Electrocatalytic hydrogen evolution of palladium nanoparticles electrodeposited on nanographene coated macroporous electrically conductive network

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Electrocatalytic hydrogen evolution of palladium nanoparticle electrodeposited on nanographene coated macroporous electrically conductive network was studied in KOH electrolyte. The surface nanographene on nickel nanoparticles can increase the electron conductivity and protect the metal particles, as well as improve the electrode stability in the electrolyte. After the palladium nanoparticle electrodeposited on nanographene coated three-dimensional network, the enhancing electrocatalytic hydrogen evolution can be attributed to better surface electrochemical properties, including of the low charge transfer resistances, and improving H\textsuperscript{+} ion adsorption/desorption and reaction rate.

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I N T R O D U C T I O N

Hydrogen energy is one of the potential candidates for replacing fossil fuels in the future to minimize the CO\textsubscript{2} emissions and their effects on climate due to its clean and environmentally friendly properties [1–4]. The hydrogen evolution reaction (HER) is one key step in water splitting to obtain the hydrogen fuel. It involves the electrochemical reactions, which protons diffused from solution combine with electrons transported from the electrode to form first hydrogen atoms chemisorbed at the electrode surface and
then hydrogen gas [5–7]. The HER, which explores the mechanism of multi-electron transfer processes in electrocatalysis, always requires a fine catalyst to achieve fast kinetic for practical application. In order to improve the efficiency of catalysts, many strategies have been made toward the modification of material properties, formation of composite catalysts, fabrication of electrode with three-dimensional (3D) architecture, and or combination of the different efforts [8–11]. It was made great efforts to construct the hierarchical structures, including of macroporous pores (>50 nm in diameter), mesoporous walls (2–50 nm) and micropores (<2 nm), to improve the hydrogen atoms chemisorbed at the electrode surface [12,13]. Recently, the 3D graphene structures have attracted increasing attention due to the high porosity and large specific area [14–16] for increasing electrocatalyst loading to improve the HER efficiency. Also, the 3D architecture based on graphene can be as a network to produce the pass channel for fast electron and ion transport. For example, a 3D graphene foam can be synthesized by chemical vapor deposition (CVD) using nickel foam as the porous template on which graphene is deposited by CVD followed by removal of the template to form the 3D graphene foam [17,18]. However, the 3D electrode properties, such as the specific surface area and ion transport, were limited due to large (several tens and hundreds micrometers) and aperiodic porous structure for 3D graphene foam. Also, the degradation of fabricated 3D graphene foam appears because of spontaneous agglomeration and restacking of the graphene nanosheets due to the large Van der Waals attraction between adjacent sheets [19].

There are different kinds of 3D architectures, such as interdigital structures, nanometer- or micrometer-sized wire arrays, and microchannel plates (MCP), have been fabricated on silicon by standard microelectromechanical (MEMS) techniques [20–22]. The silicon microchannel plate (SiMCP) is a perforated through-hole and free-standing substrate formed by photo-assisted electro-chemical etching and subsequent electrochemical peeling from the Si substrate [23,24]. The microchannels have a depth of about 200 μm and square sizes of 5 × 5 μm for holes giving an aspect ratio (length/diameter of hole) of the channels of 40. The SiMCP array has a large area ratio (>70%) and the surface area gain can be larger than 100 compared to a planar one. In addition, the SiMCP can be annealed at a high temperature (more than 1000 °C) in subsequent processing steps to produce 3D electrode and has sufficient mechanical stability in non-aqueous and aqueous electrolytes containing acids and salts. After deposition of a metal such as nickel, the nickel-coated SiMCP structure (named as macroporous electrically conductive network, MECN) is also stable in alkaline media as well. Such as, the tetsubo-like Co(OH)2 nanorodes deposited on MECN electrode shows excellent HER activity, with a low overpotential and Tafel slope and high current density in 1 M KOH solution [11].

In order to improve the electrical conductivity of the 3D architecture, it has been employed to fabricate 3D nanographene on the MECN by hydrothermal carbonization. The stable 3D nanographene array is formed and will not aggregate to form graphite due to the solid silicon architecture. Then it shows that the nano-graphene coated MECN was the suitable 3D electrode to fabricate the field emission devices [25] and energy storage devices with the high power and energy density and excellent electrochemical stability [26,27]. Recently, it is also proved that the structured Pd, such as Mesoporous Pd, mesoporous Pd metal nanoarchitectonics, and/or Pd nanoparticles supported on graphene, Pd-modified structure, can provide fascinating electrocatalytic properties [28–32]. PdNi alloy structures prepared on carbon nanofibers (CNFs) exhibit bifunctional electrocatalyst properties, and show good catalytic activity and stability in both the HER and hydrogen oxidation reaction (OR), which can be attributed to the synergistic effects of the PdNi alloy and the properties of the CNF substrate [33]. It also shows that nano-dispersed interconnected crystalline phases of Ni and Pd exhibit high catalyst activity, resulting in record high performance for an alkaline membrane fuel cell [34]. In this case, it is interesting to deposit the noble metal such as Palladium (Pd) on the surface of nano-graphene 3D electrode to study the electrocatalysis properties and to get deep understanding of the function of surface nanographene. It is also necessary to understand the electrochemical properties of the 3D nanographene structure with a large electrode/electrolyte contact area and deep microchannel in an accommodated volume.

