Unzipping of Single-Walled Carbon Nanotube for the Development of Electrocatalytically Active Hybrid Catalyst of Graphitic Carbon and Pd Nanoparticles

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Supporting Information

ABSTRACT: We demonstrate a new approach for the unzipping of single-walled carbon nanotube (SWCNT) in an aqueous solution using the transition metal complex PdCl₂⁻ as a sacrificial chemical scissor and the growth of graphitic-carbon-coated Pd nanoparticles for the electrocatalytic oxidation of formic acid. The chemical unzipping and the growth of Pd nanoparticles involve the spontaneous electron transfer between SWCNT and the metal complex in an aqueous solution at room temperature. The redox potential for SWCNT and PdCl₂⁻ favors the spontaneous electron transfer reaction. The metal complex, in situ generated Pd nanoparticle, and oxygen play vital role in the oxidative unzipping of SWCNT. The Pd nanoparticles have an average size of 11 nm and are coated with the graphitic carbon layer of unzipped SWCNT (UzCNT-Pd). The Pd nanoparticle of the UzCNT-Pd hybrid material has a large electrochemically active surface area of 2.14 cm². The hybrid material exhibits excellent electrocatalytic activity toward the oxidation of formic acid. The area and mass specific activity are significantly higher than those of the traditional carbon-supported Pd nanoparticle. The synergistic effect of graphitic carbon and the metal nanoparticles controls the catalytic activity. The confinement of Pd particles inside the graphitic carbon enhances the overall performance of the catalyst.

INTRODUCTION

Graphene, the one-atom-thick, two-dimensional honeycomb carbon network has received immense interest owing to the unique properties.1-3 The high mechanical strength, excellent electrical conductivity, and large surface area made it a wonder material for various applications. Graphene-based materials including the hybrid material derived from graphene/reduced graphene oxide (rGO) and metal/metal oxide/metal nitride/metal sulfide nanoparticles have been extensively used in electrocatalysis. For instance, the hybrid materials derived from rGO and metals, metal oxides/hydroxides, carbides, nitrides, etc. have been well exploited for the development of electrocatalytic interfaces, sensors, biosensors, energy conversion, and storage devices by taking advantage of the high electrical conductivity of graphene and mechanical stability.4-8 The ideal integration of graphene/rGO and metal or metal oxide nanoparticles significantly enhances the overall performance of the hybrid possibly due to synergistic effect.9,10 However, the quality of graphene/rGO has significant contribution to the catalytic activity.11 The presence of defects and oxygen-containing functionalities in rGO and debris along with the rGO layers can limit the performance of the material.12 Moreover, the restacking of individual graphitic layers due to π−π* interaction significantly alters the properties.

Carbon nanotubes (CNTs) are made of graphene sheets seamlessly rolled into a concentric tube. The unzipping of carbon nanotube (CNT) is a promising approach to obtain high-quality graphene nanoribbon or graphene nano-strips. Several methods, including chemical oxidation, electron beam, steam and plasma etching, hydrothermal, electrochemical, intercalation, etc., have been documented in the literature for the unzipping of CNTs.13-20 In the chemical oxidation method, the overoxidation of edges generates defects and a large number of oxygen-containing functionalities. The nature of the oxidizing agent actually controls the unzipping of CNT as well as the defects in the graphene sheet. The hybrid material based on metal nanoparticle and unzipped CNT can be a promising catalyst for electrocatalytic applications. The in situ growth of metal nanoparticles and unzipping of CNT will ensure the ideal integration of the metal nanoparticle with the honeycomb carbon network and the possible encapsulation of metal particles with graphitic carbon layer. Moreover, presence of nanoscale metal particles can effectively prevent the restacking of individual carbon nanolayers. Such hybrid materials and carbon-encapsulated catalysts are expected to be electrocatalytically highly active due to possible synergistic effect.4-9,21,22 The metal and metal oxide nanoparticles encapsulated in graphitic carbon are very promising for...
The confinement of catalyst particles into the carbon layer assures the long-time stability and durability during catalytic process. The electronic interaction between the graphitic layers and the metal catalyst contributes to enhanced activity. The loss of surface area due to aggregation of the catalyst particles and the unwanted adsorption of the reactant/product can be avoided with such encapsulated catalyst. In an attempt to synthesize an electrocatalytically active hybrid material of honeycomb carbon network and Pd nanoparticles, we developed a new one-pot approach using a single-walled CNT (SWCNT) and Pd complex. The unzipping of SWCNT and the synthesis of hybrid material are achieved at room temperature without using any harsh oxidizing agent. Although several unzipping methods have been developed, including the metal-assisted unzipping procedure in the presence of harsh oxidizing agent, to the best of our knowledge, this is the first report that describes the use of Pd-based metal complex as a sacrificial chemical scissor and the one-pot synthesis of hybrid electrocatalyst of unzipped SWCNT and Pd nanoparticles in the absence of any additional oxidizing agent for electrocatalytic application.

