# Ultrafine FePd Nanoalloys Decorated Multiwalled Cabon Nanotubes toward Enhanced Ethanol Oxidation Reaction

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S Supporting Information

**ABSTRACT:** Ultrafine iron-palladium (FePd) nanoalloys deposited on $\gamma$-$Fe_2O_3$, FePd–$Fe_2O_3$, further anchored on carboxyl multiwalled carbon nanotubes (MWNTs–COOH), FePd–$Fe_2O_3$/MWNTs, were successfully synthesized by a facile one-pot solution based method as thermally decomposing palladium acetylacetonate ($Pd(acac)_2$) and iron pentacarbonyl ($Fe(CO)_5$) in a refluxing dimethylformamide solution in the presence of MWNTs–COOH. A 3.65 fold increase of peak current density was observed in cyclic voltammetry (CV) for ethanol oxidation reaction (EOR) compared with that of Pd/MWNTs after normalizing to Pd mass. The greatly enhanced tolerance stability toward poisoning species and largely reduced charge transfer resistance were also obtained in chronoamperometry and electrochemical impedance spectroscopy due to the downward shifted d-band center of FePd alloy, easily formed oxygen containing species on $Fe_2O_3$, and the stabilizing role of the MWNTs.



**KEYWORDS:** ethanol oxidation reaction, palladium-based catalysts, iron–palladium alloy, gamma phased iron oxide, carbon nanotubes

## 1. INTRODUCTION

Palladium (Pd)-based catalysts have attracted much attention during the last decades owing to their versatile roles in many catalytic reactions involving carbon–carbon formation,[1] hydrogenation of many organic compounds,[2−4] oxidation of hydrocarbons,[5] isomerization,[6] and decomposition of nitrogen monoxide.[7] Among the numerous applications, direct alcohol fuel cells (DAFCs) are greatly highlighted due to their merits such as zero pollution, high volumetric energy density, easy transportation, renewable, and relatively low operating temperature.[8,9] Among different alcohol fuels, ethanol is more competitive with less toxicity, sustainability, and higher energy density.[10] For direct ethanol fuel cells (DEFCs), the anode catalyst Pd is in greater demand than the more common platinum (Pt) catalysts due to its lower cost, greater tolerance to CO species, and higher electrocatalytic activity in alkaline medium.[11−13]

The strategies to further minimize catalyst cost and to achieve full utilization of Pd atoms include clean Pd surface, small size, formation of alloy with cheaper metals, or fixture on the substrates.[14,15] To prevent the aggregation of small particles arising from the increased surface energy inherent with the small sizes,[16] considerable efforts have been devoted to stabilize the particles by using surfactants, polymers or ligands.[17,18] However, the strongly bonded organic materials on the catalytic nanoparticles (NPs) surface will inevitably prevent the full access to the electrolyte surroundings, which largely limit their performances.[18,19] In this case, introducing proper supports as another alternative is found to be advantageous because they can not only make low loading catalysts possible but also endow additional properties to the catalysts. The Pd-based

alloys can not only minimize the usage of Pd but also demonstrate enhanced electrocatalytic activities. The introduced doping metal can alter the d-band center of alloy, thus facilitating the desorption of fuel species and making more active sites available on the catalytic metal.[20] For example, PdSn,[21] PdCo,[22] PdNi,[23] and PdAu[24] bimetallic catalysts have shown much higher catalytic activity and stability toward electrooxidation of formic acid, ethanol and oxygen reduction reaction (ORR) than the commercial Pd/C catalysts. Among the Pd-based alloys, iron−palladium (FePd) alloys with different nanostructures such as sphere,[25] rod,[26] core−shell,[27] leaf,[28] and ultrathin wire[29] have received dramatic interest due to their excellent catalytic performances in ORR, methanol oxidation and dechlorination.

Transition metal oxides have also shown to be effective promoters or appropriate supporting materials for Pd-based electrocatalysts.[30−33] Metal oxides can alter the electronic structure of Pd through interfacial bonding, accelerating electron transfer between metal and oxide, or both.[34] Catalysts with Pd supported on different oxide/C such as $CeO_2$, $Co_3O_4$, $Mn_3O_4$, and NiO have displayed much higher catalytic activity and stability than Pd/C or Pt/C electrocatalysts under comparable experimental conditions.[35] Among numerous transition metal oxides, magnetite and maghemite are of scientific and technological importance due to their intrinsic magnetic features, and intrigued electronic properties.[36,37]

However, simple magnetic iron oxides are easily aggregated due to the dipole−dipole interactions and van der Waals forces.[38] The conductivity will also be largely limited due to the poor conductivity of iron oxides. To overcome these problems, another substrate is further needed to disperse iron oxide particles. Nowadays, carbon materials such as carbon nanotubes (CNTs) have attracted intense interests due to their excellent electronic properties, good physicochemical stability, and large specific surface area.[39] Carboxylic groups on MWNTs have demonstrated a unique function to anchor the magnetic NPs uniformly on the carboxyl MWNTs (MWNTs−COOH),[15] and the MWNTs behaved as spacers in the final catalysts to facilitate good electrolyte access. In summary, an optimal combination of catalytic metal alloys, metal oxides promoter and highly conductive carbon substrate could incorporate all the specific advantages in the final catalysts and contribute to an excellent catalytic performance.

Herein, we report a facile one-pot solution-based method as in situ thermal decomposition of $Pd(acac)_2$ and $Fe(CO)_5$ in a refluxing dimethylformamide (DMF) solution where ultrafine FePd alloy was first formed and deposited on the $Fe_2O_3$ NPs, which were formed and evenly distributed on the MWNTs surface. The formed nanocatalysts were termed as "FePd−$Fe_2O_3$/MWNTs". Different iron substrates as $Fe_3C$ and $\gamma$-$Fe_2O_3$ were obtained with varying the $Fe(CO)_5$ precursor dosage. The Pd/MWNTs and $Fe_3O_4$/MWNTs were also obtained as control experiments. The compositions of these iron-containing specimens were determined by Mössbauer spectrometer and X-ray photoelectron spectroscopy (XPS). The crystalline structures and morphologies of Pd/MWNTs, $Fe_3O_4$/MWNTs, FePd−$Fe_3C$/MWNTs, and FePd−$Fe_2O_3$/MWNTs were investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The variation of defects on the tube wall surface after the deposition of NPs was characterized by Raman spectroscopy and XPS. The thermal properties and final loadings of the as-synthesized nanocomposites were determined by thermogravimetric analysis (TGA). The electrocatalytic performances of these catalysts were evaluated toward ethanol oxidation reaction (EOR) using cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS).

