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Article

New strategy of S,N co-doping of conductive-copolymer-derived carbon nanotubes to effectively improve the dispersion of PtCu nanocrystals for boosting the electrocatalytic oxidation of methanol

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ABSTRACT

Efficacious regulation of the geometric and electronic structures of carbon nanomaterials via the introduction of defects and their synergy is essential to achieving good electrochemical performance. However, the guidelines for designing hybrid materials with advantageous structures and the fundamental understanding of their electrocatalytic mechanisms remain unclear. Herein, superfine Pt and PtCu nanoparticles supported by novel S,N-co-doped multi-walled CNT (MWCNTs) were prepared through the innovative pyrolysis of a poly(3,4-ethylenedioxythiophene)/polyaniline copolymer as a source of S and N. The uniform wrapping of the copolymer around the MWCNTs provides a high density of evenly distributed defects on the surface after the pyrolysis treatment, facilitating the uniform distribution of ultrafine Pt and PtCu nanoparticles. Remarkably, the Pt₁Cu₂/SN-MWCNTs show an obviously larger electroactive surface area and higher mass activity, stability, and CO poisoning resistance in methanol oxidation compared to Pt/SN-MWCNTs, Pt/S-MWCNTs, Pt/N-MWCNTs, and commercial Pt/C. Density functional theory studies confirm that the co-doping of S and N considerably deforms the CNTs and polarizes the adjacent C atoms. Consequently, both the adsorption of Pt₁Cu₂ onto the SN-MWCNTs and the subsequent adsorption of methanol are enhanced; in addition, the catalytic activity of Pt₁Cu₂/SN-MWCNTs for methanol oxidation is thermodynamically and kinetically more favorable than that of its CNT and N-CNT counterparts. This work provides a novel method to fabricate high-performance fuel cell electrocatalysts with highly dispersed and stable Pt-based nanoparticles on a carbon substrate.

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1. Introduction

Direct methanol fuel cells (DMFCs), which are green, easy to transport and store, and high-energy density conversion devices, have been widely investigated in recent years [1,2]. The methanol oxidation reaction (MOR) plays a vital role in determining the efficiency of DMFCs. At present, Pt-based materials are widely considered to be the most effective and commercially available catalysts for the anode process of DMFCs. However, several key obstacles including the scarcity, low effective utilization, and easy poisoning of the noble metal Pt still limit the large-scale application of Pt-based materials [3]. Therefore, the question of how to reduce the cost of Pt-based catalysts, improve their catalytic utilization efficiency, and enhance their electrocatalytic properties presents an intriguing challenge and has become a popular research area in the development of DMFCs. To date, various strategies have been exploited to address the above issues. For example, studies have focused on carbon nanomaterial supports (e.g., carbon nanotubes or graphene) [4–6], alloying with other transition metals [7,8], metal oxide/carbide/sulfide co-catalysts [9–11], and controlling the morphology of the catalytic particles [12,13]. In particular, the performance of Pt-based catalysts mainly depends on the properties of the support and the interactions between catalytic particles and support. Therefore, the supporting materials can significantly affect the dispersibility, utilization efficiency, and even electrocatalytic properties of the metal nanoparticles in the catalyst [14,15]. Although XC-72 carbon-black-supported Pt or PtRu has been commercially used as the anode electrocatalyst for DMFCs, the drawbacks of such carbon black supports (e.g., small pore size and poor stability under electrochemical operating conditions) still prevent them from meeting the practical requirements of high-performance electrocatalysts [16]. In this context, various alternative carbon supports, e.g., mesoporous carbon [17], carbon hollow microspheres [18], carbon fiber [19,20], carbon nanotubes [21], and graphene [22], have been extensively studied and developed. Among such materials, carbon nanotubes (CNTs) have been considered to be ideal catalyst carrier materials due to their outstanding advantages of low cost, excellent electrical conductivity, large surface-to-volume ratio, and high electrochemical stability [23]. However, the chemical inertness of the surfaces of pristine CNTs is unconducive to the deposition and dispersion of catalytic nanoparticles, thereby hindering enhancement of their electrochemical performance [24]. Accordingly, modifying the surfaces of CNTs while maintaining their unique properties remains a challenge for the development of highly efficient CNT-based catalysts.

Theoretical and experimental investigations have demonstrated that doping heteroatoms into CNTs can not only enhance their conductivity and hydrophilicity, but also provide abundant anchoring sites for the deposition of metal nanoparticles [25,26]. Such doped CNTs are expected to be promising electrocatalytic materials for electrochemical energy devices, and, thus, many CNT-based composites doped with foreign heteroatoms such as B [27], N [25,28], P [29], and S [15,30] have been exploited as electrode materials toward methanol

