

Electrophoretic Deposition of Carbon Nanotubes onto Zinc Substrates for Electrode Applications

(Pemendapan Elektroforetik Nanotub Karbon ke dalam Substrat Zink untuk Aplikasi Elektrod)

NAPAPON MASSA-ANGKUL, JESPER T.N. KNIJENBURG, PORNNAPA KASEMSIRI, CHAIYAPUT KRUEHONG, GÜNTHER G. SCHERER, PRINYA CHINDAPRASIRT & KAEWTA JETSRISUPARB*

ABSTRACT

Carbon nanotubes (CNTs) as nanostructured materials have been widely used to improve electrochemical performance of electrode materials for various batteries and electrolyzers. The purpose of this work was to investigate the electrophoretic deposition (EPD) of multi-walled CNTs (MWCNTs) onto Zn plates for application in aqueous Zn ion batteries. The effects of MWCNTs on Zn oxidation and reduction were assessed using cyclic voltammetry. Before EPD, the MWCNTs were modified using H_2SO_4/HNO_3 under reflux to improve dispersion stability in water. Acid modification shortened the MWCNTs but did not cause significant changes in crystallinity, tube diameter, and interlayer spacing. In a second step, the acid modified MWCNTs were homogeneously deposited onto a conductive Zn plate by EPD. Cyclic voltammetry data indicate that the coating of Zn with MWCNTs does not affect the Zn oxidation and reduction potential. Oxidation of Zn eventually leads to formation of a ZnO film, protecting the Zn surface from corrosion. When the protective ZnO film is dissolved, the underlying Zn is oxidized, leading to unfavorable loss of Zn. The presence of MWCNTs reduces oxidation during the cathodic sweep, implying that the MWCNT coating partially protects the underlying Zn surface from oxidation during charging. In addition, the MWCNT coated electrodes also facilitate hydrogen formation and show less oxygen limitation reaction, and could thus be envisaged as possible electrode materials for energy storage devices such as bifunctional electrodes for electrolyzers or air cathodes for batteries or fuel cells.

Keywords: Carbon nanotubes; electrochemistry; electrophoretic deposition; zinc electrode

ABSTRAK

Nanotub karbon (CNTs) sebagai bahan nano telah digunakan secara luas untuk menambahbaik prestasi elektrokimia bahan elektrod dalam pelbagai bateri dan bahan elektrod. Tujuan kajian ini ialah untuk mengkaji pemendapan elektroforesis (EPD) CNTs berbilang dinding (MWCNTs) ke atas plat Zn untuk kegunaan dalam bateri ion Zn akues. Kesan MWCNTs ke atas pengoksidaan dan penurunan Zn telah dikaji menggunakan voltametri berkitar. Sebelum EPD, MWCNTs telah diubah suai menggunakan H_2SO_4/HNO_3 untuk menambahbaik kestabilan penyebaran dalam air. Pengubahsuaian asid memendekkan MWCNTs tetapi tidak menyebabkan perubahan nyata dalam kehabluran, diameter tiub dan jarak antara lapisan. Pada langkah kedua, MWCNTs terubah suai asid telah dimendap ke atas plat Zn melalui proses EPD. Data voltametri berkitar menunjukkan bahawa salutan MWCNTs ke atas Zn tidak menjejaskan pengoksidaan Zn dan potensi penurunan. Pengoksidaan Zn telah menyebabkan pembentukan lapisan ZnO yang melindungi permukaan Zn daripada kakisan. Setelah lapisan ZnO terlarut, Zn pada lapisan bawah telah teroksida dan menyebabkan kehilangan Zn. Kehadiran MWCNTs telah mengurangkan pengoksidaan semasa sapuan katod, menunjukkan bahawa salutan MWCNTs telah melindungi sebahagian permukaan Zn di bawah daripada pengoksidaan semasa pengecasan. Tambahan pula, elektrod bersalut MWCNTs juga membantu pembentukan hidrogen dan menunjukkan tindak balas pengehadan oksigen, dan boleh diramal sebagai bahan elektrod dalam peralatan penyimpanan tenaga seperti elektrod dwifungsi untuk bahan elektrod atau katod udara untuk bateri dan sel fuel.

Kata kunci: Elektrokimia; elektrod zink; nanotub karbon; pemendapan elektroforesis

INTRODUCTION

Rising energy demand and increasing global environmental concerns are the main drive for energy storage technologies

to couple with renewable energy sources such as wind or solar power. The aqueous zinc (Zn) battery is a promising technology for large scale energy storage due to the high availability, stability, safety, and cost-effectiveness of Zn

(Fu et al. 2017). However, low Zn utilization caused by dendrite formation over several charge/discharge cycles and self-corrosion can eventually shorten the battery cycle life (Fu et al. 2017; Lu et al. 2018; Wang et al. 2015).

