

Synthesis and Characterization of Nano-hybrid Noble Metals/N doped TiO₂/MWCNTs Electrocatalysts

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Abstract—Novel metal catalysts are easily poisoned by CO adsorption or leaching in oxidation of formic acid that leads to decrease the performances of catalyst. To increase the catalyst activity and poison tolerance in fuel cells, novel metal nanoparticles are usually supported on modified support materials to enhance its performance. In this study, TiO₂/MWCNTs are synthesized by sol-gel method. Also, ammonium is used to dope nitrogen into TiO₂ to modify its electrical and chemical property. MWCNTs, TiO₂/MWCNTs and N-doped TiO₂/MWCNTs are three supporters using in this study to examine the effects of supporters on the electrocatalytic performance of Pd and AuPd catalysts. The synthesized metal nanoparticles are uniformly dispersed on the surfaces of MWCNTs, TiO₂ and N-doped TiO₂ modified MWCNTs. The electrochemical analysis illustrate that Pd/N-doped TiO₂/MWCNTs (molar ratio of NH₄OH:TiO₂=4:1) catalyst exhibits higher activity and better stability than that of Pd/MWCNTs either/or Pd/TiO₂/MWCNTs catalyst in formic acid electrooxidation. Same results are observed in AuPd series of catalysts. It indicates that suitable N-doping TiO₂ improves dramatically on the performance of Pd or AuPd-based catalysts in electrochemical reaction. Thus, hybrid AuPd/N-doped TiO₂/MWCNTs (molar ratio of NH₄OH:TiO₂=4:1) materials have potentially to be used in the direct formic acid fuel cells (DFAFCs) in the future.

Keywords—Fuel cells, Formic Acid, Pd, AuPd, N-doped TiO₂, catalyst, MWCNTs

1. Introduction

In the past decades, direct liquid fuel cell is an intensive research as candidate for portable power supply applications [1]. Direct formic acid fuel cells (DFAFCs) have attracted significant attention as more convenient and less dangerous when handled, stored, or transported at room temperature as compared with gaseous hydrogen fuel cell. As calculated from the Gibbs free energy, formic acid has a higher theoretical electro-motive force (EMF) than hydrogen or direct methanol fuel cells [2-5].

DFAFCs also demonstrate a potential use in future fuel cell devices, although further research is needed in improving formic acid electro-oxidation catalysts. In previous works, Pt has commonly been used as a catalyst for formic acid. However, it was revealed that Pt catalysts used in the electro-oxidation of formic acid were severely poisoned by an adsorbed CO intermediate [6]. In contrast to the Pt catalysts, Pd catalysts are able to catalyze formic acid oxidation (FAO) through a more direct pathway, bypassing the strongly bound CO intermediate [7]. Hence, Pd catalysts are less prone to CO poisoning and deactivation than Pt. However, the catalytic activity and durability of Pd catalysts still need to be substantially improved for higher power output in working DFAFCs.

Noble metal particles such as Pt, Pd and Au can be highly dispersed on carbon surface [8, 9]. This allows for much lower noble metal loading in the catalyst layer while providing high surface area on the carbon support. However, the size distribution and activity of the metal catalysts on the carbon surface depends strongly on the surface morphology of the carbon. To enhance the CO tolerance and corrosion resistance, transition metal oxide based materials, such as TiO₂, CeO₂ and WO₃, were added as electrocatalyst support materials [10-12]. It is expected that this carbon temple modification by metal oxides will greatly enhance the performance of the noble metal-based catalysts for formic acid oxidation. And many attempts have been made to modify the electrical chemical property of TiO₂. So we mainly focus on the doping with transition metals [13-16], but shortcomings of metal doped TiO₂ such as lower conductivity and thermal instability, its tendency to form charge carrier recombination centers, as well as the expensive ion implantation facilities make metal-doped TiO₂ impractical [17]. Some researchers interested in the anion doping (such as N, C, S, P, and F) of TiO₂. Among these anion dopants, nitrogen seems to be the most effective dopant due to its similar size to oxygen, metastable AX (acceptor (A) deactivated (X)) center formation, and small ionization energy [18]. Computational studies[19] and valence band (VB) XPS data[20,21] support the suggestion that nitrogen doping forms new localized states in the band gap just above the VB maximum, leading to substantial reduction of the energy necessary to form oxygen vacancies in bulk TiO₂ [22]. The conductivity of TiO₂ will increase by the doping.