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Palladium(II) acetylacetonate ($Pd(C_5H_7O_2)_2$, 99%, $M_w$ = 304.64 g/mol), iron(0) pentacarbonyl ($Fe(CO)_5$, 99%, $M_w$ = 195.90 g/mol), potassium hydroxide (KOH, BioXtra, ≥ 85% KOH basis), dimethylformamide (DMF, 99%) and ethanol ($C_2H_5OH$, ≥ 99.5%) were obtained from Sigma-Aldrich. Carboxylic group functionalized multiwalled nanotubes (MWNTs−COOH) (Stock no. 1272YJF; content of MWNTs, ≥ 95 wt %; content of −COOH, 0.47−0.51 wt %; o.d., 50−80 nm, i.d., 5−15 nm; length, 10−20 $\mu$m) were provided by Nanostructured & Amorphous Materials, Inc. (Houston, TX). All the chemicals were used as-received without any further treatment.

**2.2. Synthesis of Catalysts.** A facile one-pot solution-based method was employed to synthesize Pd/MWNTs, $Fe_3O_4$/MWNTs, and FePd-alloyed nanocatalysts. Briefly, 100.0 mg MWNTs−COOH was first dispersed in 60 mL DMF solution undergoing 1 h of sonication, the solution was then transferred to a 250 mL three-neck flask and heated to reflux (~160 °C) in ~20 min. For the synthesis of FePd-based nanocatalysts, 202.0 mg $Pd(acac)_2$ in 20 mL DMF was added to the refluxing MWNTs−COOH/DMF solution. $Fe(CO)_5$ (130.2, 437.0, and 875.0 mg) was then added to the solution after boiling again in ~5 min, and the products were denoted as FePd−$Fe_3C$/MWNTs, FePd−$Fe_2O_3$(3:5)/MWNTs, and FePd−$Fe_2O_3$(3:10)/MWNTs, respectively. For the control synthesis of Pd/MWNTs and $Fe_3O_4$/MWNTs, only 202.0 mg $Pd(acac)_2$ or 875.0 mg $Fe(CO)_5$ was added to the refluxing MWNTs−COOH/DMF solution. All the solutions were maintained refluxing for additional 3 h to complete the whole reaction. Finally, after cooling to room temperature, the solid iron containing products were removed from the suspension using a permanent magnet, while Pd/MWNTs were filtered under vacuum. All the final products (FePd−$Fe_3C$/MWNTs, FePd−$Fe_2O_3$(3:5)/MWNTs, FePd−$Fe_2O_3$(3:10)/MWNTs, Pd/MWNTs, and $Fe_3O_4$/MWNTs) were rinsed with acetone three times and collected after vacuum drying at 60 °C for 24 h.

**2.3. Preparation of Working Electrode.** The working glassy carbon electrode with a diameter of 3 mm was successively polished with 1.0 and 0.05 $\mu$m alumina powders on a microcloth wetted with doubly distilled water to produce an electrode with a mirror-like surface. For the preparation of a catalyst coated electrode, 1.0 mg catalyst was added to 1.0 mL ethanol solution of nafion (the content of nafion is 0.1 wt %), the mixture was then treated for 30 min with ultrasonication to form a uniform suspension. The obtained suspension (5 $\mu$L) was dropped on the surface of well-treated glassy carbon electrode. Finally, the resultant modified glassy carbon electrode was dried naturally at room temperature.

**2.4. Characterizations.** The Mössbauer spectrometer was set to produce a high-precision Doppler velocity modulation of the source $\gamma$ radiation. The effects of the Doppler velocity modulation on the absorption of $\gamma$ radiation were recorded synchronously in the 1024 channels of the multichannel analyzer. The result was 1024 numbers representing registered gamma quanta (representing a singular quantum) passing through the absorber under the condition of different Doppler velocity. A separate calibration procedure was used to establish the exact correspondence channel-velocity (Spectrometer calibration was performed by measuring a standard $\alpha$-Fe absorber, which produces a well-known six line spectrum. The whole velocity range was calibrated using these six velocity points). The shape of absorption spectrum was fitted to a theoretical model line shape, which was a superposition of singlets, doublets and sextets ($^{57}$Fe case) of a Lorentzian form. The result was investigated by chi 2 criterion and the theoretical line shape was tailored to fit experimental spectrum by the adjustment of spectral parameters like isomer shift, quadrupole splitting, hyperfine magnetic field, and so on.

The powder X-ray diffraction (XRD) analysis of the samples was carried out with a Bruker AXS D8 Discover diffractometer with General Area Detector Diffraction System (GADDS) operating with a Cu Kα radiation source filtered with a graphite monochromator ($\lambda$ = 1.5406 Å). The 2θ angular region between 10 and 80° was explored at a scan rate of 1° min$^{-1}$.

Transmission electron microscopy (TEM) was used to characterize the morphology of the as-prepared nanocomposites in a JEOL 2010F microscope at a working voltage of 200 kV. The samples were prepared by drying a drop of ethanol suspension on a 400-mesh carbon-coated copper grid (Electron Microscopy Sciences).

Raman spectra were obtained using a Horiba Jobin-Yvon LabRam Raman confocal microscope with 785 nm laser excitation at a 1.5 cm$^{-1}$ resolution at room temperature.

Thermogravimetric analysis (TGA) was conducted using a TA Instruments Q-500 at a heating rate of 10 °C min$^{-1}$ and an air flow rate of 60 mL min$^{-1}$ from 25 to 700 °C.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos AXIS 165 XPS/AES instrument. The samples were scanned with a monochromatic Al X-ray source at the anode of 10 kV and beam current of 15 mA. The peaks were deconvoluted into the components on a Shirley background

**2.5. Electrochemical Evaluations.** The electrochemical experiments were conducted in a conventional three-electrode cell. The as-prepared glassy carbon electrode deposited with catalyst was used as the working electrode, while saturated calomel electrode (SCE; 0.241 V vs SHE) connected to the cell through a Luggin capillary served as reference electrode. All the potentials were referred to the SCE. All electrochemical measurements were performed on an electrochemical working station VersaSTAT 4 potentiostat (Princeton Applied Research). Stable cycle voltammogram (CV) curves were recorded after potential sweeping for several cycles until the CV curve became stable in the potential region from −1.0 to 0.3 V. Chronoamperometry (CA) toward EOR was performed at −0.3 V in 1.0 M KOH solution containing 1.0 M ethanol for a duration of 1000 s. The electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 100 000 to 0.1 Hz with a 10 mV amplitude at −0.4 V.