To subdue formation of dendrites, different approaches have been proposed, primarily by introducing additives (e.g. polymers, organic molecules, metal ions) to electrolytes and electrodes (Lu et al. 2018). The presence of additives, however, increases the polarization and fails to sustain a high battery performance (Lu et al. 2018). Long-term cycling stability has been achieved through backside plating configuration, which can effectively reduce dendrite formation, but comes with the cost of lower energy density (Higashi et al. 2016). Since metallic Zn is unstable in aqueous environment, corrosion leading to limited battery shelf life is an undeniable phenomenon. Recently, coating of ionomers such as Nafion onto Zn particles and implementation of electrolyte additives enables mitigation of corrosion by preserving concentration of zincate ions into the electrolyte and, hence, the cycle life of rechargeable Zn ion battery is improved (Mainar et al. 2018). However, this comes with the cost of limited rate capability and capacity.

Another effective method to improve the utilization of Zn is through incorporation of porous (nano)materials like activated carbon (Huq et al. 2016) or zeolite into the Zn electrode (Cychosz et al. 2017). The well-defined structure may restrict diffusion of oxidation products, hence providing a better control of Zn redistribution. However, the effects of nanostructured materials on the electrochemical behavior of Zn are not fully understood.

As one of the most widely used materials, carbon nanotubes (CNT) are a nanostructured material with a high tensile strength, high electrical conductivity and high ion affinity, making it suitable for various electrochemical applications (Chen et al. 2018). In contrast to other carbonaceous materials, such as graphite or activated carbon, CNT bundles construct a network structure which may accommodate nanosized materials. Frequently, CNTs are added to electrode composites to improve electronic conductivity or as catalyst supports (Chen et al. 2018) or as current collector (Hu et al. 2016). It is also shown that the presence of CNTs improves cyclic behavior and discharge capacity of porous Zn electrode in an alkaline battery (Huq et al. 2016), and electrodeposition of CNTs with Zn reduced steel corrosion in 3.5 wt. % NaCl compared to pure Zn coating (Praveen et al. 2007). Binders are commonly used to hold CNTs in the electrode matrix and ensure good electrical connection. Yet, the presence of binder generates the weight increase of the electrode as well as increased charge transport resistance, resulting in a lower battery performance. In addition, organic solvents used to disperse and blend the

polymeric materials could harm the environment. Thus, one of effective ways to improve electrode performance is to develop binder-free electrodes.

Electrophoretic deposition (EPD) is a widely used coating technique, due to its simplicity, versatility, and scalability (Thomas et al. 2005; Ye et al. 2016). In the EPD process, an electric current is used to attract charged colloidal particles to deposit onto the oppositely charged electrode. The coating layers formed typically exhibit higher conductivity and better mechanical stability than electrodes prepared by conventional methods due to excellent physical connectivity between film and the substrate, even without the requirement for a binder (Ye et al. 2016).

Herein, we prepared Zn/MWCNT composite electrodes by a one-pot modification and deposition process. First, the MWCNTs underwent acid modification to improve their hydrophilicity and colloidal stability. The acid modified MWCNTs were subsequently electrophoretically deposited onto a Zn plate. In this one-pot process the MWCNTs are kept in aqueous suspension throughout the modification and deposition process, eliminating the requirement for tedious separation of MWCNTs after acid modification. The prepared Zn/MWCNT electrodes were characterized by cyclic voltammetry to assess the effects of the modified MWCNTs on the electrochemical behavior of Zn.

MATERIALS AND METHODS

MATERIALS

Distilled and deionized water (18.2 M Ω) was used in all experiments. Multi-walled carbon nanotubes (MWCNTs, outer diameter 10 nm, >90% purity) were purchased from Nano generation Co. Ltd. (Chiang Mai, Thailand). Analytical grade sulfuric acid (96% H₂SO₄) and nitric acid (65% HNO₃) were purchased from RCI Labscan Ltd. AR grade potassium hydroxide pellets (KOH) were purchased from QReC limited. The chemicals were used as received without further purification. Zinc plate (99.94% purity, optical emission spectrometry) was generously received from the Department of Physics, Khon Kaen University. The Zn plate was cut into small pieces by size of 2×1 cm² and rinsed with acetone before the electrophoretic deposition.