**RESULTS AND DISCUSSION**

**Unzipping of SWCNT and Characterization of Hybrid Catalyst.** The synthesis of UzCNT-Pd hybrid catalyst involves the K₂PdCl₄-assisted unzipping of SWCNT and the growth of Pd nanoparticles, as shown in Figure 1. It is known that SWCNTs can undergo redox reaction with metal ions of suitable redox potential and such a galvanic displacement reaction has been exploited for the electroless deposition of metal nanoparticles. The redox potential of SWCNT is +0.5 V (standard hydrogen electrode) and, in principle, the metal ions having the reduction potential >0.5 V can undergo spontaneous galvanic displacement reaction with SWCNTs in an aqueous condition.
solution.\textsuperscript{28,29} Dai’s group has explored the deposition of metal nanoparticles on CNTs without any reducing agents. The galvanic displacement reaction between CNT and the metal precursors yields metal nanoparticles. However, the oxidative cleavage/opening of CNT has not been noticed earlier. In our case, the reduction potential of PdCl\textsubscript{4}\textsuperscript{2−}/Pd redox couple (0.599 V) is higher than that of SWCNT and hence a spontaneous electron transfer between SWCNT and PdCl\textsubscript{4}\textsuperscript{2−} is expected. Such an electron-transfer reaction converts the metal complex into metal atom without any additional reducing agent. The subsequent nucleation and growth produces Pd nanoparticles. On the other hand, the spontaneous electron-transfer reaction oxidatively unzips the SWCNT. To follow the unzipping and the growth of Pd nanoparticles, the TEM measurements have been performed at different time intervals (Figure 2). The length of purified SWCNT is > 5 μm and the integrity of SWCNT does not change during the purification process by acid treatment (Figure S1). However, significant change in the morphology was observed after the treatment with PdCl\textsubscript{4}\textsuperscript{2−}. For instance, the sample collected at 12 h of the reaction evidences the growth of Pd nanoparticles without any significant change in the morphology of SWCNT. Partial unzipping of SWCNT is noticed when the reaction time is increased to 24 h and complete unzipping is observed in 48 h. It should be mentioned here that no such morphological change is noticed in the absence of Pd complex, indicating the vital role of the complex. The in situ produced Pd nanoparticles are not uniform in size. Although few particles have the size of >25 nm, most of the Pd nanoparticles are coated with a graphene layer (Figure 2D). The in situ produced Pd nanoparticles are not uniform in size. The high-resolution TEM (HRTEM) image shows that the Pd particles are coated with a graphene layer (Figure 2D–F). Because the diameter of SWCNT is 2 nm, the unzipped CNT sheet from a single SWCNT cannot encapsulate the Pd particle. However, as the length of SWCNT is >5 μm, the UzCNT sheets from two or more SWCNTs can encapsulate/coat the Pd nanoparticles. The fringe spacing of Pd nanoparticle corresponds to (111) plane of face centered cubic lattice. The spotty selected area electron diffraction (SAED) pattern shows the crystalline nature of the Pd nanoparticles. The lattice fringe spacing of the graphitic carbon in the hybrid catalyst is measured to be 0.37 nm, which is close to that of the other unzipped CNT available in the literature.\textsuperscript{30} The X-ray diffraction (XRD) measurements show (Figure 3) characteristic diffractions at 40.12, 46.65, 68.04, 81.91, and 86.42° corresponding to the (111), (200), (220), (311), and (222) planes of face-centered cubic Pd (JCPDS 46-1043). The broad diffraction observed at ~23.34° is ascribed to the graphitic carbon network of the unzipped SWCNT. The TEM image of physical mixture of SWCNT/Pd (experimental section for details) shows the Pd nanoparticles have an average size of 10 nm (Figure S1).