# 3. RESULTS AND DISCUSSION

**3.1. Characterizations of Nanocatalysts.** *3.1.1. Mössbauer Spectra Analysis.* Room temperature $^{57}$Fe Mössbauer spectra as a powerful technique determining iron compounds were first employed to investigate the chemical environment of the as-synthesized nanocatalysts to determine the composition.[40] Figure 1 shows the spectral curves and the detailed data are listed in Table 1. For the FePd−Fe$_3$C/MWNTs, Figure 1a, only one component as Fe$_3$C is obtained after curve fitting,

**Table 1. Room-Temperature Mössbauer Spectral Data of the Measured Samples**

| samples | composition (%) | | |
|---|---|---|---|
| | Fe$_3$C | Fe$^{2.5+}$ | Fe$^{3+}$ |
| FePd−Fe$_3$C/MWNTs | 100 | | |
| FePd−Fe$_2$O$_3$(3:10)/MWNTs | 5 | | 95 |
| Fe$_3$O$_4$/MWNTs | | 39 | 61 |
| FePd−Fe$_2$O$_3$(3:5)/MWNTs | 9 | | 91 |

which is evidenced by isomer shift (IS) of 0.15 mm/s and the corresponding quadrupole splitting (QS) of 0.54 mm/s. Two components as Fe$^{3+}$ and Fe$_3$C are obtained after curve fitting of FePd−Fe$_2$O$_3$(3:10)/MWNTs, Figure 1b, The main component Fe$^{3+}$(95%) is located at IS (0.33 mm/s), hyperfine filed (HI) (490 kOe); IS (0.35 mm/s), HI (466 kOe) and IS (0.35 mm/s), HI (417 kOe), indicating the Fe$^{3+}$ is in the frustrated oxygen sites of γ-Fe$_2$O$_3$ where the iron ions in octahedral-sites have different number with the nearest occupied octahedral-sites. The second component as Fe$_3$C (5%) is located at IS of 0.15 mm/s, QS of 0.60 mm/s. For curve fitting of Fe$_3$O$_4$/MWNTs, Figure 1c, Fe$_3$O$_4$ is confirmed as Fe$^{3+}$ (61%) in tetrahedral sites of Fe$_3$O$_4$ (IS, 0.32 mm/s, HI, 492 kOe) and Fe$^{2.5+}$ in octahedral sites of Fe$_3$O$_4$ (IS, 0.63 mm/s, 454 kOe and IS, 0.50 mm/s, 450 kOe). Similar to FePd−Fe$_2$O$_3$(3:10)/MWNTs, the curve fitting of FePd−Fe$_2$O$_3$(3:5)/MWNTs indicates two components as 9% Fe$_3$C and 91% Fe$^{3+}$, Figure 1(d), the Fe$^{3+}$ in the frustrated oxygen sites is demonstrated by IS of 0.35 mm/s, HI of 482 kOe (47%), IS of 0.35 mm/s, HI of 456 kOe (29%), and IS of 0.35 mm/s, 414 kOe (16%). In addition, Fe$^{3+}$ (3%) in the distorted oxygen octahedral is demonstrated by IS of 0.35 mm/s, QS 0.53 mm/s. Finally, The 9% Fe$_3$C is located at IS of 0.1 mm/s with QS of 0.53 mm/s. It is noticed that different precursor combinations have produced different iron components, Fe$_3$O$_4$ for simple decomposing Fe(CO)$_5$ in the DMF solution, Fe$_3$C with relatively lower Fe(CO)$_5$ precursor dosage, and γ-Fe$_2$O$_3$ for high Fe(CO)$_5$ dosage in the presence of Pd(acac)$_2$.

*3.1.2. X-ray Diffraction.* Figure 2 shows the XRD patterns of Pd/MWNTs, FePd−Fe$_3$C/MWNTs, FePd−Fe$_2$O$_3$(3:5)/MWNTs, FePd−Fe$_2$O$_3$(3:10)/MWNTs and Fe$_3$O$_4$/MWNTs, respectively. The standard diffraction pattersn of γ-Fe$_2$O$_3$ (PDF



**Figure 1.** Mössbauer spectra of (a) FePd−Fe$_3$C/MWNTs, (b) FePd−Fe$_2$O$_3$(3:10)/MWNTs, (c) Fe$_3$O$_4$/MWNTs, and (d) FePd−Fe$_2$O$_3$(3:5)/MWNTs.



**Figure 2.** XRD patterns of (a) Pd/MWNTs, (b) FePd−Fe$_3$C/MWNTs, (c) FePd−Fe$_2$O$_3$(3:5)/MWNTs, (d) FePd−Fe$_2$O$_3$(3:10)/MWNTs and (e) Fe$_3$O$_4$/MWNTs, standard cards of Fe$_3$O$_4$, γ-Fe$_2$O$_3$ and Pd are shown at the bottom (red, Fe$_3$O$_4$; black, γ-Fe$_2$O$_3$; and blue, Pd).

39-1346), $Fe_3O_4$ (PDF 65-3107) and Pd (PDF 88-2335) are also provided at the bottom of Figure 2. For Pd/MWNTs, four main diffraction peaks as C (002) centering at 25.97° (PDF 26-1077), Pd (111), (200), and (220) centering at 40.01, 46.54 and 67.65°, (PDF 88-2335), are clearly observed, suggesting the successful deposition of Pd on MWNTs, Figure 2a. For $Fe_3O_4$/MWNTs, Figure 2e, partial characteristic peaks centering at 30.24, 35.63, 43.28, 53.73, 57.27, 62.93, and 74.47° are consistent with the (220), (311), (400), (422), (511), (440), and (533) planes of $Fe_3O_4$ (PDF 65-3107), respectively, indicating the successful deposition of $Fe_3O_4$ on MWNTs. However, because the standard patterns of $\gamma$-$Fe_2O_3$ (PDF 39-1346) and $Fe_3O_4$ (PDF 65-3107) are similar, Mössbauer spectra as a reliable technique evaluating the state of the synthesized iron oxides are referred as the final standard. For FePd−$Fe_3C$/MWNTs, FePd−$Fe_2O_3$(3:5)/MWNTs, and FePd−$Fe_2O_3$(3:10)/MWNTs (Figure 2c,d), besides the main diffraction peaks of MWNTs, $Fe_3C$ and $\gamma$-$Fe_2O_3$, one characteristic peak corresponding to the (111) plane of FePd (PDF 65-3253) is clearly observed, confirming from the positive shift from Pd (111) (39.79°) to FePd (111) (40.47°).[41] In addition, the peak intensity of FePd (111) and C (002) is observed to decrease with increasing the $Fe(CO)_5$ precursor dosage due to the produced dominant iron oxide, the average crystallite size of $Fe_2O_3$ and Pd NPs can be estimated using the Debye−Scherrer equation 1.

$$L = 0.89\lambda/(\beta \cos \theta_B) \qquad (1)$$

where $L$ is the particle size, $\lambda$ is 1.5406 Å for the wavelength of Cu K$\alpha$ radiation, $\beta$ is the full width at half-maximum (fwhm), and $\theta_B$ is the diffraction angle. The fwhm was calculated from the diffraction peak of the (311) plane of $\gamma$-$Fe_2O_3$ or $Fe_3O_4$ and (111) plane of Pd or FePd, the corresponding crystallite sizes of $Fe_3O_4$, $\gamma$-$Fe_2O_3$, Pd and FePd NPs in Pd/MWNTs, FePd−$Fe_3C$/MWNTs, FePd−$Fe_2O_3$(3:5)/MWNTs, FePd−$Fe_2O_3$(3:10)/MWNTs, and $Fe_3O_4$/MWNTs are calculated and shown in Table 2. The size of iron oxide particle is