ACID MODIFICATION OF MWCNTS

A schematic of the acid modification and EPD process is given in Figure 1. To form a colloidal suspension in water, 1 g of pristine MWCNTs was treated in 60 mL concentrated H₂SO₄/HNO₃ (3:1 v/v) at 120 °C for 60 min (Maiaugree et al. 2016; Sezer & Koç 2019). After cooling down, the solid was separated by centrifugation

(9500 rpm, Mikro 200 Centrifuge) and washed with distilled water until neutral pH. The resulting acid modified MWCNTs were kept in aqueous suspension and its concentration was measured by UV-Vis spectroscopy as described herewith to determine the required dilution

for the EPD process. Such MWCNT suspensions were stable for several months. A portion of the modified MWCNTs was separated and oven-dried for solid state characterization, and for preparation of the UV-Vis calibration curve as described herewith.

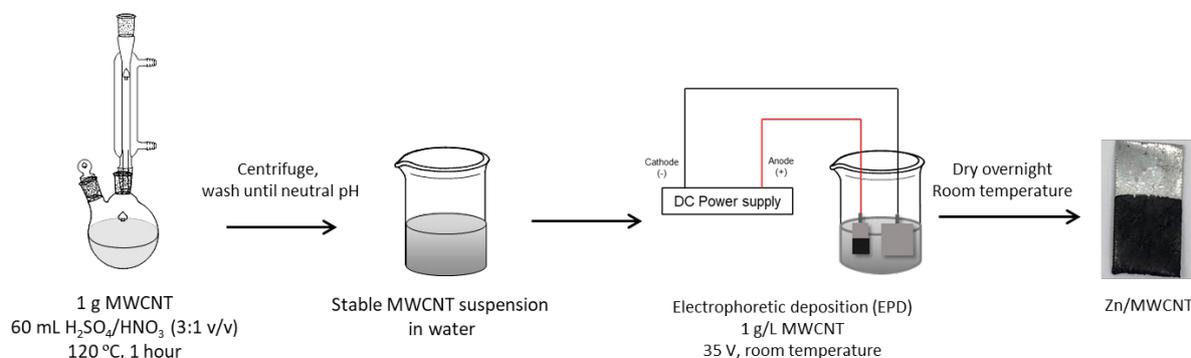


FIGURE 1. Schematic of the one-pot acid modification and electrodeposition (EPD) process of MWCNT in water onto Zn plates

ELECTROPHORETIC DEPOSITION (EPD) OF MWCNTS

The EPD of modified MWCNTs was carried out using a DC power supply (Twintex DC power supply, model TP150-5S). In a typical EPD experiment (Figure 1) the modified MWCNTs (1 g L⁻¹ in water) were deposited onto a Zn plate (2 × 1 cm²) as working anode. Another Zn plate (2 × 2 cm²) was used as counter electrode. A voltage of 35 V was applied, and the inter-electrode distance was 1 cm. The deposition time was varied from 5 sec to 90 m. After deposition, the Zn/MWCNT electrodes were dried overnight at room temperature (Figure 1).

CHARACTERIZATION OF PRISTINE AND MODIFIED MWCNTS

The Fourier-transform infrared (FTIR) spectra of pristine and modified MWCNTs were measured using a Bruker TENSOR27 spectrometer in the range 4000-450 cm⁻¹ (4 cm⁻¹ resolution), accumulating a total of 16 scans. The X-ray diffraction (XRD) analysis of dried CNTs powder was carried out using a D8 Advance (Bruker). The voltage and current were set at 40 kV and 40 mA, respectively. The diffraction angle 2θ is scanned from 5° to 60° at scanning speed of 1° min⁻¹. Nitrogen adsorption isotherms were measured at 77 K on an ASAP2460 (Micromeritics). The specific surface area (SSA) and pore size distribution of MWCNTs were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

The concentration of the MWCNTs in aqueous suspension was measured by UV-Vis spectroscopy (SPECORD 200, Analytik Jena) following Zhao and Gao (2003). A calibration curve was prepared using known concentrations of activated MWCNTs in water prepared from dried activated MWCNTs, and the peak absorbance at 255 nm was measured.

The optical contact angle (OCA) was determined using the OCA15EC (Dataphysics) using sessile drop technique. A water droplet was dispensed through a manual syringe with dosing volume of 5 μL, and the contact angle was calculated using SCA20 software.

Transmission electron microscopy (TEM) images were taken on a TECNAI G2 20 S-TWIN (FEI, Czech Republic) operated at 200 kV. Samples were dispersed on copper grids for analysis. The interlayer spacing d_{002} was determined from the SAED patterns using ImageJ software (version 1.52p). Field emission scanning electron microscopy (FESEM) images were taken on a Carl Zeiss Auriga using 3 kV acceleration voltage.