To further ascertain the unzipping of SWCNT and the growth of Pd nanoparticles, X-ray photoelectron spectroscopy (XPS) measurements have been performed. Figure 4A is the surface survey scan profile of a UzCNT-Pd hybrid material. Characteristic signatures for Pd, C, and O are obtained. The deconvoluted C 1s spectra of both purified SWCNT and UzCNT-Pd hybrid material show the presence of C≡C (283.9 eV), C−C (284.5 eV), and C−O (285.46 eV).\textsuperscript{31} The (π−π*) shakeup satellite characteristic of delocalized π-conjugation is observed at 290.1 eV.\textsuperscript{32} However, in the case of UzCNT-Pd, a significant decrease (32−47%) in the ratios (C=C/C−C) and (C=C/C−O) of the areas corresponding to C≡C, C−C, and C−O compared to the purified SWCNT is noticed. Such a decrease implies the increase in C−C and C−O in the carbon network due to the unzipping of SWCNT. The high-resolution Pd 3d XPS profile (Figure 4B) shows the characteristic 3d\textsubscript{5/2} and 3d\textsubscript{3/2} signatures corresponding to the metallic Pd at 335.5 and 340.8 eV, respectively.\textsuperscript{33} A close look at the Pd 3d profile of UzCNT-Pd shows a slight downshift (~0.4 eV) with respect to SWCNT/Pd (Figure S2), suggesting a decrease in the D-band center.\textsuperscript{34,35} Such a downshift can weaken the chemisorption of oxygen-containing species and favor the facile oxidation of formic acid. The chemical unzipping of SWCNT is known to increase the defects by decreasing the sp\textsuperscript{3} domain. Raman spectroscopy is a powerful technique to characterize the ordered and disordered environments in the carbon network.\textsuperscript{32} In a typical Raman spectral profile of graphene or rGO, the D-band is ascribed to the defects introduced into the sp\textsuperscript{2} hybridized carbon networks and the intensity of this band is proportional to the defects concentration.\textsuperscript{36} The G-band arises from the E\textsubscript{2g} vibrational mode of sp\textsuperscript{2}-carbon network. The ratio of the intensity (I\textsubscript{D}/I\textsubscript{G}) can be used as a qualitative measure of the defects in the carbon network.\textsuperscript{37} As shown in Figure 5A, the I\textsubscript{D}/I\textsubscript{G} ratio of the UzCNT-Pd is ~4 times higher than that of the as-purchased and purified SWCNT possibly due to the generation of oxygen-containing functionalities. Furthermore, the chemical unzipping affects its regular tubular structure, as seen from the TEM images (Figure 2B,C) and observable increase in the intensity of D-band is noticed and hence the I\textsubscript{D}/I\textsubscript{G} ratio. The Fourier transform infrared (FTIR) spectral profile evidences the increase in the intensity of the bands corresponding to the oxygen-containing functionalities such as carboxyl C≡O (~1720 cm\textsuperscript{−1}), epoxy C−O (~1220 cm\textsuperscript{−1}), alkoxy C−O (~1100 cm\textsuperscript{−1}), and hydroxyl −OH (~3410 cm\textsuperscript{−1}), further confirming the oxidative unzipping of SWCNT (Figure 5B). The presence of C=C band (~1650 cm\textsuperscript{−1}) in the FTIR spectral profile reveals that the graphitic structure is retained upon unzipping, though a slight decrease in band intensity at 1650 cm\textsuperscript{−1} is observed.\textsuperscript{3,5,15,58} Such a decrease in the intensity is in agreement with the Raman spectral measurements. The new peaks observed at 2860 and 2930 cm\textsuperscript{−1} are ascribed to sp\textsuperscript{3} C−H stretching vibration.

Time-dependent UV−vis spectral measurement is performed to confirm the reduction of PdCl\textsubscript{4}\textsuperscript{2−} to Pd(0). PdCl\textsubscript{4}\textsuperscript{2−} is known to show a strong absorption in the tail end of the UV region (200−270 nm) and a weak absorption at ~413 nm.\textsuperscript{39} A
gradual decrease in the spectral bands in the visible and UV regions corresponding to $\text{PdCl}_4^{2-}$ was noticed during the reaction (Figure 6A), indicating that the metal complex is consumed during the reaction. The disappearance of the characteristic signature of metal complex confirms the reduction of metal complex (Figure 6A). It may be argued that the decrease in the absorbance could be due to the irreversible adsorption of $\text{PdCl}_4^{2-}$ onto the SWCNT surface. Although such an adsorption of the complex on the surface of SWCNT may not be ruled out, no spectral signature for the adsorbed complex is noticed, ascertaining that the decrease in the absorbance is actually due to the reduction of the complex to Pd(0). It is worth pointing out here that no observable decrease in the absorbance is noticed when the reaction is conducted in an inert atmosphere (Figure 6B), suggesting that (i) PdCl$_4^{2-}$ does not irreversibly adsorb on SWCNT and (ii) atmospheric oxygen has role in the unzipping and reduction of the PdCl$_4^{2-}$. The palladium-catalyzed cleavage of the C–C double and triple bonds in the presence of oxygen has been demonstrated in the past. In our case, although the detailed mechanism of unzipping is not well understood in the present stage, it is considered that the room temperature oxidative cleavage of SWCNT could be similar to the Pd-catalyzed C–C cleavage of the alkene-involving PdCl$_4^{2-}$, in situ generated Pd(0), and oxygen. The metal complex, in situ generated Pd

Figure 4. XPS surface survey scan (A), deconvoluted high-resolution Pd 3d (B), and C 1s (C) spectral profile of UzCNT-Pd. Deconvoluted C 1s spectra of purified SWCNT is shown in (D).