oxidation and oxygen reduction reactions. To date, the most widely studied non-metal dopants have been nitrogen and sulfur [31,32]. The similar atomic radii of N (0.70 Å) and C (0.77 Å) make it easy for N atoms to be doped into the carbon lattice. Additionally, the difference in electronegativity between N (3.04) and C (2.55) can effectively improve the conductivity of N-doped carbon nanomaterials [33]. As for sulfur, its atomic radius (1.04 Å) is obviously larger than that of C, which can result in more defects and induce charge localization in S-doped carbon nanostructures. In particular, it has been found that S and N dual-doped CNTs (SN-CNTs) can present the advantages of both dopants and increase the synergistic electronic effect of various components in the catalysts, thereby improving the electrocatalytic performance [24,26,34,35]. For example, Shi *et al.* [34] utilized aniline and sulfur as sources to synthesize S and N co-doped CNTs (SN-CNTs), which showed augmented oxygen reduction reaction (ORR) activity in both acidic and alkaline electrolytes compared with N-CNTs. Wang *et al.* [35] prepared S and N co-doped CNTs with enhanced oxygen reduction activity by annealing a mixture of thiourea and CNTs. However, most reported SN-CNTs have been synthesized by using small molecular substances with heteroatoms (e.g., NH_3 , urea, thiourea, and CS_2) as the precursors. The weak interactions between the small precursor molecules and CNTs can influence the number and uniformity of the distribution of the heteroatom-based active sites. According to our previous results, conductive polymers such as polyindole (PI) and poly-3,4-ethylenedioxythiophene (PEDOT) can effectively grow and coat the surface of CNTs via an in-situ polymerization route, following which S-doped and N-doped CNTs with uniform sites for the highly efficient anchoring of Pt nanoparticles can be obtained by a pyrolysis procedure [15,28]. Unfortunately, very few studies have focused on the conductive-polymer-based preparation of S and N double-doped carbon nanomaterials and their electrocatalytic applications in fuel cells. Therefore, we herein design and fabricate S and N co-doped multiwalled carbon nanotubes (SN-MWCNTs) via the facile pyrolysis of PEDOT/polyaniline (PANI) copolymer-coated MWCNTs (PEDOT-PANI/MWCNTs). The SN-MWCNTs are then employed as the support for highly efficient Pt or PtCu alloy nanoparticles, which are used as the anode electrocatalyst in DMFCs. Fourier-transform infrared (FTIR), Raman, X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and electrochemical tests were used to ascertain the structure, particle size, morphology, and electrocatalytic MOR behavior of the as-prepared composites. The results show that the co-doping of S and N creates a high density of evenly distributed active sites on the MWCNT surface to achieve the uniform deposition of highly dispersed Pt and PtCu nanoparticles, which can, in turn, enhance the charge transfer interaction from the catalytic nanoparticles to the SN-MWCNT support. The fabricated Pt/SN-MWCNT and $\text{Pt}_{10}\text{Cu}_2$ /SN-MWCNT catalysts exhibit better MOR electrocatalytic activity, durability, and anti-CO poisoning ability than the single-doped MWCNT/supported Pt (e.g., Pt/N-MWCNTs, Pt/S-MWCNTs) and commercial Pt/C catalysts.

2. Experimental

2.1. Materials

The MWCNTs (diameter 40–60 nm, length 5–15 μm , purity 98%) from Shenzhen Nanotech Port Co. Ltd., China, 3,4-ethylenedioxythiophene (EDOT) and Nafion solution (5 wt%) from Sigma-Aldrich, CuSO_4 and sodium dodecyl sulfate (SDS) from Aladdin Reagent Co., Ltd., aniline, ethylene glycol (EG), methanol, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, HNO_3 , and H_2SO_4 from Sinopharm Chemical Reagent Co., Ltd., and a commercial Pt/C catalyst (20 wt%) from Alfa Aesar were of analytical grade and were used as received. Triply distilled water was used to prepare the aqueous solutions.

2.2. Preparation of SN-MWCNTs and PtCu/SN-MWCNTs

Typically, the MWCNTs were firstly pre-acidized as described in a previous report [36], after which they were referred to as AO-MWCNTs. Then, 2.307 g SDS was dissolved into 20 mL triply distilled water under stirring. 20 mg of AO-MWCNTs was ultrasonically dispersed in the above colorless solution for 2 h. Subsequently, 180 μL EDOT and 120 μL aniline were added to the suspension and stirred vigorously (2 h). $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution (20 mL, 0.04 mol L^{-1}) was rapidly injected into the obtained mixture. The mixture was subjected to additional stirring (24 h), and the PEDOT-PANI-coated MWCNT (PEDOT-PANI/MWCNTs) composites were obtained by centrifugation, washed, and finally dried at 60 $^\circ\text{C}$ overnight. Next, the as-obtained PEDOT-PANI/MWCNTs were annealed at 800 $^\circ\text{C}$ for 3 h with flowing Ar in a tube furnace, and the resulting products were labeled as SN-MWCNTs. For comparison, S-MWCNTs (without aniline) and N-MWCNTs (without EDOT) were also prepared by a similar protocol.

To disperse PtCu alloy nanoparticles onto the SN-MWCNT surface, 20 mL of EG containing 20 mg of SN-MWCNTs, 5.2 mg of CuSO_4 , and 797 μL of H_2PtCl_6 solution (0.0193 mol L^{-1}) were mixed to form a uniform suspension under ultrasonication for 2 h. This suspension was then infused to a 30 mL reaction vessel. After hydrothermal treatment at 160 $^\circ\text{C}$ for one day, the final catalyst was obtained after centrifugation, washing, and drying (denoted as $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNTs}$). Simultaneously, we also investigated the effects of various Pt:Cu atomic ratios on the performance of the PtCu alloy catalysts. According to the ICP-MS results, the Pt:Cu ratios of the $\text{Pt}_1\text{Cu}_{0.4}/\text{SN-MWCNTs}$, $\text{Pt}_1\text{Cu}_1/\text{SN-MWCNTs}$, $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNTs}$, and $\text{Pt}_1\text{Cu}_3/\text{SN-MWCNTs}$ were 1:0.43, 1:0.86, 1:1.54, and 1:2.70, respectively, which were in good agreement with the feed ratios. For comparison, Pt/SN-MWCNTs, Pt/S-MWCNTs, and Pt/N-MWCNTs were also prepared by a similar protocol. Additionally, the Pt mass fractions of the as-prepared $\text{Pt}_1\text{Cu}_{0.4}/\text{SN-MWCNTs}$, $\text{Pt}_1\text{Cu}_1/\text{SN-MWCNTs}$, $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNTs}$, $\text{Pt}_1\text{Cu}_3/\text{SN-MWCNTs}$, Pt/SN-MWCNTs, Pt/S-MWCNTs, and Pt/N-MWCNTs as measured by ICP-MS were 18.30%, 11.17%, 7.05%, 10.14%, 19.8%, 17.67%, and 18.33%, respectively, which are close to the raw amounts in the precursor solutions.