ELECTROCHEMICAL CHARACTERIZATION

Cyclic voltammetry (CV) analysis of the electrodes was carried out in 1 M KOH solution with a Gamry R600 potentiostat using a three-point-probe configuration (Triamthaisong et al. 2018). The working electrodes were composed of either a bare Zn plate (2 × 1 cm²) or a Zn/MWCNT electrode (2 × 1 cm²), whereas a 2 × 2 cm² Zn plate was used as counter electrode. A Luggin capillary

filled with saturated KCl salt bridge was placed in the electrolyte near the working electrode, and Ag/AgCl in saturated KCl was used as reference electrode. The CV measurements were carried out with a scan rate of 10 mV s⁻¹ at room temperature.

RESULTS AND DISCUSSION

CHARACTERIZATION OF PRISTINE AND MODIFIED MWCNTS

The MWCNTs need to be prepared as a stable suspension for the EPD process. For this purpose, the MWCNTs are typically treated with concentrated acids to incorporate acid-functional groups on the surface that improve their aqueous dispersibility (Maiaugree et al. 2016; Sezer & Koç 2019). In this work, the MWCNTs were treated under reflux using concentrated H₂SO₄/HNO₃. The resulting acid modified MWCNTs were well-dispersed in water and the suspension is stable for several months. In contrast, the pristine MWCNTs floated on the water surface or settled to the bottom when centrifugation was applied.

The FTIR analysis was carried out to confirm the success of acid modification. Figure 2(a) shows the FTIR spectra of pristine and modified MWCNTs samples. The spectrum of the pristine MWCNTs show the typical vibrational peaks at 2906 and 2865 cm⁻¹ that can be ascribed to symmetric methyl and asymmetric/symmetric methylene groups, respectively. Such groups are typically found at defect sites on the nanotube sidewall surface (Scheibe et al. 2010). Other peaks related to hydrocarbon

groups can be found at 895 cm⁻¹ (=C-H bending) (Wei et al. 2019). The peaks at 1000-1200 and 1313 cm⁻¹ are typically associated with C-O bonds (Saleh 2011; Wei et al. 2019). This indicates that the pristine MWCNTs already contain some oxygen-containing groups such as ethers (Scheibe et al. 2010). Furthermore, the presence of carboxylic groups on the pristine MWCNTs can be seen at 1734 (carboxylic C=O) and 1427 cm⁻¹ (O-H) (Varga et al. 2017). The small absorbance peak at 1643 cm⁻¹ can be assigned to C=C stretching (Wei et al. 2019) or C-O stretching (Saleh 2011). The peaks at 3200-3400 cm⁻¹ are from hydroxyl groups that may be from moisture adsorbed from the air (Wei et al. 2019). The peaks at 1990-2320 cm⁻¹ were artefacts from the FTIR equipment (Nazeeruddin et al. 2003).

After acid modification, there are no major changes in the FTIR peak positions. The peak at 1025 cm⁻¹ is reduced in intensity relative to the other peaks, indicating cleavage of the C-O and C-O-C groups by the H₂SO₄/HNO₃ acid mixture (Scheibe et al. 2010). There was no significant shift in the carboxylic C=O peak at 1734 cm⁻¹, in agreement with Zhang et al. (2003) for short treatment times. In addition, nitric and sulfonic groups may have been grafted onto the modified MWCNT (Mansor et al. 2012; Qu et al. 2016). Even though the hydrophilicity (as discussed later) and dispersibility in water improved after acid treatment, the increase in functional group content could not be verified with FTIR analysis; functional groups are difficult to see with FTIR as they only account for a small percentage of the total MWCNT mass (Kim et al. 2005).

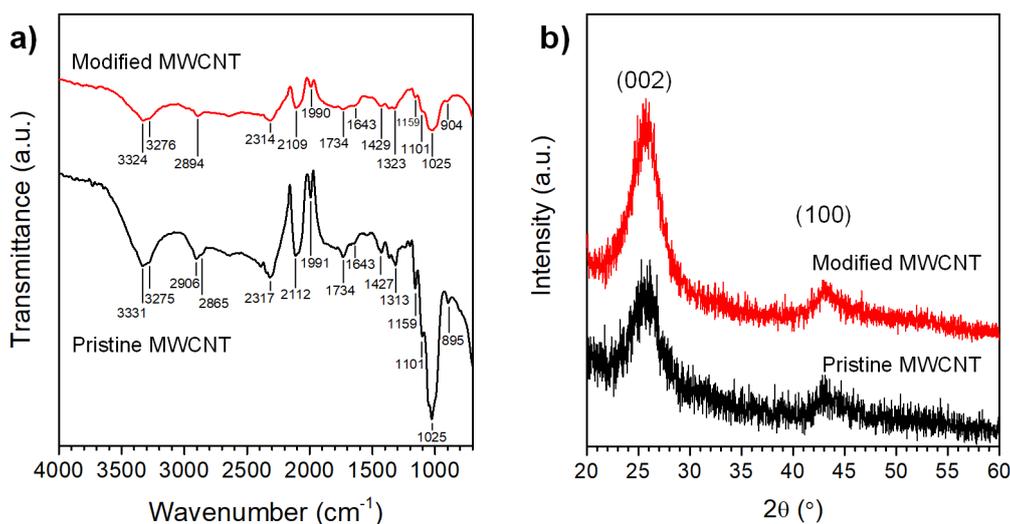


FIGURE 2. a) FTIR spectra and b) XRD patterns of pristine and modified (acid treated) MWCNTs