**Table 2. Particle Size of Deposited Particles in Different Nanocomposites**

| nanocatalysts | $Fe_3O_4$ or $Fe_2O_3$ size (nm) | Pd or FePd size (nm) |
|---|---|---|
| $Fe_3O_4$/MWNTs | 31.4 | |
| Pd/MWNTs | | 8.5 |
| FePd−$Fe_2O_3$(3:10)/MWNTs | 15.6 | 2.5 |
| FePd−$Fe_2O_3$(3:5)/MWNTs | 10.6 | 4.3 |
| FePd−$Fe_3C$/MWNTs | | 3.8 |

observed to increase with increasing the $Fe(CO)_5$ precursor dosage. In contrast, the Pd/FePd particle size is also observed to decrease with increasing the $Fe(CO)_5$ dosage, which is probably due to the increased $Fe_2O_3$ particle surface area.

*3.1.3. Raman Spectroscopy.* Raman spectroscopy is a useful technique to characterize carbonaceous materials, especially for analyzing the surface structure and distinguishing sp$^2$ and sp$^3$ hybridized forms of carbon. Figure 3 shows the Raman spectra of the as-received MWNTs−COOH, FePd−$Fe_2O_3$(3:10)/MWNTs, $Fe_3O_4$/MWNTs Pd/MWNTs, FePd−$Fe_2O_3$(3:5)/MWNTs, and FePd−$Fe_3C$/MWNTs, respectively. All the samples exhibit the characteristic D, and G bands around ~1335 and 1580 cm$^{-1}$. The D band is a "dispersive" band, which is ascribed to the edges, other defects and disordered



**Figure 3.** Raman spectra of (a) MWNTs−COOH, (b) FePd−$Fe_2O_3$(3:10)/MWNTs, (c) $Fe_3O_4$/MWNTs, (d) Pd/MWNTs, (e) FePd−$Fe_2O_3$(3:5)/MWNTs, and (f) FePd−$Fe_3C$/MWNTs.

carbon, whereas G band is related to the stretching mode of crystal graphite. The intensity ratio of D to G bands ($I_D/I_G$) denoted as $R$ is a measurement of the degree of disorder and average size of the sp$^2$ domain,[42] the higher the $R$, the larger the degree of defects. The calculated $R$ values from Figure 3 of FePd−$Fe_2O_3$(3:10)/MWNTs (1.7656), $Fe_3O_4$/MWNTs (1.7570), Pd/MWNTs (1.7483), FePd−$Fe_2O_3$(3:5)/MWNTs (1.7810) and FePd−$Fe_3C$(2:1)/MWNTs (1.6202) are all higher than that of the as-received MWNTs−COOH (1.5239). This similar phenomenon has also been observed in the GO and CNFs,[43,44] indicating a possible chemical interactions or bonds between the NPs and MWNTs.

*3.1.4. TGA Analysis.* TGA analysis is considered as a useful tool to determine the thermal stability and metal loading of carbon supported catalysts. Figure 4 shows the TGA curves of



**Figure 4.** TGA curves of (a) $Fe_3O_4$/MWNTs, (b) Pd/MWNTs, (c) FePd−$Fe_2O_3$(3:5)/MWNTs, (d) FePd−$Fe_2O_3$(3:10)/MWNTs and (e) FePd−$Fe_3C$/MWNTs, and (inset) enlarged view of the area indicated by the green rectangle.

$Fe_3O_4$/MWNTs, Pd/MWNTs, FePd−$Fe_2O_3$(3:5)/MWNTs, FePd−$Fe_2O_3$(3:10)/MWNTs, and FePd−$Fe_3C$/MWNTs. For $Fe_3O_4$/MWNTs (Figure 4a), a slight weight-up begins at 150 °C is observed due to the oxidation of $Fe_3O_4$, which is consistent with the Mössbauer result and different from the other four nanocomposites (Figure 4b−e). Slight weight-losses are first observed for the Pd containing nanocatalysts due to the continuous decomposition of remained acetylacetonate (acac) on the Pd surface.[15] However, a following weigh increase is observed due to the oxidation of metal Pd or FePd. A common

fast weight decrease is observed for all these five nanocatalysts as the temperature reaches 500 °C due to the burning of MWNTs. The final residue percentages of $Fe_3O_4$/MWNTs, Pd/MWNTs, FePd−$Fe_2O_3$(3:5)/MWNTs, FePd−$Fe_2O_3$(3:10)/MWNTs, and FePd−$Fe_3C$/MWNTs are determined to be 78.80, 41.42, 74.92, 79.54 and 60.55%. The loading of Pd in Pd/MWNTs is determined to be 37.85% from the TGA result. For $Fe_3O_4$/MWNTs, FePd−$Fe_2O_3$(3:10)/ MWNTs, FePd−$Fe_2O_3$(3:5)/MWNTs, and FePd−$Fe_3C$/ MWNTs, the varying trend of the final residue is in good accordance with the iron precursor dosage. However, the final residue of 80% indicates a saturation of MWNTs when further increasing the $Fe(CO)_5$ dosage. Energy-dispersive X-ray spectroscopy (EDS) is introduced to determine the Pd loading, Figure S1. The element Pd, Fe, C, and O are clearly observed, suggesting the successful synthesis of FePd−$Fe_2O_3$/MWNTs or FePd−$Fe_3C$/MWNTs nanocatalysts. The Pd loading is determined to be 13.12, 20.66, and 30.03% for the FePd−$Fe_2O_3$(3:10)/MWNTs, FePd−$Fe_2O_3$(3:5)/MWNTs, and FePd−$Fe_3C$/MWNTs nanocatalysts by selecting an entire area as 125 um by 125 um.