Figure 5. Raman (A) and FTIR spectral profiles (B) of SWCNTs and UzCNT-Pd.
nanoparticles, and oxygen play important role in the oxidative scissoring of SWCNT.

**Electrocatalytic Oxidation of Formic Acid.** The electrochemical oxidation of formic acid on metal electrode surface can follow either (i) dehydration or (ii) dehydrogenation pathway, depending on the nature of the electrode material. The dehydration pathway involves the generation of a poisonous surface-adsorbed intermediate, CO. The dehydrogenation pathway produces CO2 by the direct oxidation of formic acid. The latter pathway is preferred, as it does not involve catalyst poisoning. The traditional Pt catalyst is known to follow the dehydration pathway, whereas the Pd-based catalysts favor the dehydrogenation pathway. Because the carbon-supported catalysts are known to show high catalytic activity and the Pd-based catalysts promote the dehydrogenation pathway for the electrochemical oxidation of formic acid, we have exploited the UzCNT-Pd hybrid material for the oxidation of formic acid. The hybrid material shows the characteristic voltammetric signature corresponding to the surface oxide formation and its reduction and hydrogen

Figure 6. (A) Time-dependent spectral profile obtained during the unzipping of SWCNT. (B) Spectral profile of K2PdCl4 illustrating the role of oxygen in the unzipping of SWCNT.

Figure 7. Characteristic cyclic voltammetric (A) and CO stripping profiles (B) of UzCNT-Pd, SWCNT/Pd, rGO/Pd, and Pd in 0.5 M H2SO4 at a scan rate of 50 mV s⁻¹. CO stripping was performed in CO saturated electrolyte.

Figure 8. Cyclic voltammograms illustrating the electrocatalytic activity of UzCNT-Pd hybrid catalyst toward formic acid oxidation in 0.5 M H2SO4 at a scan rate of 50 mV s⁻¹. The area- and mass-normalized current is shown in (A) and (B).
ad sor ption and desorption (Figure 7A). The careful analysis of the voltammetric profiles reveals that the potential corresponding to surface oxide reduction on the UzCNT-Pd is more positive (∼60 mV) compared to as-synthesized unsupported Pd nanoparticle. Such a shift can be ascribed to the reduced oxophilicity and weak bonding of oxygen-containing species, such as OHad and COOad on the surface of Pd nanoparticle.34,35,42 The graphitic carbon confinement of the Pd nanoparticle plays an important role in controlling the surface property of the nanoparticles. The electrochemically accessible surface area (ECSA) of Pd is estimated by the CO-stripping method.35,43 The magnitude of the stripping peak is proportional to the ECSA of Pd nanoparticles, and the charge associated with the stripping (Figure 7B) of adsorbed CO (QCO) is used to calculate the surface area.44 The ECSA of Pd in UzCNT-Pd, SWCNT/Pd, rGO/Pd, and unsupported as-synthesized Pd nanoparticles are calculated to be 2.14, 1.21, 1.02, and 0.8729 cm², respectively. The CO-stripping peak potential of UzCNT-Pd is significantly less positive (∼60 mV) than that of the as-synthesized unsupported Pd nanoparticles, indicating the facile oxidation of CO due to weak adsorption. It is well known that the CO tolerance of catalysts plays an important role in achieving facile electron transfer for the oxidation of formic acid. On Pd-based electrocatalyst, CO is formed during the electrochemical reduction of in situ generated CO₂ rather than through the dehydration pathway of formic acid oxidation.35,46 The CO-tolerant electrocatalysts are highly preferred for the development of formic acid fuel cell. The catalyst that weakly binds to CO or favors the facile oxidation of CO at a less positive potential has a high tolerance toward poisoning CO species. As discussed earlier, the downshift in the d-band center weakens the binding of CO on the surface of Pd nanoparticles of UzCNT-Pd hybrid material.47