The XRD patterns (Figure 2(b)) show that the modified MWCNTs have a similar crystalline structure as the pristine MWCNTs, indicating that the crystallinity and microstructure of the MWCNTs has not substantially changed after acid treatment (Gómez et al. 2016). Two prominent peaks were found at ca. $2\theta = 26$ and 43° that can be attributed to (002) and (100) planes, respectively (Saleh 2011). The (002) peak corresponds to the interlayer spacing (d_{002}) between graphene sheets while (100) peak is characteristic for the in-plane graphitic structure (Che et al. 2015).

To confirm any structural changes by acid modification, FESEM and TEM images of pristine and modified MWCNTs were analyzed (Figure 3). The pristine MWCNTs appear as smooth long tubes with high aspect

ratio and an outer diameter of approximately 10-15 nm (Figure 3(a)-3(c)). The interlayer spacing (d_{002}) between tubes was found to be 0.33 nm as typical for MWCNTs (Kharissova & Kharisov 2014). The modified MWCNTs are shorter than the pristine MWCNTs and their surface roughness has increased (Figure 3(e)). Moreover, the modified MWCNTs are strongly aggregated (Figure 3(d)) that may have caused a decrease in their SSA (Table 1). The acid treatment, however, did not significantly affect the tube diameter and d_{002} (Figure 3(f)). An increase in the interlayer spacing d_{002} was previously observed for longer acid treatment (>24 h) (Chiang et al. 2011); the duration of the acid treatment in our experiment (60 min) was likely too short to induce significant changes.

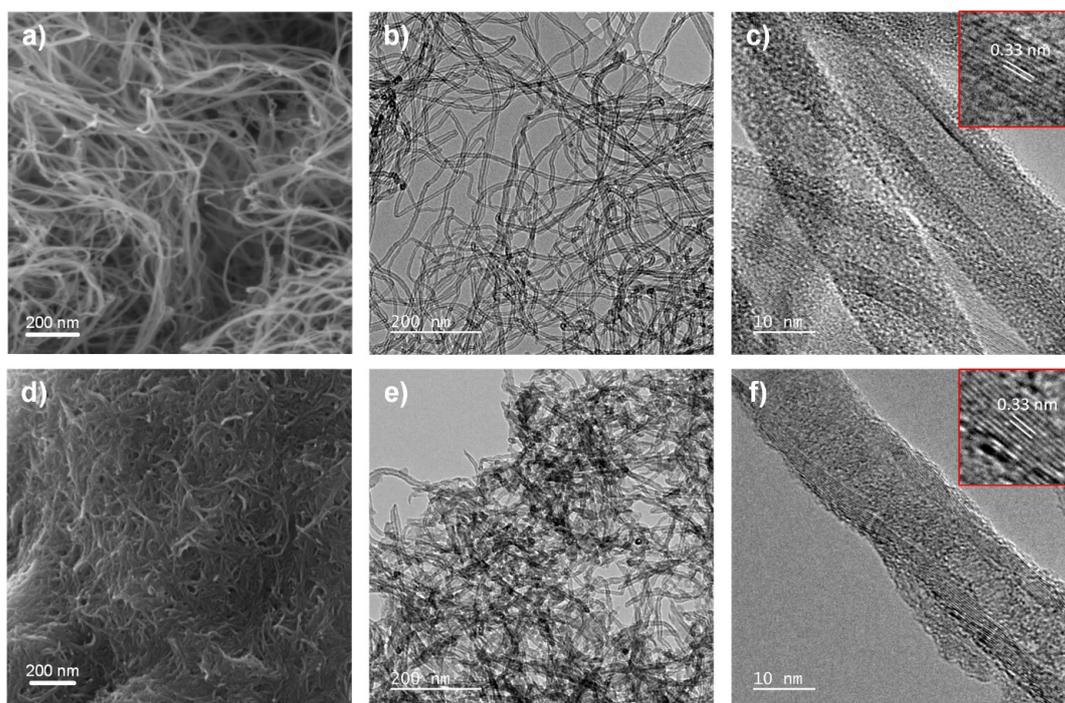


FIGURE 3. a) SEM image of pristine MWCNTs. b,c) TEM images of pristine MWCNTs at low (b) and high magnification (c). d) SEM image of acid-modified MWCNTs. e,f) TEM images of acid-modified MWCNTs at low (e) and high magnification (f). The insets in c) and f) indicate the interlayer spacing d_{002} as calculated from the SAED patterns

After modification, the surface area and pore volume of MWCNTs decreased from 269 to 65 m^2g^{-1} and from 0.99 to 0.17 cm^3g^{-1} , respectively (Table 1), which could have been caused by pore entrance blockage by the

formation of functional groups (Lu & Chiu 2008) or by aggregation of MWCNTs (Figure 3(d)) during separation/drying for solid state characterization.