**3.1.5. TEM Characterizations.** Figure 5 shows TEM microstructures of the Pd/MWNTs, $Fe_3O_4$/MWNTs and

synthesis of Pd/MWNTs, which is also consistent with the XRD result. For $Fe_3O_4$/MWNTs (Figure 5d), the $Fe_3O_4$ NPs with an average diameter of 30 nm are clearly observed anchoring on the tube wall surface, demonstrating the facile synthesis of $Fe_3O_4$/MWNTs. A lattice fringe of 4.67 Å belonging to the (111) plane of fcc $Fe_3O_4$ is clearly observed in the HRTEM image, Figure 5e. For the SAED pattern shown in Figure 5f, the planes of (111), (220), (311), (400), (422), (440), (533), and (511) of $Fe_3O_4$ are well distinguished, indicating the existence of $Fe_3O_4$, consistent with the Mossbauer spectra. For Pd−$Fe_3C$/MWNTs, the formed NPs are observed randomly distributed on the MWNTs with serious agglomeration (Figure 5g). Irregular NPs covered on the tube wall surface and the clear lattice spaces of 2.21, 2.25, and 2.02 Å belonging to FePd (111), $Fe_3C$ (002) and $Fe_3C$ (220), are observed (Figure 5h). For the SAED pattern (Figure 5i), apart from the $Fe_3C$ planes of (210), (102), (301), (040), (211), and (222), the (111) plane of FePd is also obtained, indicating the formation of FePd alloy and consistent with the XRD result.[46−49]

Figure 6a shows the TEM image of FePd−$Fe_2O_3$(3:10)/ MWNTs, relatively larger $Fe_2O_3$ NPs are observed to disperse

**Figure 5.** (a, d, and g) TEM image and (b, e, and h) corresponding HRTEM image with clear lattice fringe (c, f, i) as well as SAED pattern with marked facet of (a−c) Pd/MWNTs, (d−f) $Fe_3O_4$/MWNTs, and (g−i) Pd−$Fe_3C$/MWNTs.

**Figure 6.** (a−c) TEM, SAED pattern and HRTEM image of FePd−$Fe_2O_3$(3:10)/MWNTs, corresponding EFTEM maps as (d) Fe + C, (e) Fe + C + Pd, (f) Fe + C + O and (g) Fe + C + Pd + O of FePd−$Fe_2O_3$(3:10)/MWNTs; (red) oxygen, (blue) carbon, (green) iron, and (pink) palladium. (h and i) TEM and HRTEM images of FePd−$Fe_2O_3$(3:5)/MWNTs, and (j) mapping result of corresponding elements of FePd−$Fe_2O_3$(3:5)/MWNTs.

Pd−$Fe_3C$/MWNTs with corresponding HRTEM images and selected area electron diffraction (SAED) patterns. For Pd/ MWNTs, the Pd NPs are observed to be uniformly decorated on the tube wall surface with an average particle size of ∼15 nm (Figure 5a). Clear lattice space of 2.28 and 2.38 Å are observed belonging to the (111) plane, and kinematically forbidden reflections of Pd 1/3(422) of face-centered cubic (fcc) Pd, respectively (Figure 5b).[45] In addition, four planes assigned to Pd (111), (220), (200), and (311) are also clearly noticed in the SAED pattern (Figure 5c). Both the distinguished lattice fringes and the marked SAED facets indicate a successful

on the tube wall surface with a slight agglomeration. However, ultrafine NPs are observed further deposited on the surface of $Fe_2O_3$ NPs at a closer look. The morphology of ultrafine NPs is further confirmed by the HRTEM image, Figure 6b, the small FePd particles are uniformly distributed on the surface of $Fe_2O_3$ NPs. Clear Lattice fringes of 2.21 and 2.71 Å belonging to FePd (111) and FePd (110) are observed, indicating the formation of FePd alloy. Pure Pd NPs are also obtained on the tube wall surface or $Fe_2O_3$ surface as indicated by the Pd (111) plane. SAED pattern further discloses the crystallization, both FePd (110, 220 and 200) and γ-$Fe_2O_3$ (311, 511 and 440) are

**Figure 7.** (A) Wide-scan survey of FePd−Fe$_2$O$_3$(3:5)/MWNTs, curve fitted elements in FePd−Fe$_2$O$_3$(3:5)/MWNTs as (B) C 1s, (C) Fe 2p, and (D) Pd 3d, (E and F) wide-scan survey and curve fitting spectra of Pd/MWNTs and Pd 3d.

observed in Figure 6c, indicating the existence of γ-Fe$_2$O$_3$ and FePd alloy as confirmed by the XRD results.

Energy-filtered TEM (EFTEM) is also performed to provide a 2-dimensional (2-D) elemental distribution. In the EFTEM image, a brighter area always represents a higher concentration of the corresponding element in this area.[50] Figure 6d−g shows the element maps of C + Fe, C + Fe + Pd, C + Fe + O, and C + Fe + Pd + O. The irons are observed evenly distributed on the surface of MWNTs (whereas the lacy grid is also made of carbon; Figure 6d). Compared with Figure 6d, bright pink dots representing the Pd elements are clearly seen on the surface of large green particles (Figure 6e). Figure 6f displays a uniform coverage of red oxygen based on Figure 5a, confirming the formation of iron oxides. Finally, the summation of C, Fe O and Pd distributions is shown in Figure 6g, the pink Pd dots are evenly distributed on the green Fe, which are further anchored on the blue nanotubes together with a coverage of red O. All these results suggest the containment of Pd, Fe, O, and C elements and further confirm the unique structure of

FePd−Fe$_2$O$_3$/MWNTs nanocatalysts. Similarly, Figure 6h−j shows the TEM and corresponding HRTEM images of C, O, and Fe mappings of FePd−Fe$_2$O$_3$(3:5)/MWNTs nanocatalysts, and a similar structure is observed, showing that the ultrafine NPs are first deposited on the Fe$_2$O$_3$ NPs, which are further dispersed on the tube wall surface. However, the relatively sparse dispersion of Fe$_2$O$_3$ NPs compared with that in FePd−Fe$_2$O$_3$(3:10)/MWNTs is probably due to the lower Fe(CO)$_5$ precursor dosage. Finally, similar distributions of C, O, and Fe elements are also observed in Figure 6j, which are consistent with that of FePd−Fe$_2$O$_3$(3:10)/MWNTs.

*3.1.6. XPS Analysis.* XPS is a powerful tool for providing valuable insights into the surface of solid samples, identifying the atomic composition of the solid surface, and allowing the valence state of elements to be determined based on the specific binding energy measured from a particular type of photoelectron. Figure 7A is the wide scan survey of FePd−Fe$_2$O$_3$(3:5)/MWNTs over a range of 0−1000 eV. Five main spectra peaks centering at ca. 85.46, 279.14, 330.15, 527.84, and

**Figure 8.** Cyclic voltammetry (CV) of (a) $Fe_3O_4$/MWNTs, (b) Pd/MWNTs, (c) FePd−$Fe_2O_3$(3:10)/MWNTs, (d) FePd−$Fe_3C$/MWNTs, and (e) FePd−$Fe_2O_3$(3:5)/MWNTs in (A) 1.0 M KOH and (B) 1.0 M KOH solution containing 1.0 M ethanol with current density normalized to catalyst area at a scan rate of 50 mV/s. Panels C and D show the same CV spectra as shown in panels A and B with current density normalized to Pd mass.