Experimental details

All the chemical reagents were analytical grade (AR) and used as received without further purification. Palladiumchloride (PdCl2), ethylene diaminetetraacetic acid (EDTA), Nickel chloride hexahydrate (NiCl2·6H2O), and ammonium chloride (NH4Cl) were purchased from Aladdin Reagent and triethylene glycol (C6H14O4), sodium hypophosphite monohydrate (NaH2PO2·H2O), ethanol, hydrochloric acid (HCl), triton X-100 and some other chemical reagents were bought from Sinopharm Chemical Reagent Co. Ltd. Deionized water was used throughout the experiments.

The fabrication process of three kinds of 3D architectures based on SiMCP, Ni-coated SiMCP (marked as MECN), carbon–nickel alloy coated MECN (marked as NiCMECN), and nano-graphene coated MECN (marked as NGMECN), were reported before [25–28]. First step, the SiMCP structures were produced by the standard microelectronics fabrication steps on a p-type (100) silicon wafer with a thickness of 525 μm. Some important steps include of the pre-etching of lithography patterned Si wafer electrodes in a tetramethyl ammonium hydroxide (TMAH) solution, anodized etching and self-peeling processes on a computer-controlled photo-assisted electrochemical system. The SiMCP was cut into 1 cm × 1 cm square pieces for further processing. More details about the process can be found in Refs. 24 and 25. Second step, the MECN electrodes were obtained through electroless deposition of the porous nano-Ni films in a vacuum oven at the temperature 90 °C for 30 min to make nickel cover the inner sidewalls of the SiMCPs smoothly. Third step, the mixed solution of Sodium acetate trihydrate and triethylene glycol were transferred to a Teflon-sealed stainless steel autoclave with MECSNs samples. The tighten autoclave was inserted into a vacuum oven Teflon-sealed stainless steel autoclave with MECSNs samples. The tighten autoclave was inserted into a vacuum oven heated for 6 h at temperature 250 °C to produce the carbon–nickel alloy coated MECN (labeled as NiCMECN). Fourth step, the NiCMECN samples were placed in a tube furnace for 1 h at temperature 650 °C in argon to produce nano-graphene layer coated MECSNs (labeled as NGMECN). More details about the
from 10 to 100 mVs/C. An appropriate amount of NH₄OH was added to adjust the pH to 7–9, as well as the bath temperature needed to keep at 55 °C. After electroplating for 30 min with the current density of 50 mA cm⁻², different samples, including of Pd/MECN, Pd/NiCMECN and Pd/NGMECN, were also taken down to wash with deionized water and dry on heat-plate with temperature 80 °C.

The morphology and microstructure of the samples were examined by scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan) and the crystal structures were determined by X-ray diffraction (XRD, Rigaku, RINT2000, Japan, Cu Kα1 radiation, λ = 0.154 nm). The electrochemical tests were performed on a CHI660D electrochemical workstation (Shanghai Chenhua CHI660D) in the three-electrode mode in which the sample, platinum electrode, and saturated calomel electrode (SCE) served as the working electrode, counter electrode, and reference electrode, respectively. The samples were exposed to 1.0 mol L⁻¹ KOH at room temperature (25 °C) and the cyclic voltammograms (CV) were acquired in the potential range between −1.2 and 0.6 V vs. SCE at different scanning rates from 10 to 100 mVs⁻¹. The Tafel plots were obtained from the potentiodynamic polarization tests conducted at sweeping rates of 1 mV s⁻¹ in the anodic direction. The data in the Tafel plots in the range of ±200 mV from the open circuit potential were selected. Electrochemical impedance spectroscopy (EIS) was conducted in the frequency range from 100,000–0.1 Hz at the open circuit potential (OCP). In the Mott–Schottky analysis, the impedance-potential curves were obtained by sweeping the potential in the positive direction at an excitation voltage of 5 mV and frequencies from 1 to 1000 Hz. The data were normalized by the footprint area.