TABLE 1. Specific surface area, average pore diameter, and pore volume of pristine and modified MWCNTs determined by nitrogen adsorption at 77 K

Sample	Surface area (m^2g^{-1})	Pore diameter (nm)	Pore volume (cm^3g^{-1})
Pristine MWCNTs	269	7.62	0.99
Modified MWCNTs	65	9.09	0.17

The water OCA onto a typical Zn/MWCNT electrode was used to study the wettability of the modified MWCNTs. Figure 4 shows that the Zn/MWCNT electrode surface is hydrophilic with a water contact angle of $35.9\text{--}39.1^\circ$, comparable to Cho et al. (2009). This low contact angle is likely due to the presence of hydrophilic carboxyl and hydroxyl functional groups on the modified MWCNTs. Similar results were found by Silva et al. (2012), who report that the acid functional

groups introduced onto the walls of MWCNTs from acid modification caused a change in the contact angle due to hydrogen bonding interaction. A low water OCA is necessary for electrocatalysis, especially for water splitting, to ensure a good contact between electrocatalyst and aqueous electrolyte (Xu et al. 2018). In contrast, pristine MWCNTs demonstrate a non-wetting behavior (Silva et al. 2012; Werder et al. 2001), which may also explain their poor dispersibility in water.

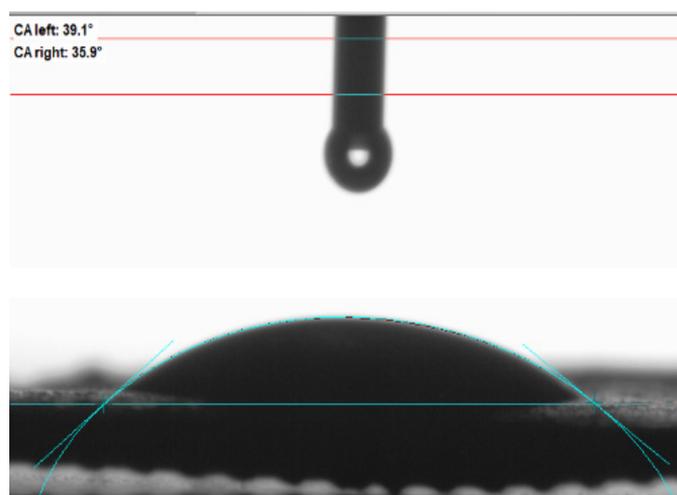


FIGURE 4. Water optical contact angle (OCA) on Zn/MWCNT electrode

ELECTROPHORETIC DEPOSITION KINETICS

The obtained deposited MWCNT film after 60 min shows a smooth and optically homogeneous surface (Figure 1). A lower potential (<30 V) typically results in inhomogeneous films that are loosely bound to the substrate (Thomas et al. 2006), whereas potentials of >35 V may negatively affect the morphology and stability of deposited films due to gas evolution via water electrolysis (Cho et al. 2009). Therefore, a deposition voltage of 35 V

was applied in this study. Figure 5(a) shows the weight of electrophoretically deposited MWCNT onto Zn substrate as a function of time at 35 V. These deposition kinetics are in the same order as previous EPD studies of CNTs on stainless steel substrates (Moore et al. 2012; Thomas et al. 2006). A rapid increase in the deposited mass is observed in the first 10 min and levels off. At prolonged deposition time, the deposited MWCNT layer acts as a shielding film that causes a high electrical resistance,

decreasing the driving force for MWCNT deposition onto the electrode (Cho et al. 2009; Du et al. 2002). Although a higher deposited weight may be obtained by EPD using non-aqueous solvents (Nie et al. 2012), EPD in aqueous media has the advantages of lower voltage required, lower cost, and avoiding environmental issues with organic solvents (Besra & Liu 2007; Cho et al. 2009). Figure

5(b) shows a typical FESEM image of a Zn/MWCNT electrode. The MWCNTs are randomly oriented and form a homogeneous layer on the Zn plate. Compared to the modified MWCNTs powder (Figure 3(d)), when deposited onto a Zn plate using EPD the MWCNTs are less aggregated and an open structure is formed.