2.3. Physical characterizations

A 360 E.S.P. model Nicolet spectrometer, Renishaw-InVia confocal microscopic Raman spectrometer, D/MAX 2500 v/pc X-ray diffractometer, Talos F200S high-resolution transmission electron microscope (HRTEM), and ESCALAB 250Xi XPS system were used to collect the FTIR spectra, Raman spectra, XRD patterns, HRTEM/TEM images, and XPS spectra of the samples, respectively. All the binding energies of the XPS spectra were calibrated according to an internal standard i.e., the reference C 1s at 284.5 eV. The metal contents in the catalysts were detected using a NexION300X inductively coupled plasma mass spectrometry (ICP-MS) system.

2.4. Electrochemical measurements

In the typical three-electrode test system, a platinum foil (1 cm^2), saturated calomel electrode (SCE), and glassy carbon electrode (GCE, diameter 5.0 mm) served as the counter electrode, reference electrode, and working electrode substrate during electrochemical measurements. All the catalyst-modified GCEs were prepared as follows: 3 mg of catalyst was dispersed in 3 mL of triply distilled water and 50 μL of Nafion to form a homogeneous suspension, after which 15 μL of the catalyst suspension was pipetted onto the pre-polished GCE and allowed to dry naturally. The electrocatalytic performance of the catalysts toward MOR was recorded using an electrochemical workstation (CHI 660D), and a 0.5 M CH_3OH + 0.5 M H_2SO_4 solution and a 0.5 M H_2SO_4 solution were used as the electrolytes for methanol oxidation and CO stripping measurements at the requested scan rate. The current density was normalized per mg of Pt.

3. Results and discussion

To confirm the successful synthesis of the PEDOT-PANI/MWCNTs and SN-MWCNTs, these MWCNTs-based composites were first characterized using FTIR. As can be observed from Fig. 1(a), the acid-treated MWCNTs (AO-MWCNTs) show no obvious absorption peak below 1000 cm^{-1} ; the signal peak appearing at 1642 cm^{-1} belongs to the -COOH stretching vibration (black line). In the spectrum obtained for the PEDOT-PANI/MWCNTs (red line), the characteristic peaks at 1540, 1461 and 1307 cm^{-1} are indexed to the stretching vibrations of the quinone ring in PANI, C=C in the benzene ring, and Ar-N (Ar represents an aromatic group), respectively [37]. Additionally, the peaks observed at 1093 and 703 cm^{-1} correspond to the vibration of the C-O-C bond of the ethylene dioxy group and the C-S bond of the thiophene ring of PEDOT, respectively [38]. Interestingly, for the SN-MWCNTs (blue line), the characteristic signals for PEDOT and PANI disappear, indicating that the structure of the PEDOT/PANI copolymer is completely destroyed during the pyrolysis. It is noted that the IR absorption signals for the C-N and C-S bonds can be hardly detected in the SN-MWCNT spectrum, probably due to the low doping content of N and S atoms, which is confirmed in subsequent XPS analysis. The effect of

Fig. 1. (a) FTIR spectra for AO-MWCNTs, PEDOT-PANI/MWCNTs and SN-MWCNTs. (b) Raman spectra of AO-MWCNTs, PEDOT-PANI/MWCNTs and SN-MWCNTs. (c) XRD spectra of Pt/SN-MWCNTs, Pt/N-MWCNTs and Pt/S-MWCNTs. (d) XRD spectra for Pt₃Cu₃/SN-MWCNTs, Pt₂Cu₂/SN-MWCNTs, Pt₁Cu₁/SN-MWCNTs, Pt_{0.4}Cu_{0.4}/SN-MWCNTs and Pt/SN-MWCNTs.

SN-doping on the MWCNT structure was also investigated by Raman spectroscopy. As depicted in Fig. 1(b), all three samples present the D ($\sim 1347\text{ cm}^{-1}$) and G ($\sim 1578\text{ cm}^{-1}$) bands. The disordered D band is related to the degree of defects existing in the MWCNTs, and the G band is related to the sp^2 carbon atom bonding vibration in the graphite layer [13,39]. Furthermore, the G band for the PEDOT-PANI/MWCNTs shows an obvious blue shift of approximately 10 cm^{-1} relative to that for the AO-MWCNTs and SN-MWCNTs, which may be due to the insertion of the PEDOT/PANI copolymer into the bundle of MWCNTs [40]. Generally, the ratio of the D and G peak intensities (I_D/I_G) is an indicator used to evaluate the extent of defects on the MWCNT surface [35]. The I_D/I_G value (~ 0.64) for the PEDOT-PANI/MWCNTs was much higher than that for the AO-MWCNTs (~ 0.49), demonstrating the significantly increased surface disorder of the MWCNTs due to the non-covalent PEDOT/PANI copolymer coating [41]. After the SN-doping of the MWCNTs, the I_D/I_G value was found to be slightly increased to ~ 0.68 , suggesting that the incorporation of S and N atoms further disturbs the surface structure of the MWCNTs.