711.67 eV are clearly observed corresponding to Fe 3p, C 1s, Pd 3d, O 1s, and Fe 2p emissions, indicating the successful synthesis of FePd−$Fe_2O_3$(3:5)/MWNTs.[51,52] In contrast, for the wide scan survey of Pd/MWNTs, only three characteristic peaks as O 1s, Pd 3d, and C 1s are observed (Figure 7E), further demonstrating the successful synthesis of Pd/MWNTs and the introduction of Fe in the FePd−$Fe_2O_3$/MWNTs nanocatalysts as confirmed by the wide scan survey of FePd−$Fe_2O_3$(3:5)/MWNTs (Figure 7A). For the high-resolution scan survey of FePd−$Fe_2O_3$(3:5)/MWNTs, Figure 7B is the curve fitting of C 1s, and four peaks indicating C−C, C−O, C═O, and O−C═O are smoothly deconvoluted, demonstrating that the structure of functionalized MWNTs has not been destroyed during the synthesis process. For the deconvolution of Fe 2p (Figure 7C), the centers of electron-binding energy of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ are 710.72 and 724.15 eV, respectively. The shakeup satellite structures at the higher binding energy sides of the main peaks are the fingerprints of the electronic structure of r-$Fe_2O_3$, which are in good agreement with the previously reported spectra of γ-$Fe_2O_3$.[53−55] For the curve fitting of Pd 3d in FePd−$Fe_2O_3$(3:5)/MWNTs (Figure 7D), great differences are observed compared with that of Pd/MWNTs (Figure 7F). The XPS spectrum of the Pd 3d in Pd/MWNTs is curve-fitted with four peaks, that is, 334.71 and 340.30 eV correspond to the orbits of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ of metal Pd, and the peaks located at 336.59 and 342.36 eV are assigned to the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ orbits of Pd(2+).[56] However, for FePd−$Fe_2O_3$(3:5)/MWNTs, only two peaks centering around 335.89 and 341.52 are deconvoluted to metal Pd $3d_{5/2}$ and Pd $3d_{3/2}$ (Figure 7D). The peaks of metal Pd $3d_{5/2}$ and Pd $3d_{3/2}$

are both observed to shift to higher values compared with that of Pd/MWNTs, confirming the "FePd" alloy-like formation.[41] This shift of binding energy is probably due to the modification of electronic structure of Pd as the electron will transfer from Fe to Pd due to the electronegativity of Fe. The d band of Pd will also be altered due to the intra- or inter-atomic charge transfers between Fe and Pd after they are alloyed together.[41,57−59] This electron transfer will probably contribute to the enhanced tolerance stability of CO species, which can greatly facilitate EOR.[60] This strong evidence of the formation of FePd alloy is also consistent with the aforementioned XRD and TEM results. For $Fe_3O_4$/MWNTs, FePd−$Fe_2O_3$(3:10)/ MWNTs, and FePd−$Fe_3C$/MWNTs, the high-resolution scan surveys of Fe 2p are provided in Figure S2A and compared with that of FePd−$Fe_2O_3$(3:5)/MWNTs, typical features of different iron oxides are clearly observed, consistent with the Mössbauer spectra. In addition, similar Pd 3d peak phenomena are also observed in FePd−$Fe_2O_3$(3:10)/MWNTs and FePd−$Fe_3C$/ MWNTs, Figure S2B, indicating the formation of FePd alloy.

**3.2. Electrocatalytic Evaluations.** *3.2.1. Electroactivity Evaluation.* Cyclic voltammetry (CV) is a useful and convenient technique for estimating the electrochemically active surface area (ECSA) of Pd−based catalysts. The ECSA can not only provide important information about the active sites of catalysts but also evaluate the access of conductive paths to transfer electrons to and from the electrode surface.[61] Figure 8A,C presents the CVs of $Fe_3O_4$/MWNTs, Pd/MWNTs, FePd−$Fe_2O_3$(3:10)/MWNTs, FePd−$Fe_3C$/MWNTs, and FePd−$Fe_2O_3$(3:5)/MWNTs in 1.0 M KOH solution at a scan rate of 50 mV/s with current density normalized to

catalyst area and Pd mass, respectively. For $Fe_3O_4$/MWNTs (Figure 8A,a), negligible peaks are observed due to its nonactivity compared with that of Pd−containing nanocatalysts, which are all characterized with flat anodic peak ($E$ = 0.3 V) and strong cathodic peak ($E$ = −0.4 V) representing the formation and reduction of palladium oxide (PdO), respectively. Furthermore, the FePd−$Fe_3$C/MWNTs, FePd−$Fe_2O_3$(3:10)/MWNTs, and FePd−$Fe_2O_3$(3:5)/MWNTs (Figure 8A,c−e) are observed to exhibit remarkable higher specific current magnitudes and wider potential reduction ranges than that of Pd/MWNTs during the reduction of PdO (Figure 8C). The ECSA of Pd−based nanocatalysts for EOR in alkaline medium is usually measured on the basis of the columbic charge for the reduction of PdO during the negative scan and using eq 2.[62]

$$ECSA = Q/SL \qquad (2)$$

where $S$ is the proportionality constant used to relate charges with area under an assumption that a monolayer of PdO is covered on the surface, the charge produced by the reduction of the monolayer PdO is 405 $\mu$C cm$^{-2}$. $L$ is the catalyst loading (g). The calculated ECSA values for Pd/MWNTs, FePd−$Fe_2O_3$(3:10)/MWNTs, FePd−$Fe_3$C/MWNTs and FePd−$Fe_2O_3$(3:5)/MWNTs are shown in Table 3. The ECSA value

**Table 3. CV Results for Different Nanocatalysts**

| nanocatalysts | ECSA ($m^2$ $g^{-1}$) | $j_p$ (mA/$cm^2$) | $j_p$ (A/mg $_{Pd}$) |
|---|---|---|---|
| Pd/MWNTs | 25.35 | 9.026 | 0.326 |
| FePd−$Fe_2O_3$(3:10)/MWNTs | 115.3 | 6.485 | 0.698 |
| FePd−$Fe_3$C/MWNTs | 64.09 | 10.76 | 0.501 |
| FePd−$Fe_2O_3$(3:5)/MWNTs | 120.4 | 17.52 | 1.191 |

of Pd/MWNTs is greatly increased after introducing Fe. In addition, the ECSA value of Pd−$Fe_3$C/MWNTs is also increased when continue increasing the Fe(CO)$_5$ precursor dosage. However, the ECSA values keep almost constant when further increasing Fe(CO)$_5$ as indicated by FePd−$Fe_2O_3$(3:5)/MWNTs (120.4 $m^2$ g$^{-1}$) and FePd−$Fe_2O_3$(3:10)/MWNTs (115.3 $m^2$ g$^{-1}$) due to the fully utilized Pd element. The highest ECSA value (120.4 $m^2$ g$^{-1}$) is achieved in FePd−$Fe_2O_3$(3:5)/MWNTs probably due to the optimal ratio of MWNTs to $Fe_2O_3$ NPs and the increased active sites after introducing FePd

alloy and $Fe_2O_3$ substrate. Finally, detectable positive shifts of the PdO on-set reduction peaks are clearly seen after the introduction of Fe, demonstrating easier reductions of PdO after modified with Fe due to the electronegativity of Fe.[63]