In this study, ammonium will be used to dope nitrogen into TiO₂ to modify its electrical and chemical property. Three supporters: MWCNTs, TiO₂/MWCNTs and N-doped TiO₂/MWCNTs will be prepared and examines the effects of supporters on the electrocatalytic performance of Pd and AuPd catalysts.

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II. Experimental

The multi-walled carbon nanotubes (MWCNTs, QF-MCNTs-30, China. Purity 98-99%), with diameter in 10~50 nm and several micrometers length, were acidized by nitric acid under 115°C for 9 hours to form hydroxyl group (-OH) and carboxyl group (-COOH) on both tips and sidewalls of the nanotubes. The created defects can act as nucleation sites for metal clusters.

The nano hybrid of TiO₂/MWCNTs and N doped TiO₂/MWCNTs were synthesized via sol-gel process. The Ti precursor of titanium tetra-isopropoxide was added into HNO₃/IPA (isopropyl alcohol). The deionized water is added to initialize the sol-gel process. Then HNO₃ aqueous solution was added to control the pH to 1.5 to avoid the aggregation of nanoparticles (Solution A). The purified MWCNTs were dispersed in IPA via sonication for 1 hour (Solution B). HNO₃ aqueous solution was added to control the pH, too. Then, solution A was dropped into solution B slowly and stirred vigorously. The mixture was heated and kept 80°C for 24hrs to form a uniform mixture of MWCNTs in the sol-gel solution. When the reaction completed, the gel became gray nanoparticles. The final product was sintered in a tube furnace under argon atmosphere with heating rate of 5 °C/min to 900 °C and kept for 1.5 hour. The synthesis process of N doped TiO₂/MWCNTs is similar as that of TiO₂/MWCNTs: solution A was first prepared by adding proper amount of ammonia solution to IPA as the doped N source. A typical preparation flowchart of N doped TiO₂/MWCNTs is shown in Figure 1, which has the molar ratio of ammonia to TiO₂ as 4 to 1.

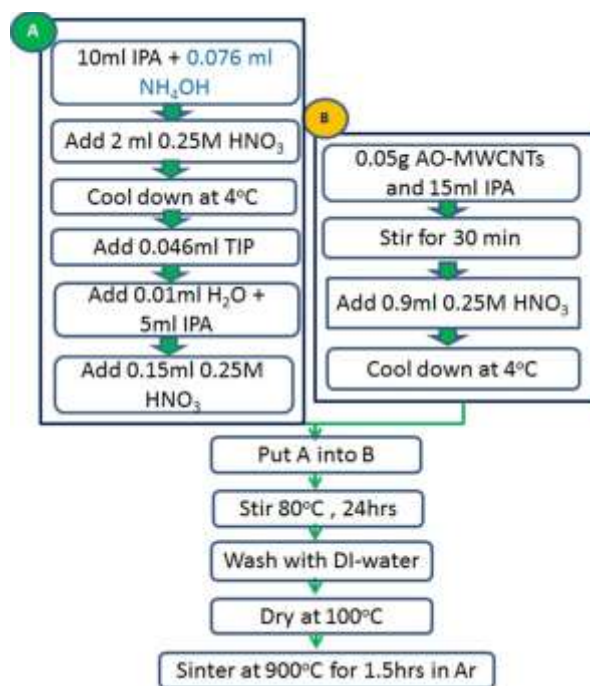


Figure 1. Preparation flowchart of N doped TiO₂/MWCNTs -4:1

Hybrid 20wt%Pd or bimetallic 10wt% Au/10wt%Pd nanomaterials deposited on various modified MWCNTs are prepared by polyol process. The acidized or titania modified