Figure 8 illustrates the electrocatalytic response of the hybrid material toward the oxidation of formic acid. The large anodic peak obtained while sweeping from a less positive to a more positive potential corresponds to the oxidation of formic acid. As can be seen, only one voltammetric peak is noticed, suggesting that the hybrid material promotes the dehydrogenation pathway for the oxidation of formic acid. The electrocatalytic activity is evaluated in terms of the onset potential and current density. The hybrid catalyst shows the onset and the oxidation peak potential in the forward sweep at 183 and 620 mV, respectively. The ECSA and mass-normalized current density at the potential of 0.62 V is found to be 117 mA cm⁻² and 1.995 A mgPd⁻¹, respectively. This is significantly higher (3–6 times) than those of the SWCNT/Pd and as-synthesized unsupported Pd nanoparticles, highlighting the high electrocatalytic activity of the hybrid material. To highlight the electrocatalytic activity of the hybrid material, the formic acid oxidation has also been performed with SWCNT/Pd, unsupported as-synthesized Pd, and rGO/Pd (Figures 8 and S3). The ECSA and mass-normalized current density on the hybrid material are significantly higher than those of SWCNT/Pd, unsupported as-synthesized Pd, and rGO/Pd nanoparticles, further highlighting the excellent catalytic activity of the hybrid material. The electrocatalytic activity of the hybrid material is largely dependent on the mass loading on the electrode surface (Figure S4). The effect of mass loading on the catalytic activity is evaluated in terms of mass-normalized current density in the forward sweep at the potential of 0.62 V. A high mass activity and a less positive oxidation peak potential are obtained at a mass loading of 0.0247 mgPd cm⁻².

The electrocatalytic response of the UzCNT-Pd hybrid material is highly stable; the peak current and peak potential do not change upon repeated sweeps. To further evaluate the stability of the electrode, amperometric measurements at the potential of 620 mV for 3600 s are performed (Figure S5) and then the same electrode is subjected to voltammetric experiment for the oxidation of formic acid. Unlike the as-synthesized unsupported Pd and SWCNT-supported Pd nanoparticles, the amperometric response at the UzCNT-Pd hybrid materials is highly stable for a long time. Moreover, the shape of the voltammogram, peak current, and oxidation peak potential does not change significantly (Figure S5) even after subjecting to amperometric experiment. The hybrid material retains 94% of the initial current even after subjecting to chronocoulometric measurements for 3600 s, implying the durability of the catalyst; it does not undergo poisoning during the oxidation of formic acid. The high stability can be attributed to the ideal integration of Pd nanoparticles and the UzCNTs. The UzCNT layer on the Pd nanoparticles ensures the enhanced durability and overall electrocatalytic performance. In the case of SWCNT/Pd and as-synthesized unsupported Pd, ∼15–20% drop in the initial current is noticed, suggesting the lack of durability of these catalysts. Although SWCNT/Pd has a carbon support, it cannot retain the initial catalytic activity, possibly due to the loss of surface area by the aggregation of Pd nanoparticles. In terms of mass-specific activity, the performance of our hybrid catalyst is superior to that of the other Pd-based catalysts available in the literature (Table S1). For instance, Matsumoto’s group has prepared recently carbon-supported Pd/Pb intermetallics and achieved a mass-normalized current density of ∼4.5 mA mgPd⁻¹.45 Zhang’s group obtained a mass-normalized activity of 1655.7 ± 74.6 mA mgPd⁻¹ with PdCu bimetallic alloy.46 Sun’s group achieved a mass activity of ∼1600 mA mgPd⁻¹ using tungsten oxide nanorod-supported Pd nanoparticles.47 The ternary Pd-Ni-P/CNT hybrid catalyst exhibits a mass activity of 1457 mA mgPd⁻¹.50 Feng’s group achieved 1250 mA mgPd⁻¹ with the core–shell Au@AuPd catalyst.49 Our hybrid catalyst exhibits a high mass- and area-normalized current density and has a high durability compared to the bimetallic and intermetallic electrocatalysts. The graphitic confinement prevents the sintering of Pd nanoparticles during the electrocatalytic reaction and enhances the overall catalytic performance.

## SUMMARY

A new approach for the unzipping of SWCNT and the synthesis of electrocatalytically active hybrid catalyst based on the unzipped SWCNT and Pd nanoparticle is demonstrated for the first time. The present approach does not involve the use of harsh oxidizing agent for the unzipping of SWCNT. The PdCl₂ complex, in situ generated Pd nanoparticles, and oxygen are involved in the oxidative unzipping of SWCNT. The method presented here has the advantage of producing graphitic-carbon-coated electrocatalytically active Pd nanoparticle and unzipped CNT in one pot. The electrocatalytic performance is evaluated with the oxidation of formic acid. Unlike the traditional carbon-supported Pd nanoparticles, the hybrid material has a high electrocatalytic activity and efficiently catalyses the oxidation of formic acid. The synergistic effect of unzipped SWCNT and nanosize Pd nanoparticles facilitates the electron transfer for the oxidation of formic acid. The
confinement of Pd nanoparticles inside the graphitic carbon layer actually plays an important role in enhancing the overall electrocatalytic performance.