The electrocatalytic activities of these five nanocatalysts toward EOR were studied in a mixture of 1.0 M KOH aqueous solution containing 1.0 M ethanol at a scan rate of 50 mV s$^{-1}$ from −1.0 to 0.3 V (Figure 8B). The corresponding CVs with current density normalized to Pd mass are also shown in Figure 8D. For $Fe_3O_4$/MWNTs, no oxidation peak of EOR is observed due to the nonactivity of $Fe_3O_4$/MWNTs (Figure 8D,a). For Pd containing nanocatalysts (Figure 8D,b−e), typical voltammetric characteristics of electrooxidation of ethanol are clearly seen, such as EOR oxidation peak during the forward scan at around ∼ −0.25 V and another shape anodic peak during the reverse scan associated with the oxidation of fresh ethanol after the reduction of PdO at ∼ −0.43 V. The mass peak current density ($j_p$) and onset potential in the forward scan are main parameters to evaluate their eletrocatalytic activities for EOR. The electrocatalytic activities are observed to follow the order: FePd−$Fe_2O_3$(3:5)/MWNTs > FePd−$Fe_3$C/MWNTs > Pd/MWNTs > FePd−$Fe_2O_3$(3:10)/MWNTs based on catalyst area. However, the order changes to FePd−$Fe_2O_3$(3:5)/MWNTs > FePd−$Fe_2O_3$(3:10)/MWNTs > FePd−$Fe_3$C/MWNTs > Pd/MWNTs after normalizing to Pd mass, suggesting that the catalytic activity of Pd can be greatly enhanced after the introduction of Fe. In addition, the onset potential also follows the same trend as $j_p$, suggesting an easier EOR after the introduction of Fe. Finally, the $j_p$ of FePd−$Fe_2O_3$(3:5)/MWNTs (1.2 A/mg Pd) is observed to largely outweigh others and the onset potential is also the lowest one among all the nanocatalysts, both indicating the highest activity of FePd−$Fe_2O_3$(3:5)/MWNTs as indicated by the ECSA analysis.

*3.2.2. Tolerance Stability.* To further probe the long-term tolerance of these nanocatalysts toward intermediate carbonaceous species, we performed chronoamperometric (CA) measurements at −0.3 V for a duration of 1000 s in 1.0 M KOH solution containing 1.0 M ethanol. Figure 9A,B shows the CA curves after normalizing the current to catalyst area and Pd mass, respectively. All the polarization currents decay rapidly during the initial period, implying the poisoning of nanocatalysts by the intermediate carbonaceous species. Gradually, the current is decayed and a pseudosteady state is achieved.



**Figure 9.** (A) Chronoamperometry (CA) curves of EOR on (a) $Fe_3O_4$/MWNTs, (b) Pd/MWNTs, (c) FePd−$Fe_2O_3$(3:10)/MWNTs, (d) FePd−$Fe_3$C/MWNTs and (e) FePd−$Fe_2O_3$(3:5)/MWNTs at −0.3 V (vs SCE) with catalyst area-based current density, (B) CAs with the current density normalized to Pd mass.

Among all the nanocatalysts in Figure 9B, Pd/MWNTs (Figure 9B,a) exhibit a fast decay rate and achieve the lowest extreme current, demonstrating a poor tolerance stability toward poisoning species. However, for FePd−Fe$_2$O$_3$/MWNTs catalysts, an enhanced stability is observed after the normalization to Pd mass, which is probably due to the formed FePd alloy and the positive effects of Fe$_2$O$_3$ and MWNTs substrates. In addition, the FePd−Fe$_2$O$_3$(3:5)/MWNTs are observed to display the slowest decay rate and are able to maintain the highest stable current density for the whole duration of time, indicating the best tolerance stability of FePd−Fe$_2$O$_3$(3:5)/MWNTs toward poisoning species.

*3.2.3. Reaction Kinetics Evaluation.* Electrochemical impedance spectroscopy (EIS) has been demonstrated to be a sensitive electrochemical technique for the study of the electrooxidation kinetics toward EOR. Semicircular Nyquist plots of imaginary ($Z''(\Omega)$) versus real ($Z'(\Omega)$) components of impedance are shown in Figure 10. The illustrations are



**Figure 10.** EIS spectra of (a) Fe$_3$O$_4$/MWNTs, (b) Pd/MWNTs, (c) FePd−Fe$_3$O$_4$(3:10)/MWNTs, (d) FePd−Fe$_3$C/MWNTs and (e) FePd−Fe$_2$O$_3$(3:5)/MWNTs in 1.0 M KOH solution containing 1.0 M ethanol at −0.4 V vs SCE. (Inset) Equivalent circuit used to fit the impedance spectra.

obtained with the potential fixing at −0.4 V with respect to SCE. For Fe$_3$O$_4$/MWNTs (Figure 10a), the observed nearly straight line indicates a huge transfer resistance and further demonstrates the noncatalytic activity of Fe$_3$O$_4$/MWNTs. For Pd/MWNTs, FePd−Fe$_2$O$_3$(3:10)/MWNTs, FePd−Fe$_3$C/MWNTs and FePd−Fe$_2$O$_3$(3:5)/MWNTs, Figure 10(b-e), typical characteristics of EIS plots are observed as a semicircle in the high frequency region and a tail followed in the low frequency region. The diameter of the primary semicircle can be used to measure the charge transfer resistance ($R_{ct}$) of the catalyst, which has a physical meaning to evaluate how fast the

rate of charge transfer is during the oxidation process.[64] Therefore, a decrease in the diameter of the semicircular Nyquist plot signifies a decrease in $R_{ct}$ and an enhancement of charge transfer reaction kinetics. The $R_{ct}$ values of the nanocatalysts are estimated by fitting the EIS curves with the software ZSimpWin based on an equivalent electric circuit as shown in the inset of Figure 10. In this $R_s$ ($R_{ct}$ CPE) circuit, $R_s$ represents the uncompensated solution resistance, $R_{ct}$ represents the charge-transfer resistance while the meaning of constant phase element (CPE) is a parameter related to the capacitor property. The parallel combination of $R_{ct}$ and CPE takes into account the nonequilibrium charge transfer through the thin electrode film and the whole ethanol adsorption and oxidation process. The parallel combination ($R_{ct}$ CPE) leads to a depressed semicircle in the corresponding Nyquist impedance plot. The values for all the parameters $R_s$, $R_{ct}$, CPE and their associated % error are summarized in Table 4. The $R_s$ values are observed to be almost the same, Table 4, due to the same solution resistance. However, the $R_{ct}$ values of FePd−Fe$_2$O$_3$/MWNTs nanocatalysts are much smaller than that of Pd/MWNTs, implying greatly enhanced charge transfer kinetics due to the formation of FePd alloy and the Fe$_2$O$_3$ substrate. For details, the $R_{ct}$ value of FePd−Fe$_2$O$_3$(3:10)/MWNTs is observed to be ten times smaller than that of Pd/MWNTs, suggesting a big enhancement of the activity due to the formed FePd and Fe$_2$O$_3$. However, the $R_{ct}$ value further decreases with decreasing the Fe(CO)$_5$ precursor dosage as indicated by FePd−Fe$_3$C/MWNTs and FePd−Fe$_2$O$_3$(3:5)/MWNTs due to the improved conductivity by decreasing Fe amount. The lowest $R_{ct}$ value of FePd−Fe$_2$O$_3$(3:5)/MWNTs is a strong evidence for the highest reaction rate and is also consistent with the CV and CA results, implying an optimal combination of catalytic FePd with Fe$_2$O$_3$ and MWNTs substrates.