MWCNTs were added in ethylene glycol (EG) and distributed via sonication for 1hour. KOH solution was added into the MWCNTs-suspension to adjust pH value to 8. Then, the MWCNTs-suspension was moved to a heating apparatus with magnet stirring. When the temperature was heated to 170°C, the proper amounts of PdCl₂ and HAuCl₄ solution with adjusted pH 11 were added into the preheated MWCNTs-suspension, kept 170°C for 20 min. After cool to room temperature, the resulting black solid products were centrifuged and washed with distilled water, and dried at 100 °C in air. Finally, the black products were annealed at 200 °C in 5% Hydrogen and 95% Argon for 1 hour.

The prepared hybrid nanomaterials were conducted the measurements of FTIR, XRD, XAS, FESEM and TEM to confirm the structure and morphology of the products. The metal compositions of the hybrid nanoparticles were analyzed via ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer) by dissolving the samples in aqua regia for three days, proper filtrating and diluting in volumetric flask. Elemental Analyzer (EA) was used to determine the N amount in the samples.

The electrochemical properties of the hybrid catalysts were characterized by using a potentiostat/galvanostat instrument (CHI Instrument Model 600-D) with a three-electrode cell system including working electrode, platinum counter electrode and Ag/AgCl reference electrode. The rotating velocity of working electrode was 1600 rpm with the scan rate of 10mV/s. During the experiment, argon gas was kept purging. The electrolyte solution is 1M sulfuric acid for electrochemical surface area measurement, and 1M sulfuric acid and 3M formic acid mixture for the analysis of cyclic voltammetry, chronoamperometry and impedance.

III. Results and discussion

The results of elemental analysis is shown in Table I. AO-MWCNTs has 0.103wt% of nitrogen due to the nitric acid treatment. The results indicate increasing the molar ratio of NH₄OH to TiO₂, the contents of nitrogen are also increased.

TABLE I. EA results of the sample composition.

Sample Name	Content of N (wt%)
MWCNTs	-
AO-MWCNTs	0.103
TiO ₂ /MWCNTs	0.115
N-doped TiO ₂ /MWCNTs-3:1	0.126
N-doped TiO ₂ /MWCNTs-4:1	0.309

XAS Ti 2p peaks in the energy range of 450–470 eV are assigned to L3-t_{2g}, L3-e_g, L2-t_{2g}, and L2-e_g. The two small pre-peaks in the absorption spectra are predominantly triplet character, which are mixed through the spin-orbit interaction and the coulomb repulsion into the main L3 edge.

L3 and L2 features are due to spin-orbit coupling splitting of the initial 2p states into 2p_{3/2} and 2p_{1/2} [23, 24], and are further split into t_{2g} and e_g features because of the low

symmetry of the O_h ligand field compared to the spherical field.

XAS Ti 2p spectra of N-doped TiO_2 /MWCNTs ($NH_4OH:TiO_2$ molar ratio=3:1, 4:1, 5:1) is very similar to that of TiO_2 /MWCNTs but all shift to higher absorption energy. The energy splitting from the center of Ti $t_{2g}-e_g$ at the L2 edge is larger in $TiO_{2-x}N_x$ than that in TiO_2 . This is attributed to possible crystal field changes due to the incorporation of the N atoms [24]. The results reveal that NH_4OH are successfully doped nitrogen in TiO_2 by sol-gel process in this study. And the change of energy state may benefit the conductance of N doped TiO_2 .