**MATERIALS AND METHODS**

**Materials.** SWCNT of ∼2 nm diameter and 5–15 μm length was purchased from TCI (Japan) chemicals. Potassium tetrachloropalladate (K₂PdCl₄), Nafion (5% in lower aliphatic alcohol), and formic acid were obtained from Sigma-Aldrich. All of the other chemicals were of analytical grade. All of the solutions used in this investigation were prepared with Millipore water (Milli-Q system).

**Instrumentation.** Transmission electron microscopy (TEM) images of the nanoparticles are obtained with FEI-TECNAI G2 20S-TWIN electron microscope operating at 200 kV voltages. Carbon-coated copper grids (400 mesh) were used to prepare the TEM sample. X-ray diffraction (XRD) analysis was performed with a Bruker D8 advance unit using Cu Kα (λ = 1.54 Å) radiation. X-ray photoelectron spectroscopy (XPS) analysis was carried out with custom-built laboratory version ambient pressure photoelectron spectrometer (Lab-APPES). Raman spectra were acquired using 488 nm argon–krypton mixed ion gas laser (power 80 mW) as an excitation source in backscattering geometry, equipped with a single monochromator (model T64000, Jobin Yvon Horiba, France) with an objective × 100 diameter. Fourier transform infrared (FTIR) spectroscopic measurements were performed with a Perkin-Elmer FTIR spectrophotometer RX1. Electronic absorption spectra were recorded using a CARY 5000 UV–vis–NIR spectrophotometer. All of the electrochemical experiments were performed with a CHI643B electrochemical analyzer attached to a Faraday cage/picoampere booster (CH Instruments, Austin, TX). A two-compartment three-electrode cell with glassy carbon (GC) working, Pt wire auxiliary, and Ag/AgCl reference electrodes was used for electrochemical measurements. All of the potentials are referred against reversible hydrogen electrode.

**Purification of SWCNT.** The as-purchased SWCNT was purified by acid treatment. Typically, SWCNT (2.5 mg) was dispersed in 5 mL HNO₃ solution (1 M) and sonicated for 1 h to remove the impurities. The purified SWCNT was collected by centrifugation after repeated washing with copious amount of Millipore water.

**Unzipping of SWCNT and Synthesis of Hybrid Catalyst.** In a typical procedure, purified SWCNT (0.5 mg mL⁻¹) was dispersed in 5 mL H₂O by ultrasonication. An aqueous solution of K₂PdCl₄ (5 μM) was then added to the dispersion under constant stirring and the stirring was continued for 48 h at room temperature. The product (UzCNT-Pd) was then collected at different time intervals (12, 24, and 48 h) by centrifugation and washed with water and dried under vacuum. The supernatant solution was collected and characterized with UV–vis measurement to check the presence of Pd complex. The SWCNT-supported Pd nanoparticle (SWCNT/Pd) was synthesized according to the following procedures. An aqueous solution of K₂PdCl₄ (5 mM) was mixed with the required amount of reducing agent NaBH₄ under constant stirring. The Pd nanoparticle was then mixed with an aqueous dispersion of SWCNT (0.5 mg mL⁻¹) under stirring in a magnetic stirrer for 12 h. The mixture was centrifuged to collect SWCNT/Pd and dried under vacuum before subjecting to further analysis. The reduced graphene oxide (rGO)-supported Pd nanoparticle (rGO/Pd) was prepared in two steps. Graphene oxide (GO) was first reduced to rGO by conventional borohydride reduction method. In a typical procedure, NaBH₄ (200 mg) was slowly added to the GO dispersion in H₂O (1 mg mL⁻¹) and stirred for 20 min. The black product was then collected by centrifugation and dried in vacuum. The rGO/Pd was obtained by mixing the required amount of Pd nanoparticles with an aqueous rGO dispersion (0.5 mg mL⁻¹) and stirring the mixture for 12 h. The rGO/Pd was collected by centrifugation and dried in vacuum.

