch (3436 cm^{-1}) than the same peaks in VC. Upon oxidation, the aromatic ring stretch shifts from 1650 cm^{-1} in VC to 1635 cm^{-1} in O-VC. This shift is consistent with a carbonyl conjugated with the aromatic ring system, which increases the intensity of the peak and shifts the aromatic ring stretch to lower wavenumbers [17,21]. Note that these peaks are very weak in the VC spectrum since the surface oxidation is uncontrolled for this sample, whereas the O-VC sample has been oxidized to a carboxylic acid as indicated in the synthetic scheme of Fig. 1. The strong C=O and O-H stretches of the O-VC spectrum indicate that this oxidation reaction was successful.

After amidation, the 4AMP-VC spectrum (blue spectrum) shows a prominent new peak at 3739 cm^{-1} corresponding to the N-H stretch [22]. This single peak indicates that a secondary N is present in the sample [20]. In addition, all of the peaks below 1800 cm^{-1} have a larger intensity in the spectrum of 4AMP-VC than in the spectra of VC and O-VC samples, due to the overlap of C-N functional groups peaks with the C-O and C=C peaks. In addition, the conjugated C=O stretch present in both the 4AMP-VC and O-VC spectra shifts from 1635 cm^{-1} in the O-VC spectrum to 1603 cm^{-1} in the 4AMP-VC spectrum. This shift is illustrated more definitively in the inset of Fig. 3, which shows a magnification of the spectral region between 1850 and 1550 cm^{-1} . This shift to lower wavenumbers upon N-functionalization is consistent with the conversion of the conjugated carboxylic acid to an amide (HN-C=O) [20]. Based on the FTIR spectra of Fig. 3 we are able to confirm the formation of 4AMP-VC as expected from the synthetic scheme of Fig. 1 and conclude that our Vulcan® has been covalently functionalized.

In order to test our functionalized 4AMP-VC as a catalyst support, Pt nanoparticles were grown *in situ* on the 4AMP-VC support using the kinetically controlled vapor

diffusion process introduced by Kong et al. and described in detail previously [23]. For comparison, Pt nanoparticles were also grown *in situ* on bare Vulcan® (VC) and O-VC using the same procedure. XPS and TEM were performed to characterize the interaction of Pt with each support and to probe the size and distribution of the resulting catalyst particles.

Fig. 3 FTIR spectra of bare VC starting material (pink), oxidized VC (red) and 4AMP functionalized VC (blue). The dotted line in the inset highlights the carbonyl peak shift at 1650 cm⁻¹.

The XPS survey scans of Pt/4AMP-VC and 4AMP-VC are shown in Fig. 4. The bottom spectrum in Fig. 4 shows the XPS survey scan of 4AMP-VC. This spectrum has a large peak at 284.6 eV corresponding to C 1s electrons. The top of the C 1s peak was cropped and the scale of the y-axis was adjusted to better view the less intense peaks in the figure. The small peak at 399.3 eV is attributed to the N 1s electrons of 4AMP. The N/C ratio is 0.0459. In addition, a relatively large peak at 531.8 eV corresponds to the O 1s electrons of the unreacted surface oxides. These data are consistent with the FTIR data in confirming the presence of bonded N functionalities. The top spectrum in Fig. 4 shows the survey scan of Pt/4AMP-VC. The same C 1s, N 1s, and O 1s peaks are observed in

the spectrum as observed in the 4AMP-VC spectrum. The N/C ratio has decreased to 0.0290. There is an additional set of peaks centered at 73.7 eV in the Pt/4AMP-VC scan that correspond to the Pt 4f electrons, which indicates the presence of Pt on the support. A comparison of these survey scans before and after the addition of Pt reveals a decrease in the intensity of the O 1s and N 1s signals in the presence of Pt. This decrease in relative intensity is attributed to Pt nanoparticle binding near both O and N sites.

Fig. 4 XPS survey scans of Pt/4AMP-VC (top spectrum) and 4AMP-VC (bottom spectrum). In both spectra, the top of the C 1s peak was cropped and the scale of the y-axis was adjusted to better view the less intense peaks in the figure.

High resolution XPS spectra of both the N 1s and Pt 4f spectra were recorded and analyzed. Curve fitting of the high resolution spectra gave important insight into the nature of the surface groups and their interaction with Pt. Fig. 5 shows the high resolution N 1s spectrum of 4AMP-VC (bottom spectrum) and the N 1s spectrum of Pt/4AMP-VC (top spectrum). Both N 1s spectra are fitted with 3 Gaussian peaks. The two large Gaussians at 399 and 400 eV correspond to the XPS signal from the pyridine and the amide on 4AMP-VC, respectively. The smaller Gaussian at 401 eV has been assigned previously to quaternary N, such as pyridinium [24,25]. It is interesting to note

that the pyridinic peak exhibits a significant shift ($\Delta E > 0.5$ eV) to lower binding energy in the presence of Pt (top spectrum of Fig. 5). This shift toward lower binding energy was attributed to the pyridinic N groups interacting with an electropositive atom (Pt in our case) [26]. Finally, we note that the amide peak does not shift, which implies that the Pt is not binding to this site.