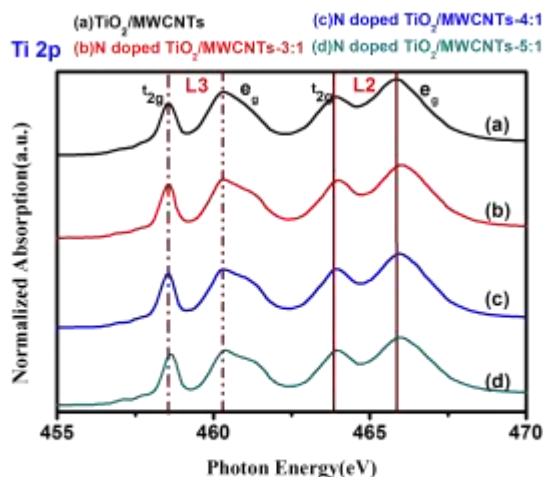


Figure 2. X-ray absorption spectroscopy of (a) TiO_2 /MWCNTs, (b) N doped TiO_2 /MWCNTs 3:1, (c) N doped TiO_2 /MWCNTs 4:1, (d) N doped TiO_2 /MWCNTs 5:1

The impedance results of the hybrid TiO_2 /MWCNTs and N doped TiO_2 /MWCNTs are shown in Figure 3. The proper doping of N can improve the electrical conductance of TiO_2 /MWCNTs as the expectation. The NH_4OH to TiO_2 molar ratio as 4 to 1, N doped TiO_2 /MWCNTs-4:1 has the smallest impedance.

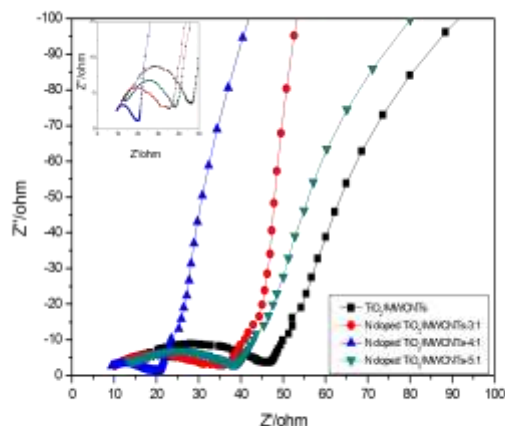


Figure 3. Impedance of TiO_2 /MWCNTs supporters.

The morphologies of the hybrid nanomaterials are shown in Figure 4. TiO_2 or N doped TiO_2 are well coated on the surface of the acidized MWCNTs with average particle size of 7-9 nm as shown in Figure 4 (a) and (b). The particle size of Pd is in the range of 6-9 nm for Pd coated on TiO_2 /MWCNTs or N doped TiO_2 /MWCNTs. SEM image for Pd/N doped TiO_2 /MWCNTs is shown in Figure 4(c).