The numerous defects on the SN-MWCNTs provide abundant active sites, which is beneficial to the deposition of highly dispersed Pt and PtCu nanoparticles. Fig. 1(c) shows the XRD patterns obtained for the Pt/SN-MWCNT, Pt/N-MWCNT, and Pt/S-MWCNT catalysts. It is found that these XRD patterns present five diffraction peaks at 2θ values of 39.8° , 46.4° , 67.6° ,

and 81.6° , corresponding to diffraction from the Pt(111), (200), (220), (311), and (222) planes, respectively [15]. According to the Scherrer formula and the independent Pt(220) diffraction peak, the average particle diameters for Pt/SN-MWCNT, Pt/N-MWCNT, and Pt/S-MWCNT were estimated to be 2.0, 2.2, and 2.6 nm, respectively. This result reveals that the S and N dual-doped MWCNTs are more conducive to improving the dispersion of the supported Pt nanoparticles compared with the single-doped MWCNTs. It is noteworthy that the addition of Cu can obviously change the diffraction peak position of Pt, as revealed in Fig. 1(d). The Pt diffraction peaks are generally shifted to higher 2θ values with increasing Cu content. According to the Bragg formula [42], the lattice parameter for the Pt₃Cu₃/SN-MWCNTs, Pt₂Cu₂/SN-MWCNTs, Pt₁Cu₁/SN-MWCNTs, Pt_{0.4}Cu_{0.4}/SN-MWCNTs, and Pt/SN-MWCNTs was calculated to be 0.3806, 0.3831, 0.3839, 0.3881, and 0.3923 nm, respectively, suggesting that the addition of Cu atoms contracts the Pt lattice and constructs a PtCu alloy nanostructure.

To directly verify the dispersion and deposition of Pt and PtCu nanoparticles on the SN-MWCNT hybrid support, the prepared catalysts were observed using TEM techniques. As exhibited in Figs. 2(a,b), PtCu nanoparticles were densely and evenly deposited on the SN-MWCNTs with a small average size of $\sim 2.87\text{ nm}$. HRTEM characterization (inset of Fig. 2(a)) shows that the lattice spacing for the PtCu nanoparticles (0.22 nm) is smaller than that for the Pt(111) plane (0.23 nm), further suggesting the formation of a PtCu alloy nanostructure [43,44].

Fig. 2. (a,b) TEM images of Pt₁Cu₂/SN-MWCNTs. The insets in (a) and (b) show the corresponding HRTEM images and size distribution histograms, respectively. (c) HAADF-STEM image of Pt₁Cu₂/SN-MWCNTs. (d-h) Element mappings for C, N, S, Pt and Cu.

Figs. 2(c–h) show the HAADF-STEM image and element mappings for the Pt₁Cu₂/SN-MWCNT nanohybrid. The elements C, N, S, Pt, and Cu are uniformly distributed over the entire cata-

lyst surface. Interestingly, the distribution for the element S is very similar to that observed for Pt and Cu, implying the presence of a stronger interaction between the doped S atoms and PtCu nanoparticles as compared to the doped N atoms. This phenomenon is due to the difference in the atomic radii of N and S. The atomic radius (0.70 Å) of N is similar to that of C (0.77 Å), while the atomic radius (1.04 Å) of S is significantly larger than that of C. Therefore, the doped S atoms can create more salutary defects in the MWCNTs and are more conducive to the approach and reduction of the Pt and Cu precursors. In addition, the deposition behavior of the Pt nanoparticles on several different doped MWCNT supports was also compared. Fig. S1 shows typical TEM images of the Pt/SN-MWCNTs, Pt/N-MWCNTs, and Pt/S-MWCNTs. Clearly, more uniform and smaller-sized Pt nanoparticles are observed for the S and N dual-doped MWCNTs (2.3 nm) compared with the other two singly doped MWCNTs (2.55 nm for N-MWCNTs, 2.78 nm for S-MWCNTs). These results demonstrate that the synergistic pairing of the co-doped S and N atoms produces abundant and uniformly distributed active sites on the surfaces of the MWCNTs, which is beneficial for the effective anchoring of catalytic nanoparticles [45].

The elemental composition and the chemical structures of the elements on the catalytic surface were characterized through XPS. Fig. 3(a) presents the XPS spectra for the Pt₁Cu₂/SN-MWCNTs, Pt/SN-MWCNTs, Pt/N-MWCNTs, and Pt/S-MWCNTs. All four catalysts present XPS signal peaks for C 1s and Pt 4d and 4f. Additionally, apparent signals for N 1s (399.8 eV), S 2p (165 eV), and S 2s (228.3 eV) are also observed for the Pt₁Cu₂/SN-MWCNTs and Pt/SN-MWCNTs (curves (1)

Fig. 3. (a) XPS survey spectra for Pt₁Cu₂/SN-MWCNTs (1), Pt/SN-MWCNTs (2), Pt/N-MWCNTs (3) and Pt/S-MWCNTs (4). (b) Cu 2p high-resolution spectrum for Pt₁Cu₂/SN-MWCNTs. Pt 4f high-resolution spectra for Pt₁Cu₂/SN-MWCNTs (c) and Pt/SN-MWCNTs (d).

and (2)) [6,33], further confirming that the N and S atoms are successfully introduced into the MWCNTs. The high-resolution Cu 2p spectrum for the Pt₁Cu₂/SN-MWCNTs (Fig. 3(b)) shows that the Cu 2p spectrum is dominated by metallic Cu⁰ (932.2 and 952.1 eV for Cu 2p_{3/2} and Cu 2p_{1/2}) [46]. The weak intensity of the Cu²⁺ signals and their satellite peaks may be due to partial oxidation by air. The high-resolution spectra measured for S 2p and N 1s in the Pt₁Cu₂/SN-MWCNTs, Pt/SN-MWCNTs, and SN-MWCNTs are shown in Fig. S2. For the Pt₁Cu₂/SN-MWCNTs (Figs. S2(a,b)), the pair of signal peaks near 164.3 and 165.6 eV (S 2p_{3/2} and 2p_{1/2}) is attributed to the C–S–C bond, while the two N 1s signal peaks observed at 398.9 and 400.9 eV originate from pyridinic-N and graphitic-N, respectively [6]. In comparison with the binding energy values for S 2p and N 1s in the SN-MWCNTs (Figs. S2(e,f), and Table S1), the deposition of Pt nanoparticles leads to a slight negative shift (0.2 eV) in the S 2p peak for the Pt/SN-MWCNTs, and the subsequent addition of alloyed Cu leads to an obvious positive shift (0.5 eV) in the S 2p peak for the Pt₁Cu₂/SN-MWCNTs. However, no significant shift occurs in the N 1s peak positions of the three samples. Figs. 3(c,d) show the high-resolution Pt 4f spectra measured for the Pt₁Cu₂/SN-MWCNTs and Pt/SN-MWCNTs, respectively. It is found that all three catalysts show two deconvoluted doublets pointing to two Pt species (i.e., Pt⁰/Pt²⁺ species). Compared to the Pt⁰ state (Fig. S3, 71.3 and 74.8 eV for 4f_{7/2} and 4f_{5/2}) in the Pt/AO-MWCNTs, the Pt⁰ 4f peaks in both the Pt₁Cu₂/SN-MWCNTs (Fig. 3(c), 71.5 and