Fig. 5 High resolution N 1s XPS spectra of 4AMP-VC (bottom spectrum) and Pt/4AMP-VC (top spectrum).

Table 1 gives the relative peak areas of the pyridinic and amide peaks as well as their ratio to one another. The peak areas were normalized by dividing their area by the area of the quaternary N peak, which we assume to be a constant signal in each spectrum. Table 1 shows that before Pt is grown on 4AMP-VC the peak area ratio of pyridine : amide is approximately 1:1, which is consistent with the structure of 4AMP. After Pt growth, however, the ratio becomes 0.758, indicating the pyridinic peak area is approximately 25% smaller than the amide peak area in the presence of Pt. As it is unlikely that the growth of Pt led to the fragmentation of the pyridine group, we attribute this decrease in pyridinic signal to the presence of Pt at the pyridine. This suggests that Pt binds

preferentially to the pyridinic N, which is consistent with previous studies of N-doped CNTs [6].

Table 1 Relative Gaussian areas of the N 1s XPS spectra shown in Fig. 5.

	Pyridine	Amide	Pyridine : Amide
Pt/4AMP-VC	2.53	3.34	0.758
4AMP-VC	1.98	2.14	0.929

Areas of the pyridinic and amide Gaussians are given as well as their ratio to one another. The areas were normalized by dividing their area by the area of the quaternary N Gaussian.

The high resolution Pt 4f spectra (Fig. 6) were fitted with 3 sets of Gaussian doublets (red, green, and pink). The bottom spectrum of Fig. 6 shows the Pt 4f peaks of the Pt/VC sample. The most intense doublet denoted by the red Gaussians (71.4 eV and 74.7 eV) is attributed to metallic Pt [27]. The broader second doublet denoted by the green Gaussians (72.1 eV and 75.4 eV) occurs at a position near a binding energy usually attributed to Pt (II). In our case, this doublet is attributed to Pt (0) atoms at the surface. The binding energy difference between Pt (0) and Pt (II) is approximately 1.4 eV [27]. The binding energy difference between these two peaks, however, is only 0.7 eV, suggesting that Pt (II) is not present in our samples. For Pt particles smaller than 2 nm, the majority of Pt atoms are on the surface [28]. Pt atoms at the interface with a carbon support lead to an XPS signal consistent with an oxidized state [29–31]. Since a large proportion of Pt atoms are at the surface of the Pt particle, it is reasonable to attribute the second doublet at higher binding energy to these Pt (0) atoms at the surface of the Pt particle. The third doublet denoted by the pink Gaussians of highest binding energy was weak and very broad (74.4 eV and 77.8 eV) is attributed to the Pt (IV) oxidation state [28]. These species could include PtO₂ and Pt(OH)₄. There are no binding energy changes when Pt is grown on O-VC in comparison to Pt/VC. The peak positions of the Gaussian doublets are identical for the fitted spectra of Pt/O-VC and Pt/VC. In the Pt 4f spectrum from the Pt/4AMP-VC sample (top spectrum of Fig. 6), however, the Gaussian attributed to Pt (0) atoms at the surface exhibited a prominent binding energy shift toward higher binding

energy ($\Delta E = 0.4$ eV), when compared to Pt/O-VC and Pt/VC. This trend is consistent with previously reported XPS data of Pt nanoparticles and is attributed to quantum size effects [29]. As the particle size decreases below 1.9 nm, there is inefficient coupling between the valence bands of the Pt particle and the support and reduces hole delocalization after photoemission [30]. The resulting localized positive charge on the Pt particle is consistent with a shift to higher binding energy in the XPS signal.

Fig. 6 High resolution Pt 4f XPS spectra of Pt/VC (bottom spectrum) and Pt/4AMP-VC (top spectrum).