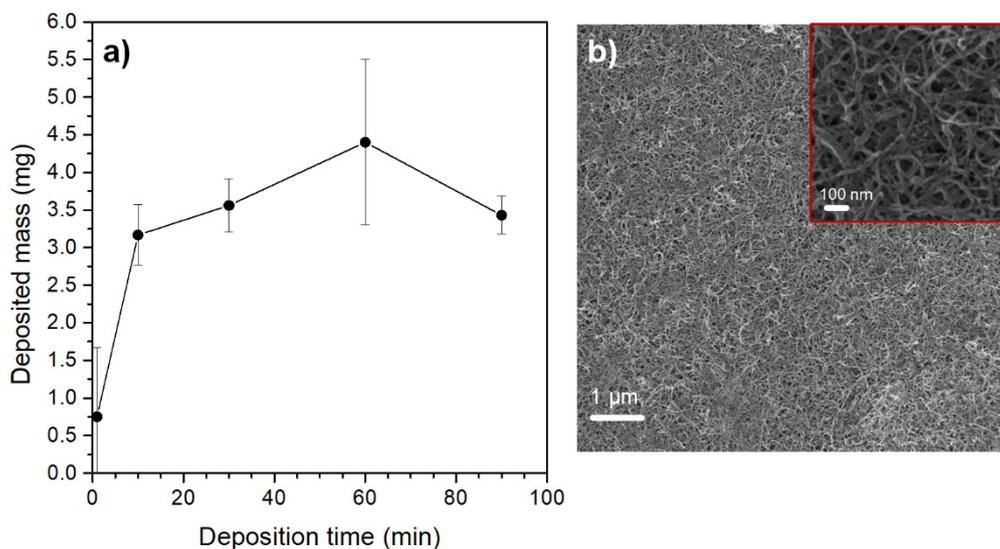


FIGURE 5. a) Electrophoretic deposition (EPD) kinetics of acid modified MWCNTs onto Zn substrate from aqueous suspension (1 g/L MWCNT) using a deposition voltage of 35 V and 1 cm interelectrode distance. Experiments were carried out in triplicate. b) FESEM image of a Zn/MWCNT electrode produced with 30 min deposition time. The inset shows a FESEM image taken at higher magnification

ELECTROCHEMICAL CHARACTERIZATION

Figure 6 shows typical cyclic voltammograms (CVs) of Zn plate and Zn/MWCNT obtained in 1 M KOH solution. The CVs of both electrodes appear almost identical except at the start of the anodic sweep where hydrogen is produced from -1.8 to -1.4 V (region A in Figure 6). The lowering of the hydrogen evolution reaction (HER) overpotential in the presence of acid modified MWCNT coating shows that the MWCNTs exhibit apparent HER activity, facilitating the formation of H_2 . The superior HER activity may be attributed to the higher electrochemical surface area due to the MWCNT coating and the catalytic property of MWCNTs (Darband et al. 2018). The MWCNT defects generated during acid modification may lead to an increase in the active sites for hydrogen production. While HER is regarded as sluggish in alkaline electrolyte media (Dubouis & Grimaud 2019),

the incorporation of acid modified MWCNTs using EPD could attribute to enhanced HER kinetics. This technique could be employed for the future design of electrodes for energy storage devices such as alkaline water electrolysis. Besides its lower HER activity, oxygen limitation reaction can be simultaneously observed in the pristine Zn electrode (region A). The presence of acid modified MWCNTs could have applications as suitable air cathode materials when a more stable substrate in alkaline electrolyte such as Ni is used.

A broad Zn anodic stripping peak is observed at around -1.4 V with respect to Ag/AgCl reference electrode for both Zn plate and Zn/MWCNTs electrodes (region B). This broad peak is likely composed of two overlapping peaks corresponding to the formation of zincate ions (i.e. $Zn(OH)_4^{2-}$ and $Zn(OH)_3^-$) due to Zn oxidation (Cai & Park 1996). These zincate ions dissolve

in the alkaline solution and eventually saturation is reached, at which point a protective ZnO layer is deposited onto the Zn surface. This passive ZnO film inhibits MWCNTs diffusion and further oxidation of Zn, causing a dramatic current drop when the potential applied is lower than -1.1 V.

During the cathodic sweep which may resemble charging of a rechargeable Zn ion battery, the anodic peak for the Zn plate starts at -1.15 V due to the dissolution of ZnO from the Zn surface in the alkaline solution (region C). After this protective film is removed, the oxidation can further take place when Zn is exposed to the electrolyte, causing a positive current density. While this phenomenon is common for Zn, it is not preferable since the current

produced during charging does not lead to useful work. The current density of the Zn/MWCNT electrode is slightly lower than that of the Zn plate, possibly because of a different local environment (e.g. the acid functional groups on MWCNT may attribute to a lower local pH on the surface). This may shift the saturation of zincate, yielding prior passive ZnO film formation compared to that of the pristine Zn plate. In addition, the coating may also act as another protective layer, thereby lowering Zn corrosion in the cathodic sweep (Bockelmann et al. 2017). Therefore, incorporation of MWCNT coating could be beneficial during charging of the Zn anode. Further reduction of both electrodes leads to Zn reduction at around -1.4 V. (region D).