74.7 eV for 4f_{7/2} and 4f_{5/2}) and Pt/SN-MWCNTs (Fig. 3(d), 71.6 and 75.1 eV for 4f_{7/2} and 4f_{5/2}) are slightly positively shifted. Furthermore, in the high-resolution Pt 4f spectrum of the Pt₁Cu₂/SN-MWCNTs, a pair of Cu 3p peaks is observed to appear at 75.1 and 78.2 eV, probably due to the alloying of Cu into the Pt lattice [47]. The above S 2p, N 1s, and Pt 4f analyses indicate that a stronger charge transfer interaction occurs between the doped S atoms and PtCu nanoparticles, which is in agreement with the HAADF-STEM results.

As mentioned above, the numerous uniform active sites on the SN-MWCNTs can significantly boost the deposition and dispersion of catalytic nanoparticles. To evaluate the number of effective active sites on the SN-MWCNT-based catalysts, we conducted electrochemical cyclic voltammetry (CV) measurements in a 0.5 M H₂SO₄ solution at 50 mV s⁻¹ for the Pt₁Cu₂/SN-MWCNTs, Pt/SN-MWCNTs, Pt/N-MWCNTs, Pt/S-MWCNTs, and commercial Pt/C catalysts. As demonstrated in Fig. 4(a), all the catalysts present CV characteristics representative of Pt-based hybrid materials in an acid electrolyte, with the hydrogen region current appearing in a lower potential window (−0.23 to 0.1 V) and the formation/reduction current for Pt oxides occurring in a higher potential window. According to a previously reported method [48], the electrochemical active surface area (ECSA) values of each catalyst were evaluated based on the integrated coulombic charge (Q_H) of the hydrogen adsorption/desorption region and the formula $ECSA = Q_H / (Q_H^{mono} \times W_{Pt})$, where Q_H^{mono} is the charge (210 μC

Fig. 4. Cyclic voltammograms for Pt₁Cu₂/SN-MWCNTs (1), Pt/SN-MWCNTs (2), Pt/N-MWCNTs (3), Pt/S-MWCNTs (4) and commercial Pt/C (5) catalysts in 0.5 M H₂SO₄ (a) and 0.5 M CH₃OH + 0.5 M H₂SO₄ (b) solutions measured at a scan rate of 50 mV s⁻¹; (c) CO stripping voltammograms for Pt₁Cu₂/SN-MWCNTs (1), Pt/SN-MWCNTs (2), Pt/N-MWCNTs (3), Pt/S-MWCNTs (4) and commercial Pt/C (5) catalysts in 0.5 M H₂SO₄ solution measured at a scan rate of 50 mV s⁻¹; (d) Current-time curves measured at 0.6 V for methanol oxidation on different catalysts in 0.5 M CH₃OH + 0.5 M H₂SO₄ solution.

cm^{-2}) corresponding to a hydrogen adsorption monolayer on polycrystalline Pt, and W_{Pt} represents the Pt loading on a catalyst-modified working electrode. Therefore, the ECSA value for the $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNTs}$ was calculated to be $148.85 \text{ m}^2 \text{ g}^{-1}$, which was much larger than those of the other four catalysts, i.e., $\text{Pt}/\text{SN-MWCNTs}$ ($130.78 \text{ m}^2 \text{ g}^{-1}$), $\text{Pt}/\text{N-MWCNTs}$ ($128.65 \text{ m}^2 \text{ g}^{-1}$), $\text{Pt}/\text{S-MWCNTs}$ ($105.56 \text{ m}^2 \text{ g}^{-1}$), and Pt/C ($54.50 \text{ m}^2 \text{ g}^{-1}$), demonstrating that the S and N dual-doped MWCNTs obviously increase the number of electroactive sites and surface utilization of the noble metal Pt.