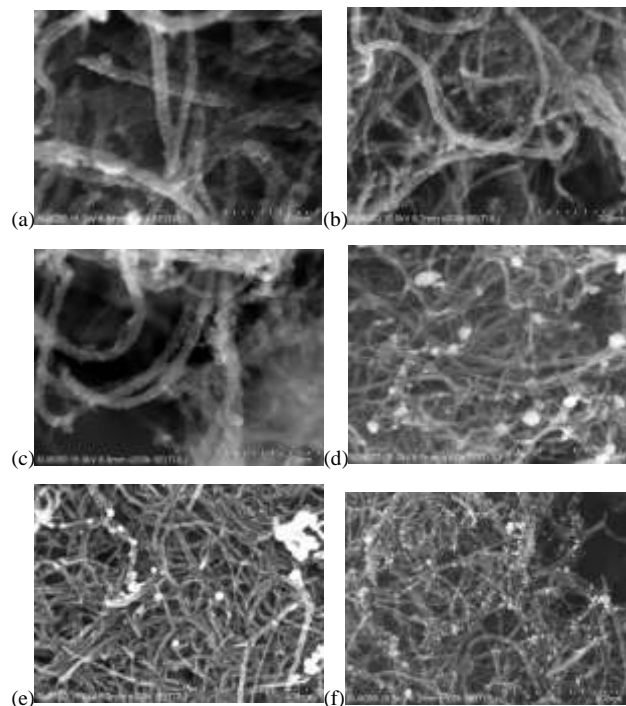


Figure 4. SEM images of the samples (a) TiO_2 /MWCNTs, (b) N-doped TiO_2 /MWCNTs-4:1, (c) Pd/N-doped TiO_2 /MWCNTs-3:1, (d) AuPd/MWCNTs, (e) AuPd/ TiO_2 /MWCNTs, (f) AuPd/N-doped TiO_2 /MWCNTs-4:1.

The images of AuPd coated on various supporters are quite different. The diameters of bimetallic Au-Pd are 19-50, 10-40 and 6-15nm for AuPd/MWCNTs, AuPd/ TiO_2 /MWCNTs and AuPd/N-doped TiO_2 /MWCNTs-4:1, respectively, as showed in Figure 4(d), (e) and (f). It reveals that the doping of N in TiO_2 changing the surface energy of TiO_2 and affecting the dispersion and nucleation of AuPd.

As further observing the HRTEM images of the catalysts, the hybrid nanoparticles can be recognized by analyzing the fringe patterns. The d space of AuPd is observed in between d spaces of pure Pd and Au. It evidences the formation of AuPd solid solution. HRTEM images in Figure 5, Pd or AuPd nanoparticles deposit on TiO_2 particles.

The electrochemical surface areas (ECSA) of catalysts can be determined by measuring the hydrogen adsorption and desorption peaks in cyclic voltammetry according to the following equation:

$$ECSA(m^2/g) = Q_H / 2(W_{Pd} \times 0.21)$$

where $Q_H [C/m^2]$ is the charge due to hydrogen adsorption and desorption, and $W_{Pd} [g/m^2]$ is the specific Pd loaded weight. Q_H can be evaluated by integrating the I-V area of the

hydrogen region, then dividing by the scan rate in V/sec and multiplying the electrode area. The constant $0.21[C/m^2]$ represents the charge required to oxidize a monolayer of H_2 on Pd [25].

The measuring results of ECSA for Pd and AuPd based catalysts are summarized in Table II. Both AuPd solid solution formation and TiO_2 modification hybrid catalysts can benefit the electrocatalytic performance. N doping to TiO_2 can further increase the ECSA area. Pd/N-doped TiO_2 /MWCNTs-4:1 and AuPd/N-doped TiO_2 /MWCNTs-4:1 have the best ECSA values in Pd and AuPd series, respectively.

TiO_2 /MWCNTs-4:1 > AuPd/N-doped TiO_2 /MWCNTs-3:1 > AuPd/N-doped TiO_2 /MWCNTs-5:1 > AuPd/ TiO_2 /MWCNTs > AuPd/MWCNTs. It is observed that:

- AuPd solid solution can enhance the electrocatalytic performance;
- TiO_2 modified and N doping TiO_2 modified hybrid catalysts have higher electro-oxidizing current density due to the efficiency support effects, lower supporter impedance, and higher ECSA area.

TABLE II. ECSA and CV results of electrocatalysts at 10th cycles.

Samples	ECSA(m ² /g) ^a	CV current density ^b
Pd/MWCNTs	21.18	203
Pd/ TiO_2 /MWCNTs	64.68	338
Pd/N-doped TiO_2 /MWCNTs-3:1	88.98	437
Pd/N-doped TiO_2 /MWCNTs-4:1	163.34	1024
Pd/N-doped TiO_2 /MWCNTs-5:1	100.23	869
AuPd/MWCNTs	97.02	411
AuPd/ TiO_2 /MWCNTs	123.23	406
AuPd/N-doped TiO_2 /MWCNTs-3:1	174.42	1184
AuPd/N-doped TiO_2 /MWCNTs-4:1	186.56	1429
AuPd/N-doped TiO_2 /MWCNTs-5:1	151.27	726