**Electrode Modification.** GC electrodes of diameter 3 mm were polished well with alumina slurry of 0.7 and 0.3 μm to obtain a mirror finish surface. The polished electrode was sonicated in Millipore water for 2–3 min and thoroughly rinsed with Millipore water and used for modification. The catalyst ink was prepared by mixing the hybrid materials (0.2 mg) with 200 μL of Nafion solution and sonicated for 60 min. Nafion solution was prepared by adding Nafion (100 μL) to the 3:2:1 mixture of ethanol/dimethylformamide/water (900 μL). Then, the catalyst ink (5 μL) was drop-casted on the cleaned GC electrode and dried at ambient condition. The mass loading of the hybrid catalyst on the electrode surface was calculated to be 0.0247 mgpd cm⁻².

**ASSOCIATED CONTENT**

**Supporting Information**

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Additional figures and table as mentioned (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Wu, J.; Pisula, W.; Müllen, K. Graphenes as Potential Material for Electronics. *Chem. Rev.* 2007, 107, 718–747.

(2) Randviir, E. P.; Brownson, D. A. C.; Banks, C. E. A decade of graphene research: production, applications and outlook. *Mater. Today* 2014, 17, 426–432.

(3) Neto, A. H. C.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. The electronic properties of graphene. *Rev. Mod. Phys.* 2009, 81, 109–162.

(4) Xie, J. L.; Guo, C. X.; Li, C. M. Construction of one-dimensional nanostructures on graphene for efficient energy conversion and storage. *Energy Environ. Sci.* 2014, 7, 2559–2579.

(5) Bonaccorso, F.; Colombo, L.; Yu, G.; Stoller, M.; Tzortzakis, S.; Ferrari, A. C.; Ruoff, R. S.; Pellegrini, V. 2D materials. Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage. *Science* 2015, 347, No. 6265.
(6) Duan, J.; Chen, S.; Jaroniec, M.; Qiao, S. Z. Heteroatom-doped graphene-based materials for energy-relevant electrocatalytic processes. ACS Catal. 2015, 5, 5207−5234.

(7) Peng, L.; Zhu, Y.; Li, H.; Yu, G. Chemically integrated inorganic-graphene two-dimensional hybrid materials for flexible energy storage devices. Small 2016, 12, 6183−6199.

(8) Shao, T.; Wang, J.; Wu, H.; Liu, J.; Aksay, I. A.; Lin, Y. Graphene Based Electrochemical Sensors and Biosensors: A Review. Electroanalysis 2010, 22, 1027−1036.

(9) Raj, C. R.; Samanta, A.; Noh, S. H.; Mondal, S.; Okajima, T.; Ohsaka, T. Emerging new generation electrocatalysts for the oxygen reduction reaction. J. Mater. Chem. A 2016, 4, 11156−11178.

(10) Bag, S.; Roy, K.; Gopinath, C. S.; Raj, C. R. Facile single-step synthesis of nitrogen-doped reduced graphene oxide-MnO2 hybrid functional material for the electrocatalytic reduction of oxygen. ACS Appl. Mater. Interfaces 2014, 6, 2692−2699.

(11) Xia, B. Y.; Yan, Y.; Wang, X.; Lou, X. W. Recent progress on graphene-based hybrid electrocatalysts. Mater. Horiz. 2014, 1, 379−399.

(12) Li, X.; Yang, X.; Jia, L.; Ma, X.; Zhu, L. Carbonaceous debris that resided in graphene oxide/reduced graphene oxide profoundly affect their electrochemical behaviors. Electrochem. Commun. 2012, 23, 94−97.

(13) Kopyinkaj, D. V.; Higginbotham, A. L.; Sinitski, A.; Lomeda, J. R.; Dimiev, A.; Price, B. K.; Tour, J. M. Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons. Nature 2009, 458, 872−876.

(14) Jiao, L.; Zhang, L.; Wang, X. R.; Diankov, G.; Dai, H. Narrow graphene nanoribbons from carbon nanotubes. Nature 2009, 458, 877−880.

(15) Zhuang, N.; Liu, C.; Jia, L.; Wei, L.; Cai, J.; Guo, Y.; Zhang, Y.; Hu, X.; Chen, J.; Chen, X.; Tang, Y. Clean unzipping by steam etching to synthesize graphene nanoribbons. Nanotechnology 2013, 24, No. 32.

(16) Jiao, L.; Zhang, L.; Ding, L.; Liu, J.; Dai, H. Aligned graphene nanoribbons and crossbars from unzipped carbon nanotubes. Nano Res. 2010, 3, 387−394.

(17) Shinde, D. B.; Majumder, M.; Pillai, V. K. Counter-ion dependent, longitudinal unzipping of multi-walled carbon nanotubes to highly conductive and transparent graphene nanoribbons. Sci. Rep. 2014, 4, No. 4363.