For the evaluation of the electrocatalytic performance of the as-prepared PtCu alloy nanoparticles, the effect of the alloyed Cu content on the MOR activity was first investigated. Fig. S4 shows the CV curves obtained for the $\text{Pt}_{1.5}\text{Cu}_{0.4}/\text{SN-MWCNTs}$, $\text{Pt}_{1.5}\text{Cu}_1/\text{SN-MWCNTs}$, $\text{Pt}_{1.5}\text{Cu}_2/\text{SN-MWCNTs}$, and $\text{Pt}_{1.5}\text{Cu}_3/\text{SN-MWCNTs}$ in $0.5 \text{ M CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$ solution at 50 mV s^{-1} . As shown in this figure, all four catalysts present irreversible current peaks for MOR at 0.62 and 0.43 V; the former corresponds to the electro-oxidation of methanol, while the latter is attributed to the elimination of the methanol oxidation intermediates produced during the forward scanning [6]. When the Pt:Cu atomic ratio is 1:2, the obtained alloy catalyst (i.e., the $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNTs}$) possesses the highest electrocatalytic activity for MOR ($1589.9 \text{ mA mg}^{-1}_{\text{Pt}}$). Notably, the MOR mass activity of the $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNTs}$ is also much higher than that of the $\text{Pt}/\text{SN-MWCNTs}$ ($1027.0 \text{ mA mg}^{-1}_{\text{Pt}}$), $\text{Pt}/\text{N-MWCNTs}$ ($801.1 \text{ mA mg}^{-1}_{\text{Pt}}$), $\text{Pt}/\text{S-MWCNTs}$ ($766.3 \text{ mA mg}^{-1}_{\text{Pt}}$), Pt/C ($375.8 \text{ mA mg}^{-1}_{\text{Pt}}$), and other state-of-the-art Pt-based materials (Fig. 4(b) and Table S2). Moreover, the current density ratio (I_f/I_b) for the forward and backward peaks in the CV curves can generally be used to qualitatively evaluate the anti-poisoning ability of the catalyst. The I_f/I_b value for the $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNTs}$ was determined to be 1.34, which is much higher than that found for the $\text{Pt}/\text{SN-MWCNTs}$ (0.74), $\text{Pt}/\text{N-MWCNTs}$ (0.65), $\text{Pt}/\text{S-MWCNTs}$ (0.66), and Pt/C (0.89), implying that the designed $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNT}$ catalyst shows a good poisoning tolerance [13]. To directly evaluate the CO tolerance of the catalysts, we further carried out CO-stripping voltammetry measurements. Fig. 4(c) displays the CO-stripping curves obtained for the $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNTs}$, $\text{Pt}/\text{SN-MWCNTs}$, $\text{Pt}/\text{N-MWCNTs}$, $\text{Pt}/\text{S-MWCNTs}$, and Pt/C in $0.5 \text{ M H}_2\text{SO}_4$ solution. Obviously, for all the catalysts, the hydrogen region current in the first CV scan is completely inhibited due to the saturated adsorption of CO onto the catalytic surface. Following the oxidization elimination of the adsorbed CO, the hydrogen region current reappears in the next CV scan. The onset potential of CO oxidation for the $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNTs}$ is negatively shifted to 0.42 V, which is much lower than other catalysts, such as the $\text{Pt}/\text{SN-MWCNTs}$ (0.44 V), $\text{Pt}/\text{N-MWCNTs}$ (0.47 V), $\text{Pt}/\text{S-MWCNTs}$ (0.50 V), and Pt/C (0.52 V), further manifesting the prominent CO poisoning resistance ability of the $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNTs}$.

The electrochemical durability of the catalysts, which is an important indicator for practical applications, was also systematically investigated using chronoamperometry (CA), CV scanning, and TEM morphology tests. Fig. 4(d) displays the CA curves obtained for the $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNTs}$, $\text{Pt}/\text{SN-MWCNTs}$,

$\text{Pt}/\text{N-MWCNTs}$, $\text{Pt}/\text{S-MWCNTs}$, and Pt/C in $0.5 \text{ M CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$ solution at 0.5 V for 7200 s. Due to the production of toxic intermediates (CO_{ads} , $\text{CH}_3\text{OH}_{\text{ads}}$, and CHO_{ads}) during MOR, all these catalysts present a sharp drop in current in the initial testing stage ($< 200 \text{ s}$). After the 7200 s durability tests, the $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNT}$ catalyst still maintained a high current density ($182.25 \text{ mA mg}^{-1}_{\text{Pt}}$) toward MOR, which was almost 1.4, 2.5, 5.6, and 32.4 times those found for the $\text{Pt}/\text{SN-MWCNTs}$ ($130.56 \text{ mA mg}^{-1}_{\text{Pt}}$), $\text{Pt}/\text{N-MWCNTs}$ ($72.13 \text{ mA mg}^{-1}_{\text{Pt}}$), $\text{Pt}/\text{S-MWCNTs}$ ($32.58 \text{ mA mg}^{-1}_{\text{Pt}}$), and Pt/C ($5.62 \text{ mA mg}^{-1}_{\text{Pt}}$). TEM characterization of the prepared catalysts before and after the 7200 s CA tests further proved that the S and N co-doping of MWCNTs can effectively decrease the agglomeration tendency of the catalytic particles under the electrochemical conditions (Fig. 5). In contrast to the obvious agglomeration of commercial Pt/C , after the 7200 s CA tests, both the $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNTs}$ and $\text{Pt}/\text{SN-MWCNTs}$ almost completely maintained their initial morphology and good dispersion of catalytic particles. Furthermore, the electrochemical cycling durability of the prepared samples was also evaluated in $0.5 \text{ M H}_2\text{SO}_4$. As revealed in Fig. S5, after 500 CV scans, the $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNT}$ and $\text{Pt}/\text{SN-MWCNT}$ hybrids retained 66.4% and 65.35% of their initial ECSA values, respectively; these values are much higher than those found for the $\text{Pt}/\text{N-MWCNTs}$ (61.31%), $\text{Pt}/\text{S-MWCNTs}$ (59.51%), and Pt/C

Fig. 5. TEM images of $\text{Pt}_1\text{Cu}_2/\text{SN-MWCNTs}$ (a,b), $\text{Pt}/\text{SN-MWCNTs}$ (c,d) and commercial Pt/C (e,f) before and after 7200 s chronoamperometry tests in $0.5 \text{ M CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$ solution at a test potential of 0.6 V .

(39.21%). Both the CA and CV results strongly demonstrate that the SN-MWCNTs significantly enhance the long-term electrochemical durability of the supported catalytic nanoparticles compared with the singly doped MWCNTs and commercial Pt/C catalyst.