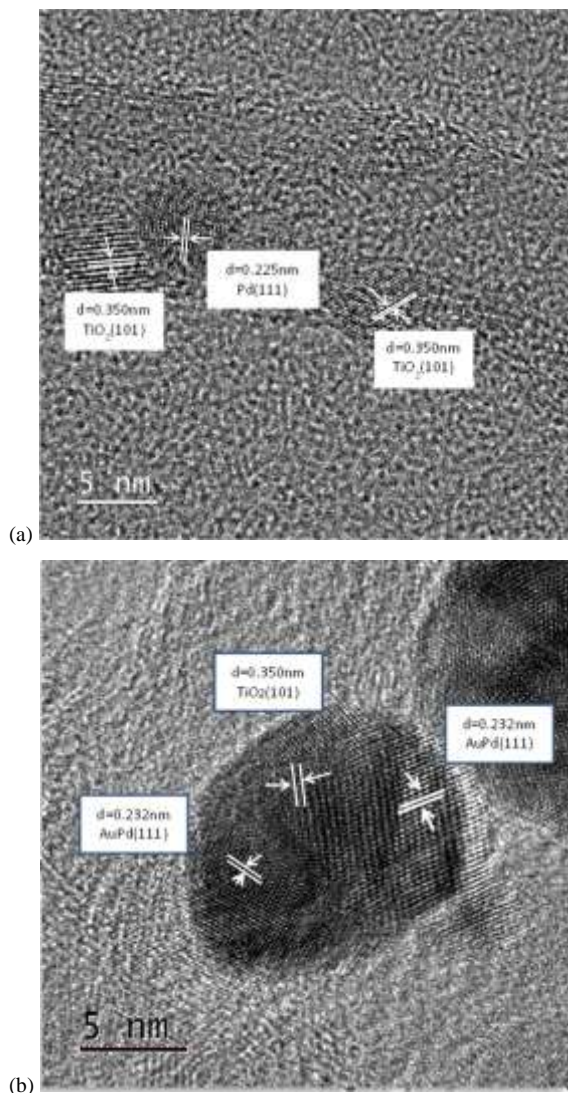


Figure 5. TEM images of the samples (a) Pd/N-doped TiO_2 /MWCNTs-4:1, (b) AuPd/N-doped TiO_2 /MWCNTs-4:1.

CV curves at 10th cycles of the prepared catalysts in 3M formic acid and 1M H_2SO_4 are shown in Figure 6. All the AuPd/metal oxide/MWCNTs catalysts show higher current density than that of AuPd/MWCNTs catalyst. The sequence of oxidation current density at 10th cycles is AuPd/N-doped

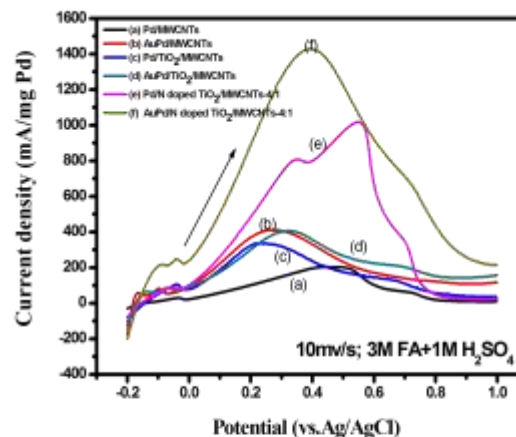


Figure 6. CV curves of (a) Pd/MWCNTs, (b) AuPd/MWCNTs, (c) Pd/ TiO_2 /MWCNTs, (d) AuPd/ TiO_2 /MWCNTs, (e) Pd/N-doped TiO_2 /MWCNTs-4:1, (f) AuPd/N-doped TiO_2 /MWCNTs-4:1 electrodes in 3M HCOOH and 1M H_2SO_4 solution for 10 cycles. (Scan rate: 10mV/s).