(18) Shinde, D. B.; Debupta, J.; Kushwaha, A.; Aslam, M.; Pillai, V. K. Electrochemical unzipping of multi-walled carbon nanotubes for facile synthesis of high-quality graphene nanoribbons. J. Am. Chem. Soc. 2011, 133, 4168−4171.

(19) Li, Y.-S.; Liao, J.-L.; Wang, S.-Y.; Chiang, W.-H. Intercalation-assisted longitudinal unzipping of carbon nanotubes for green and scalable synthesis of graphene nanoribbons. Sci. Rep. 2016, 6, No. 22755.

(20) Yang, M.; Hu, L.; Tang, X.; Zhang, H.; Zhu, H.; Fan, T.; Zhang, D. Longitudinal splitting versus sequential unzipping of thick-walled carbon nanotubes: Towards controllable synthesis of high-quality graphitic nanoribbons. Carbon 2016, 110, 480−489.

(21) Yazdi, A. Z.; Fei, H.; Ye, R.; Wang, G.; Tour, J.; Sundararaj, U. Boron/Nitrogen co-doped helically unzipped multiwalled carbon nanotube as efficient electrocatalyst for oxygen reduction. ACS Appl. Mater. Interfaces 2015, 7, 7786−7794.

(22) Li, X.; Li, T.; Zhong, Q.; Du, K.; Li, H.; Huang, J. Chemical unzipping of multiwalled carbon nanotubes for high-capacity lithium storage. Electrochim. Acta 2014, 125, 170−175.

(23) Tavakkoli, M.; Kallio, T.; Reynaud, O.; Nasibulin, A. G.; Johans, C.; Saino, J.; Jiang, H.; Kauppinen, E. L.; Laasonen, K. Single-shell carbon encapsulated iron nanoparticles: synthesis and high electrocatalytic activity for hydrogen evolution reaction. Angew. Chem., Int. Ed. 2015, 54, 4532−4538.

(24) Deng, J.; Ren, P.; Deng, D.; Yu, L.; Yang, F.; Bao, X. Highly active and durable non-precious-metal catalysts encapsulated in carbon nanotubes for hydrogen evolution reaction. Energy Environ. Sci. 2014, 7, 1919−1923.
(45) Gunji, T.; Noh, S. H.; Tanabe, T.; Han, B.; Nien, C. Y.; Ohsaka, T.; Matsumoto, F. Enhanced electrocatalytic activity of carbon-supported ordered intermetallic palladium-lead (Pd,Pb) nanoparticles toward electrooxidation of formic acid. *Chem. Mater.* 2017, 29, 2906–2913.

(46) Wang, J.-Y.; Zhang, H.-X.; Jiang, K.; Cai, W.-B. From HCOOH to CO at Pd electrodes: a surface-enhanced infrared spectroscopy study. *J. Am. Chem. Soc.* 2011, 133, 14876–14879.

(47) Bai, J.; Shen, L.; Sun, D.; Tang, Y.; Lu, T. Facile synthesis and electrocatalytic properties of dendritic palladium nanostructures. *CrystEngComm* 2014, 16, 10445–10450.

(48) Yang, N.; Zhang, Z.; Chen, B.; Huang, Y.; Chen, J.; Lai, Z.; Chen, Y.; Sindoro, M.; Wang, A.-L.; Cheng, H.; Fan, Z.; Liu, X.; Li, B.; Zong, Y.; Gu, L.; Zhang, H. Synthesis of ultrathin PdCu alloy nanosheets used as a highly efficient electrocatalyst for formic acid oxidation. *Adv. Mater.* 2017, 29, No. 1700769.

(49) Xi, Z.; Erdosy, D. P.; Mendoza-Garcia, A.; Duchesne, P. N.; Li, J.; Muzzio, M.; Li, Q.; Zhang, P.; Sun, S. Pd nanoparticles coupled to WO$_{3-x}$ nanorods for enhanced electrochemical oxidation of formic acid. *Nano Lett.* 2017, 17, 2727–2731.

(50) Liang, X.; Liu, B.; Zhang, J.; Lu, S.; Zhuang, Z. Ternary Pd-Ni-P hybrid electrocatalysts derived from Pd-Ni core-shell nanoparticles with enhanced formic acid oxidation activity. *Chem. Commun.* 2016, 52, 11143–11146.

(51) Li, D.-N.; Wang, A.-J.; Wei, J.; Zhang, Q.-L.; Feng, J.-J. Facile synthesis of flower-like Au@AuPd nanocrystals with highly electrocatalytic activity for formic acid oxidation and hydrogen evolution reactions. *Int. J. Hydrogen Energy* 2017, 42, 19894–19902.