To understand the mechanism of the performance enhancement of the Pt₁Cu₂/SN-MWCNT catalyst in depth, hybrid density functional theory (DFT) at the B3PW91 level of theory was used to explore the electro-oxidation of methanol catalyzed by the doped MWCNTs; the pseudopotential LANL2DZ was used as a basis set for the heavy metals (Pt and Cu), and 6-31G (d) was used for C, H, O, N, and S. B3PW91 and the present basis sets have been widely used to investigate alcohol oxidation catalyzed by Pt-based bimetallics [49–51]. The S,N-doped CNT was modeled using a 1.4 nm long (5,5) arm-chair single-walled carbon nanotube (C₁₀₀H₂₀N₁₂S₆, SWCNT) with four pyridine nitrogen atoms in the center surrounded by eight graphite nitrogen atoms and six sulfur atoms. Because of its similar atomic radius to C (70 vs. 77 pm), N atoms are well incorporated in the CNT geometry. On the other hand, S atoms considerably deviate from the CNT sidewall due to the larger difference in atomic radius as well as the electronic structure, with an average S–C bond length of around 1.76 Å. The doping of N and S increases both the HOMO and LUMO, which is also true for a simple model, an S,N-doped graphene sheet (C₄₈H₂₂N₆S₄, S,N-Gr, Fig. S6 and Table S3) with four pyridine nitrogen atoms in the center surrounded by two graphite nitrogen atoms and four sulfur atoms. In addition, Fig. 6 shows that the HOMO for pristine CNT is well delocalized over the sidewall, while the frontier orbital becomes rather delocalized for the S,N-doped CNT, in particular over the carbon around the nitrogen and sulfur atoms. The carbon atoms in pristine CNT are almost neutral, while for S,N-CNT and S,N-Gr, the electronegative N (approximately –0.4 e for pyridine and –0.6 e for graphite N) and electropositive S (approximately +0.7 e) polarize the surrounding carbon atoms, leading to positive and negative carbon atoms, respectively.

Based on the optimized MOR performance, Pt₁Cu₂ was used to model the bimetallic catalyst employed in the experiment. Several types of Pt₁Cu₂ adsorption sites were present on the S,N-CNT and C₄₈H₂₂N₆S₄. The adsorption (Gibbs free) energy with zero-point energy correction was calculated according to the following Eq. (1):

$$\Delta E = E(\text{Pt}_1\text{Cu}_2/\text{CNT}) - E(\text{Pt}_1\text{Cu}_2) - E(\text{CNT}) \quad (1)$$

Pt₁Cu₂ shows the strongest adsorption over the four pyridine nitrogen atoms of S,N-CNT with Pt connected to carbon (Fig. S7(a)) ($\Delta E = -4.17$ eV), followed by a single Pt atom adsorbed onto the hollow of the pyridine nitrogen ($\Delta E = -3.92$

and –4.06 eV); the weakest adsorption was found for Pt-S ($\Delta E = -3.01$ eV). The adsorption of Pt₁Cu₂ on the S,N-Gr (Fig. S7(b)) is stronger ($\Delta E = -6.81$ eV), which may be attributed to the flat surface in the latter.

In line with the above analysis that the HOMO becomes more localized due to the doping of S and N into CNT, Table S4 shows that the adsorption of Pt₁Cu₂ on S,N-CNT (S,N-Gr) is much stronger than that on pristine CNT or N-CNT. The high electron density around carbon favors coordination to the LUMO of Pt₁Cu₂. Fig. S8 reveals that the S,N-doped graphene with a higher HOMO is able to enhance the interaction of its HOMO with the LUMO of Pt₁Cu₂, resulting in stronger adsorption. Another primary contribution to the enhanced adsorption is the electrostatic contribution between the charged surface of S,N-CNT (S,N-Gr) and Pt₁Cu₂, which is absent in the case of neutral pristine CNT or a graphene surface. The rather strong adsorption of the Cu–Cu bridge over the four pyridine sites of S,N-CNT can be primarily attributed to the electrostatic attraction between positively charged Cu and negatively charged N.

The electro-oxidation of CH₃OH can be initiated by its adsorption by either hydroxyl or α -hydrogen on the metal cluster Pt₁Cu₂ supported by the doped CNT. Since the pathway through α -hydrogen is much less thermodynamically favorable compared to that through hydroxyl [50], only the adsorption of CH₃OH through hydroxyl was located on the Pt or the Cu atoms. CH₃OH favors adsorption on the Pt to adsorption on the Cu site, and the doped N and S, indeed, indirectly enhance CH₃OH adsorption (Fig. S9).

Gibbs free energy profiles for the electro-oxidation of CH₃OH catalyzed by Pt₁Cu₂ supported by pristine graphene, N-graphene, and S,N-graphene are shown in Fig. 7. As usual, at an external potential of 0 V, one assumes that $G(\text{H}^+ + \text{e}^-) = 1/2G(\text{H}_2)$ at equilibrium at 1 bar of H₂ and 298 K. The Gibbs free energy change (ΔG) for the step $\text{CH}_3\text{O}^*\text{H} \rightarrow \text{CH}_3\text{O}^* + \text{H}^+ + \text{e}^-$, for example, was calculated as Eq. (2):

$$\Delta G = G(\text{CH}_3\text{O}^*) + G(\text{H}^+ + \text{e}^-) - G(\text{CH}_3\text{O}^*\text{H}) \quad (2)$$

Similar to in the adsorption energies discussed above, the adsorption Gibbs free energy for Pt₁Cu₂ is also significantly strengthened due to the doping of S and N into Gr, which implies that the doped Gr can more strongly anchor the catalyst compared to the pristine Gr or N-Gr (ΔG : –6.18 vs. –2.69 and –0.32 eV). As shown in Fig. 7, the complete oxidation of CH₃OH to the adsorbed C*O₂ in all three cases is spontaneous, as reflected by the ΔG values of <0. Oxidation on the S,N-doped graphene is the most thermodynamically favorable path, followed by that on N-doped graphene, with that on pristine graphene being the least favorable path (ΔG : –6.72 vs. –3.31 and –0.80 eV). The first two dehydrogenations for CH₃O*H supported by S,N-Gr proceed with a minor increase in ΔG (~0.3–0.4 eV), and also exhibit an endothermic reaction with a ΔE_0 value of ~7–12 kcal mol^{–1}. The highest ΔG barrier for the S,N-Gr substrate occurs for the formation of the intermediate CHO (0.96 eV). However, for the pristine and N-doped substrates, the second dehydration step to formaldehyde (CH₂O) shows the highest Gibbs free energy barrier of 1.04 and 1.60 eV, respectively. Moreover, a comparison among the highest Gibbs free energy barriers for the stepwise electro-oxidation of CH₃OH clearly

Fig. 6. HOMO of (5,5) CNT (a) and (5,5) S,N-CNT (b) with B3PW91 (isosurface = 0.004).