Previous studies indicate Au-Pd solid solution can prevent leaching of Pd that enhance and stabilize the catalyst [26]. All the AuPd/metal oxide/MWCNTs catalysts show higher current density than that of Pd/metal oxide MWCNTs catalyst. From the point of views of CV results, it may conclude that Au-Pd solid solution can promote the catalysts performances in electrooxidation of formic acid.

According to the results of chronoamperometric analysis, it can find Au-Pd solid solution can stabilize the Pd particles on the MWCNTs. However, pure TiO₂ cannot stabilize the Pd or AuPd on the TiO₂/MWCNTs supporter. Both Pd and AuPd systems indicate the enhanced electrocatalytic activity and reliability on the N-doped TiO₂/MWCNTs supporter. Especially, Pd on N-doped TiO₂/MWCNTs has the best reliability related the other hybrid catalysts in this study. The reasons of this result may due to enhance the electron conductivity of TiO₂ by N-doping that may fast the electrooxidation reaction of formic acid.

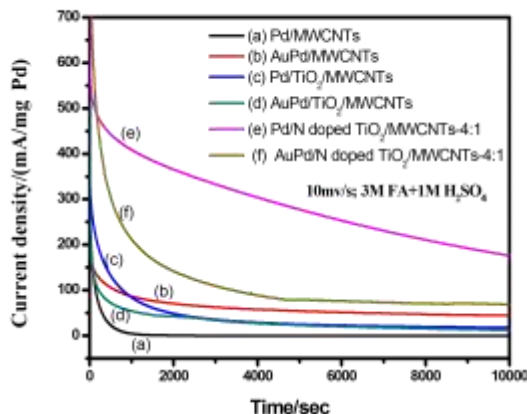


Figure 7. I-t curves of (a) AuPd/MWCNTs, (b) AuPd/TiO₂/MWCNTs, (c) AuPd/N-doped TiO₂/MWCNTs-3:1, (d) AuPd/N-doped TiO₂/MWCNTs-4:1, (e) AuPd/N-doped TiO₂/MWCNTs-5:1 electrodes in 3M HCOOH and 1M H₂SO₄ at 0.3V vs. Ag/AgCl.

Comparing the CV responses of AuPd and Pd in N-doped TiO₂/MWCNTs systems, AuPd system has the higher electrooxidation current than that of Pd one. Also, there are single electrooxidation for AuPd system, but Pd system has two reaction peaks. It reveals the reaction mechanism of AuPd/N-doped TiO₂/MWCNTs system is followed the direct reaction path. While Pd/N-doped-TiO₂/MWCNTs system has dual reactions including direct and indirect paths. However, chronoamperometric analysis at 0.3V (just at the first peak of Pd/N-doped TiO₂/MWCNTs) indicates the Pd system has higher response at 10000 seconds.

iv. Conclusion

In this study, hybrid Pd or AuPd/TiO₂/MWCNTs and Pd or AuPd/N-doped TiO₂/MWCNTs nanomaterials are successfully synthesized and characterized. MWCNTs modified by N-doped TiO₂ as supporters can enhance the electrocatalytic performance by increasing the conductivity of TiO₂ and well dispersion of Pd or AuPd nanoparticles. The 4:1 molar ratio of NH₄OH to TiO₂ obtain the optimal condition for N-doped TiO₂. The results indicate AuPd/N-doped TiO₂/MWCNTs-4:1 has the best CV current density. CA results show that Pd/N-doped TiO₂/MWCNTs-4:1 is the most stable electrocatalyst in formic acid oxidation for operation in long period of times. Thus, N-doped TiO₂/MWCNTs is a promising supporter for cathode catalyst in direct formic acid fuel cells.

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