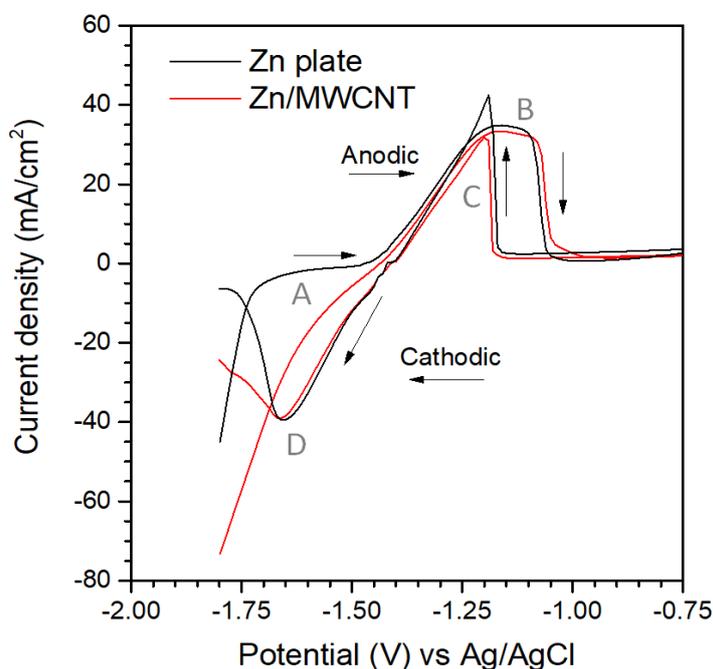


FIGURE 6. Typical cyclic voltammograms of Zn and Zn/MWCNT electrodes (3.2 mg MWCNT) in 1 M KOH using scan rate of 10 mV/s

To summarize, we have demonstrated that the binder-free EPD of hydrophilic, acid-modified, electrically conductive MWCNTs onto the Zn surface may lower the HER overpotential. This could be achieved using a facile one-pot process without the need for tedious separation of acid modified MWCNTs. It was found that the presence of acid modified MWCNT coating could be beneficial for rechargeable Zn ion battery due to reduction of Zn corrosion during charging. However, multiple cycling experiments should be conducted to confirm long-term stability.

CONCLUSION

In this work, we have demonstrated the one-pot acid modification and binder-free EPD of MWCNTs onto Zn plates. The acid modification greatly improved MWCNT dispersibility in water and shortened the MWCNTs but did not cause significant changes in crystallinity, tube diameter and interlayer spacing. The electrochemical behavior of Zn plate and Zn/MWCNT electrodes in 1 M KOH was similar, implying that incorporation of MWCNTs through EPD does not strongly affect oxidation and reduction of Zn. However, MWCNT coating

demonstrated that Zn oxidation during the cathodic sweep is reduced which could possibly enhance the performance of rechargeable Zn anode in alkaline electrolyte. Cyclic voltammetry experiments also show that MWCNTs not only contribute to high electronic conductivity but may also act as electrocatalyst for hydrogen evolution and oxygen reduction. These findings might shed light on upcoming bifunctional electrodes for energy storage devices such as alkaline electrolyzers or air electrode in alkaline batteries or fuel cells.

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- Napapon Massa-Angkul, Pornnapa Kasemsiri, Chaiyaput Kruehong & Kaewta Jetsrisuparb*
Department of Chemical Engineering
Khon Kaen University
40002 Khon Kaen
Thailand
- Jesper T.N. Knijnenburg
International College
Khon Kaen University
40002 Khon Kaen
Thailand
- Jesper T.N. Knijnenburg, Pornnapa Kasemsiri, Prinya Chindapasirt & Kaewta Jetsrisuparb*
Sustainable Infrastructure Research and Development Center
Khon Kaen University
40002 Khon Kaen
Thailand
- Günther G. Scherer
Department for Management of Science and Technology
Development
Ton Duc Thang University
Ho Chi Minh City
Vietnam
- Günther G. Scherer
Faculty of Applied Sciences
Ton Duc Thang University
Ho Chi Minh City
Vietnam
- Prinya Chindapasirt
Department of Civil Engineering
Khon Kaen University
40002 Khon Kaen
Thailand

*Corresponding author; email: kaewta@kku.ac.th

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