Table 2 shows the relative areas of the Pt 4f_{7/2} peaks. The peak areas were normalized by dividing their area by the Pt (IV) peak area (which we assume to be a constant signal in each spectrum). Table 2 illustrates key trends in the relative areas of the bulk Pt (0) and surface Pt (0) peaks. The Pt/4AMP-VC sample has a smaller bulk Pt (0) peak and a larger surface Pt (0) peak than both Pt/VC and Pt/O-VC. However, Pt/O-VC has a larger bulk Pt (0) peak and a slightly smaller surface Pt (0) peak than Pt/VC. When the Pt particles are smaller there is a greater percentage of interfacial Pt particles at the Vulcan® surface and fewer particles acting as bulk Pt (0). This implies that the ratio of Pt (0)_{surface}/Pt (0)_{bulk} can be used as an indicator of the relative particle size. In our data, the

order of increasing surface Pt (0) peak area is Pt/O-VC < Pt/VC < Pt/4AMP-VC. This implies that the Pt particle size decreases from Pt/O-VC to Pt/VC to Pt/4AMP-VC. We are able to confirm this hypothesis by imaging individual particles using TEM.

Table 2 Relative Gaussian areas of the Pt 4f XPS spectra shown in Fig. 6.

	Pt (0) _{bulk} /Pt (IV)	Pt (0) _{surface} /Pt (IV)	Pt (0) _{surface} /Pt (0) _{bulk}
Pt/4AMP-VC	1.93	2.22	1.15
Pt/O-VC	2.76	1.98	0.717
Pt/VC	2.19	2.02	0.922

Areas of the bulk Pt (0) and surface Pt (0) Gaussians are given as well as their ratio to one another. The areas were normalized by dividing their area by the Pt (IV) Gaussian area.

TEM was used to probe the size and distribution of Pt nanoparticles grown on 4AMP-VC, O-VC, and VC. Fig. 7 shows the TEM images and the size histograms of Pt/VC, Pt/O-VC, and Pt/4AMP-VC. The TEM image of Pt/VC is shown in Fig. 7a. As can be seen in the image, there is a wide distribution of particles ranging from small 0.87 nm particles to large 5.4 nm particles. The histogram in Fig. 7a. shows the average particle size was 1.91 ± 0.91 nm for Pt/VC. This histogram was formed from a distribution of over 200 particles. The TEM image of Pt/O-VC is shown in Fig. 7b. As can be seen in the image, there is a much wider distribution of particles than for Pt/VC. The particles range in size from small 1.2 nm particles to large 7.1 nm particles. The histogram in Fig. 7b. shows the average particle size was 3.04 ± 1.07 nm for Pt/O-VC. This is an interesting result since it was expected that the particle size would decrease slightly for this surface due to the increased surface roughness. We observe the loss of carbon atoms upon oxidation of the surface by the harsh oxidation conditions, which roughens the surface of O-VC. The roughened surface is expected to have an increased number of binding sites for Pt. From the image of Fig. 7b and its corresponding histogram we see this is not the case. Pt particles grown on O-VC had a larger average particle size and a wider distribution than the bare VC starting material. These results suggest that it is not simply surface defects that lead to favorable binding of Pt. The TEM image of Pt/4AMP-

VC is shown in Fig. 7c. As can be seen in the image, the 4AMP functionality led to small, well-dispersed Pt nanoparticles that are all the same size. The histogram in Fig. 7c. shows the average particle size was 1.66 ± 0.75 nm for Pt/4AMP-VC. Pt nanoparticles grown on 4AMP-VC had a much smaller average particle size and a much narrower distribution than either Pt/VC or Pt/O-VC. These results illustrate the effect of the matrix in the control of growth of the Pt nanoparticles, as previously reported for the catalytic method of synthesis used,[23] and consistent with the smaller Pt nanoparticle size and distribution previously shown for N-doped CNTs [11].

Fig. 7 TEM images and the size histograms of a) Pt/VC, b) Pt/O-VC, and c) Pt/4AMP-VC. The histograms were generated by measuring over 200 particles.

Finally, as was mentioned previously, the small, well-dispersed Pt nanoparticles have high surface area, which should result in high catalytic activity. This hypothesis was tested by measuring the electrocatalysis via cyclic voltammetry. The specific current (current per gram Pt) of the Pt nanoparticles grown on VC, O-VC, and 4AMP-VC supports was measured using hydrogen adsorption/desorption CV. The voltammograms of Fig. 8 were recorded in 0.5 M H₂SO₄. The black trace of Fig. 8 shows the hydrogen adsorption on Pt/VC. The green trace of Fig. 8 shows the hydrogen adsorption on Pt/O-VC, and the red trace shows the hydrogen adsorption on Pt/4AMP-VC. Clearly the Pt/4AMP-VC had the largest signal. Details of the Pt wt % and specific currents for each electrode can be found in the supplemental information. With approximately the same Pt loading (~ 8 wt %), the 4AMP-VC catalysts showed a two-fold increase in catalytic activity relative to Pt/VC as was expected from our highly disperse, narrow size distribution nanoscale Pt particles.