## 4. MECHANISM DISCUSSIONS

**4.1. Synthesis Mechanism.** The formation process is schematically shown in Scheme 1. The decomposition of Fe(CO)$_5$ and Pd(acac)$_2$ has been reported previously with the production of Fe and Pd atoms;[65,66] the alloying of FePd occurs when they meet together in the high temperature environment. Simultaneously, excessive Fe atoms will anchor on the tube wall surface through interacting with C=O part and the Fe$_2$O$_3$ molecules are finally obtained in the ambient atmosphere. The Fe$_2$O$_3$ molecules continue to deposit around the Fe$_2$O$_3$ nuclei and finally form the Fe$_2$O$_3$ NPs. In addition, the formed FePd NPs intend to deposit on the Fe$_2$O$_3$ surface due to the relatively lower bonding energy with Fe$_2$O$_3$ compared with that of MWNTs. However, Fe$_3$C is obtained as the decomposed Fe atoms react with C due to the relatively small amount of Fe(CO)$_5$ precursor dosage.

**Table 4. Impedance Components for Different Electrodes**[a]

| electrode | $R_s$ (Ω) | | $R_{ct}$ (Ω) | | CPE | |
|---|---|---|---|---|---|---|
| | value | error (%) | value | error (%) | value | error (%) |
| Fe$_3$O$_4$/MWNTs | 15.14 | 5.139 | 2333 | 5.757 | $1.374 \times 10^{-5}$ | 5.14 |
| Pd/MWNTs | 19.61 | 11.42 | 1.859E4 | 12.08 | $3.209 \times 10^{-6}$ | 8.506 |
| FePd−Fe$_2$O$_3$(3:10)/MWNTs | 24.63 | 10.82 | 2010 | 9.599 | $3.83 \times 10^{-6}$ | 10.66 |
| FePd−Fe$_3$C/MWNTs | 26.4 | 5.031 | 405.2 | 5.681 | $2.207 \times 10^{-5}$ | 7.824 |
| FePd−Fe$_2$O$_3$(3:5)/MWNTs | 19.86 | 4.096 | 281.5 | 4.786 | $3.606 \times 10^{-5}$ | 6.6 |

[a]Determined by fitting the experimental data using ZSimp-Win software based on the equivalent circuit presented in the inset of Figure 10.

**Scheme 1. Schematic Representation for the Synthesis of FePd−Fe$_2$O$_3$/MWNTs Nanocatalysts**



## 4.2. Improved Catalytic Mechanism Discussion.

The alloying effect of Pd with Fe is similar to the well-known bifunctional mechanism of Pt−Ru. Because the electronegativity of Fe (1.83) is much lower than Pd (2.20),[67] the alloying of Fe can modify the Pd electronic properties as the electrons will transfer from Fe to Pd and contribute to the d-band hybridization of Pd and Fe. The downward shift of d-band center relative to the Fermi level would increase the surface reactivity, thus enhancing the adsorption of OH$_{ads}$ species on the Pd surface and greatly facilitate the process of EOR. In addition, compared to fcc Pd, the slight shift of diffraction peaks of the FePd phase indicates a lattice contraction of Pd−Pd bond distance, and this strain effect can greatly lower the carbonaceous accumulation thus making the electrode more tolerant toward CO poisoning as confirmed by the CA test.[68] Furthermore, the effect of Fe$_2$O$_3$ should also be taken into consideration. Numerous reports have emphasized that the activity and stability of electrocatalysts for alcohol oxidation in alkaline media have been improved by combining catalytic Pd with metal oxides, for example, NiO, CeO$_2$, Co$_3$O$_4$, and Mn$_3$O$_4$. It has been proposed that the oxygen-containing species could form more easily on the surface of metal oxides during the alcohol oxidation reaction.[69] The buffer effect can lead to the subsequent reaction of Pd with CO-like intermediate species more easily, the produced CO$_2$ or other dissolvable products will also release the active sites for further electrochemical reaction, thus enhancing the oxidation efficiency.[70] Therefore, it is reasonable that the Fe$_2$O$_3$ substrate will have a positive effect on the electrocatalytic FePd NPs. However, excess amount of Fe$_2$O$_3$ amount can largely decrease the electrocatalytic activity due to its poor conductivity, which has been demonstrated by the decreased $j_p$ value and deteriorated tolerance stability in FePd−Fe$_2$O$_3$(3:10)/MWNTs. Therefore, there is an appropriate amount of Fe$_2$O$_3$ for the greatest enhancement of the electrocatalytic activity of the present FePd NPs. In summary, the highest electrocatalytic activity of FePd−Fe$_2$O$_3$(3:5)/MWNTs toward EOR is due to the optimal ratio of promoter Fe$_2$O$_3$ to MWNTs substrate and the enhanced FePd surface reactivity.

## 5. CONCLUSIONS

Highly catalytic active FePd−Fe$_2$O$_3$/MWNTs nanocatalysts for EOR have been successfully prepared by simple thermally decomposing Pd(acac)$_2$ and Fe(CO)$_5$ in a refluxing DMF solution in the presence of MWNTs−COOH. The formation of FePd alloy was confirmed by the crystalline structures and the composition investigations through XRD and XPS spectra. A unique structure as FePd NPs first deposited on Fe$_2$O$_3$ NPs which were further uniformly dispersed on MWNTs was disclosed by TEM. Electro-characterizations as CV, CA, and EIS demonstrated an enhanced catalytic performance of FePd−Fe$_2$O$_3$/MWNTs nanocatlysts toward EOR compared with Pd/MWNTs. Modified electronic properties of Pd by Fe, easily proceeded poisoning species on Fe$_2$O$_3$ and the optimal ratio of promoter Fe$_2$O$_3$ to MWNTs substrate are mainly account for the greatly enhanced activity. This simple method is of great significance for the facile preparation of magnetic Pd catalysts with excellent catalytic activity.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b06194.

> Supplementary figure of Energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) of as-prepared products. (PDF)

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## ■ ACKNOWLEDGMENTS

and Innovation Program of Shanghai Municipal Education Commission (No. 13ZZ138) are kindly acknowledged.

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