Fig. 7. Gibbs free energy profile (ΔG) for the electro-oxidation of CH_3OH ($\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$) catalyzed by bimetallic Pt_1Cu_2 supported on Gr (green, top), N-Gr (red, middle) and S,N-Gr (black, bottom).

indicates that the most active catalyst is the bimetallic Pt_1Cu_2 supported by the S,N-doped substrate. The decay of Pt-based catalysts due to CO poisoning is of great concern for CH_3OH oxidation. It is interesting to note that the Gibbs free energy sink due to CO adsorption on Pt_1Cu_2 decreases in the sequence S,N-Gr (0.68 eV) < Gr (0.85 eV) < N-Gr (3.33 eV). This result implies that the co-doping of S, N also relieves the poisoning effect of CO.

4. Conclusions

In summary, we propose a novel strategy to construct sulfur and nitrogen co-doped MWCNTs by taking advantage of PEDOT and PANI co-conductive-polymer-functionalized MWCNTs to support Pt and PtCu nanoalloys. Because of the co-polymer formed by PEDOT and PANI, multiple elemental species can be uniformly wrapped onto the surface of MWCNTs, which, after pyrolysis, provides a high density of uniformly distributed active sites and defects for promoting the even deposition of ultrafine Pt and PtCu nanoalloys. In particular, the as-designed $\text{Pt}_1\text{Cu}_2/\text{S,N-MWCNTs}$ show an obviously increased ECSA value ($\sim 148.85 \text{ m}^2 \text{ g}^{-1}$), higher electrocatalytic activity ($1589.9 \text{ mA mg}^{-1} \text{ Pt}$), stability, and excellent CO tolerance in methanol oxidation compared to the Pt/S,N-MWCNTs , Pt/N-MWCNTs , Pt/S-MWCNTs , and Pt/C . Moreover, DFT calculations demonstrate that the synergistic effects between the Pt_1Cu_2 nanoparticles and S,N-MWCNTs play a crucial role in the promotion of the catalyst performance. The synthesis conditions for the Pt and PtCu nanoparticle catalysts are simple, mild, and controllable, and can be used to greatly reduce costs and improve Pt utilization, providing effective theoretical support for commercial applications.

Conflict of interest

The authors declare no competing interest.

Electronic supporting information

Supporting information is available in the online version of this article.

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Graphical Abstract

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New strategy of S, N co-doping of conductive-copolymer-derived carbon nanotubes to effectively improve the dispersion of PtCu nanocrystals for boosting the electrocatalytic oxidation of methanol

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A conductive copolymer pyrolysis strategy is developed for preparing S,N co-doped carbon nanotubes, which can effectively improve the dispersion of PtCu nanocrystals and the subsequent methanol electrocatalytic oxidation.

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导电共聚物衍化新策略制备硫、氮共掺杂碳纳米管及其对改善PtCu纳米晶分散性与甲醇电催化氧化的促进作用

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摘要: 有效调控碳纳米材料的几何和电子结构的协同效应和缺陷是获得优良电化学性能的关键。然而, 如何设计一种具有优势结构的杂化材料及其电催化机理的认识尚不清楚。本文提出了一种聚(3,4-乙撑二氧噻吩)/聚苯胺导电共聚物热解

策略来制备S和N共掺杂多壁碳纳米管(MWCNTs),发现改变前驱体溶液中两种单体的比例可以调控掺杂MWCNTs中S和N原子的含量与表面活性位结构. S和N的共掺杂明显增大了碳纳米管表面的缺陷程度并暴露出更丰富的活性位点,从而有利于超细Pt和PtCu纳米颗粒的均匀分布和沉积. 透射电镜和扫描透射电镜结果表明,所制备S和N共掺杂MWCNTs(SN-MWCNTs)负载的催化剂中Pt和PtCu纳米颗粒以及掺杂的S和N原子都均匀地分布在MWCNTs上,且沉积的Pt和PtCu纳米颗粒的平均尺寸仅分别为2.30和2.87 nm. X射线光电子能谱结果表明, S和N共掺杂MWCNTs与负载的Pt基纳米颗粒之间存在强烈的电荷转移相互作用,明显改变了贵金属Pt的表面电子结构. 电化学测试结果表明,与Pt/SN-MWCNTs, Pt/N-MWCNTs, Pt/S-MWCNTs和商业Pt/C催化剂相比, Pt₁Cu₂/SN-MWCNTs表现出更大的电化学活性表面积(148.85 m² g⁻¹),更高的甲醇氧化质量活性(1589.9 mA mg_{Pt}⁻¹)、电化学稳定性和抗CO毒化能力. 密度泛函理论研究表明, S和N共掺杂导致碳纳米管极大地变形,同时极化和激活了相邻的C原子. 因此,增强了Pt₁Cu₂纳米颗粒在SN-MWCNTs上的吸附以及随后甲醇分子的吸附. 此外, Pt₁Cu₂/SN-MWCNTs对甲醇氧化的电催化活性均在热力学和动力学上优于相应的CNTs和N-CNTs基材料. 本文提供了一种新颖的在碳基材料上构建高度分散且稳定的Pt基纳米颗粒高性能燃料电池电催化剂的方法.

关键词: 甲醇氧化; 导电共聚物; 双掺杂碳纳米管; Pt基纳米颗粒; 密度泛函理论计算

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