Fig. 8 Cyclic voltammograms of hydrogen adsorption and desorption on Pt/VC (black dots), Pt/O-VC (green dashes), and Pt/4AMP-VC (red line). The inset highlights the difference between the areas of the hydrogen desorption peak.

The specific electrochemical surface area (SSA) of the Pt nanoparticles grown on 4AMP-VC, O-VC, and VC supports was calculated from the hydrogen

adsorption/desorption waves in Fig. 8 using standard methods [32,33]. The measured SSA values are given in Table 3. For comparison, SSA values were calculated using the average Pt nanoparticle diameter on each support from the TEM images in Fig. 7. The calculated SSA values are given in Table 3. It is important to note that the calculated SSA values do not take the size distribution of the Pt nanoparticles into account. Despite this, the trend is consistent and shows that the specific surface area decreases in the order Pt/4AMP-VC > Pt/VC > Pt/O-VC.

Table 3 Comparison of the specific surface area of Pt on each support.

	SSA _{measured} (m ² g ⁻¹ Pt)	SSA _{calculated} (m ² g ⁻¹ Pt)
Pt/4AMP-VC	151	169
Pt/O-VC	100	92
Pt/VC	114	146

SSA_{measured} was calculated from the cyclic voltammograms in Fig. 8. SSA_{calculated} was determined using the average Pt nanoparticle diameter from the TEM images in Fig. 7.

The oxygen reduction reaction on 4AMP-VC and VC electrodes without Pt was measured to evaluate the effect of N alone. A small current was observed for the 4AMP-VC electrode without Pt, but the observed current was more than an order-of-magnitude smaller than the current observed for the Pt/4AMP-VC. This result implies that derivatizing VC with 4AMP results in non-zero, but negligible enhancement in ORR activity. Furthermore, the agreement between the calculated and measured SSA values shown in Table 3 suggests that the smaller size of the Pt nanoparticles on 4AMP-VC is the main source of the improved catalytic activity.

The durability of the Pt nanoparticles grown on VC and 4AMP-VC supports was measured using CV to cycle the oxygen reduction reaction 800 times. The full voltammograms were recorded in O₂ saturated 0.1 M KOH and can be found in the supplemental information. Figure 9 shows the change in current at -0.8 V as a function of time for both the Pt/4AMP-VC and Pt/VC electrodes. The currents were normalized to more easily compare the rate of current

loss for each electrode. The black trace of Fig. 9 shows the current loss for the Pt/VC electrode and the red trace shows the current loss for the Pt/4AMP-VC electrode. Clearly the Pt/4AMP-VC had a much slower rate of current loss. After 100 cycles, the current of the Pt/4AMP-VC catalyst was 4.3 times larger than the current of the Pt/VC catalyst. With approximately the same Pt loading, the 4AMP-VC catalysts were more durable than Pt/VC as was expected from previous work with N-doped CNTs [11].

Fig. 9 Change in current at -0.8 V as a function of time for Pt/4AMP-VC (red line) and Pt/VC (black dots). The currents were normalized to more easily compare the rate of current loss for each electrode.

4. Conclusions

We have shown that covalent attachment of 4AMP to amorphous carbon is possible via oxidation of Vulcan® followed by amidation through an acid chloride intermediate. TGA of 4AMP-VC showed a prominent mass loss at 200 °C due to the decomposition of covalently attached 4AMP. FTIR spectra exhibited the characteristic N-H stretch and a commensurate shift of the carbonyl peak to lower wavenumbers upon functionalization with 4AMP. XPS showed N groups were present on the support at roughly 2.6 atomic %.

Upon *in situ* growth of Pt nanoparticles, the O 1s and N 1s XPS signals decrease, suggesting Pt binds to the catalyst support in the vicinity of the 4AMP. The high resolution N 1s XPS data indicates the Pt preferentially binds to the pyridinic N. This provides insight into the binding mechanism of platinum to the nitrogen-containing functional groups and points the way toward further study. In addition, the resulting Pt-decorated 4AMP-VC showed widely disperse Pt nanoparticles with smaller average size than Pt/VC or Pt/O-VC and a very narrow size distribution. Hydrogen adsorption CV confirmed that the small Pt particles on 4AMP-VC exhibited high catalytic surface area and high catalytic activity. Finally, oxygen reduction CV cycled 800 times showed that Pt/4AMP-VC is 4 times more durable than Pt/VC. These electrochemical results suggest that our Pt/4AMP-VC could be utilized as the catalyst layer in a fuel cell with high efficiency and low Pt loading. These studies are currently underway.

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