**Results and discussion**

**Structural characterization**

As shown in Fig. 1a, the top view of the SiMCP is depicted in the SEM (image I). The microchannels have a square size of 5 × 5 µm and a depth of about 200 µm and giving an aspect ratio of the microchannels of 40. The specific surface area gain is about 60 compared to a planar silicon structure. After electoreless nickel plating, the surface of the MECN is coated uniformly with a thin disordered nickel layer with a thickness about 0.5 µm composed of porous nickel grains with a size of about 50 nm (image II). Since the porous nickel balls are deposited on the outer and inner surfaces of the SiMCP and the Ni electrode is porous, the surface area of the 3D nickel layer increases by almost 100 times [36]. After hydrothermal carbonization at 250 °C for 6 h, the compact Ni–C alloy layer is formed after carbon diffusion into the MECN (image III). When carbon is introduced to the Ni layer during hydrothermal carbonization, the thickness of the Ni–C alloy is about 1.5 µm and a large amount of Ni is deposited on the projection of the silicon structure during electoreless Ni plating. Local preferential growth is observed because the thick silicon layer is retained in these regions during photo-assisted electrochemical etching forming the SiMCP, for example, at the cross points and middle of the wall (image I). However, they still retain the original 3D structure because the morphology does not change at 250 °C during hydrothermal carbonization. After annealing at 650 °C for 1 h in Ar, loose nano-balls are observed from the surface of the MECN hydrothermally carbonized (image IV). It shows that some Ni nanoballs would be exfoliated from the Ni–C alloy and the nickel layer composed of particles with loose nanometer-size balls with a diameter of about 50 nm is observed from the surface of the MECNs after post-annealing during segregation of carbon from Ni–C to form the nano-graphene on MECN [35].

After formation the different surface of 3D architecture, the metal Pd were deposited on the substrates as shown schematic images V–VII in Fig. 1a. The top and cross-sectional SEM images of Pd/NiCMECN (I, II) and Pd/NGMECN (III, IV) are shown in Fig. 1b. After electroplating Pd, the surface and sidewall of 3D NiCMECN and NGMECN were coated uniformly with a thin disordered Pd layer composed of porous Pd grains with a size of about 10–20 nm. Energy-Dispersive X-Ray Spectroscopy (EDS) spectrum (Fig. 1c) shows that there are different kinds of elements, including of carbon, oxygen, nickel, phosphorus and high-density Palladium after Pd deposited on NGMECN sample. Fig. 1d shows the X-ray diffraction (XRD) patterns of Pd/MECN, Pd/NiCMECN and Pd/NGMECN. In order to compare clearly, the related XRD data of substrates are also shown [35]. There are four high-density peaks in the XRD pattern for MECN. One peak can be attributed to the Si substrate [400] peak at 2θ = 69.3°, marked with a solid diamond) and the other three peaks arise from the cubic phase Ni metal with the (111) peak at 2θ = 44.7°, (200) peak at 2θ = 52.1°, and (220) peak at 2θ = 76.6°, marked with a hollow diamond. After Pd plating, there is one addition weak peak at the 2θ = 40.24 corresponding to the face-centered cubic phase Pd metal (111) crystal faces (marked with arrows) [37]. When carbon atoms penetrate the Ni nanoparticles forming the Ni₃C phase, the four XRD peaks of hexagonal nickel carbide appear (Ni₃C phase, marked with a circle). After Pd plating on NiCMECN, there are two peak weak at the 2θ = 40.24 and 46.78 corresponding to the face-centered cubic phase Pd metal (111) and (200) crystal faces (marked with arrows). At the same time, the XRD peaks of NiC alloy decrease and/or disappear. After annealing at 650 °C in Ar for NiCMECN, all of the hexagonal Ni₃C phase peaks disappear and a broad peak of graphite (002) (marked with a pentagram) appears at about 2θ = 25°. After Pd plating on NGMECN, there are two weak peaks at the 2θ = 40.24 and 46.78 corresponding to the face-centered cubic phase Pd metal (111) and (200) crystal faces (marked with arrows). At the same time, the wide peak of nanographene disappears. In this case, the average crystallite sizes of Pd particles D would be estimated through the Scherrer formula [37,38].

\[
D = \frac{K \lambda}{\beta \cos(\theta^*)},
\]

where K is constant number (in our case 0.93), λ the wavelength of the incide X-rays (0.154 nm), β full width at half-height of the diffracted peak and θ Bragg diffraction angle. The crystallite sizes 6.5, 13 and 10 nm can be calculated from the full width at half-height of the (111) reflections for Pd/MECN, Pd/NiCMECN and Pd/NGMECN, respectively.
Fig. 1 – (a) Top-view images of silicon microchannel plate (SiMCP, I), Ni-coated SiMCP (MECN, II), Nickel-carbon alloy coated MECN (NiCMECN, III) and nanographene-coated MECN (NGMECN, IV). The schematic of the synthesisization process of Pd nanoparticles deposited on different substrate including of MECN (V), NiCMECN (VI) and NGMECN (VII). (b) Top-view and cross-sectional images of Pd/NiCMECN (I, II) and Pd/NGMECN (III, IV). (c) EDS spectrum for Pd/NGMECN. (d) XRD patterns of MECN, NiCMECN, and NGMECN and related Pd/MECN, Pd/NiCMECN and Pd/NGMECN electrodes.
Cyclic voltammetry characterization

The cyclic voltammograms (CV) acquired from MECN and Pd/MECN in the potential range of \(-1.2\)–\(-0.6\) V vs. SCE at a scanning rate 10 mV s\(^{-1}\) are presented in Fig. 2a. The related CV curves in the potential range of \(-1.5\)–0 V vs. SCE are presented in Fig. 2b. The shapes of CV curves obtained were the same as those on the nickel and palladium in the alkaline solution [39–41]. The shapes of the CV curves obtained in our experiments were the same in all cycles (between 1st and 50th) and only the peak current density were changing during the potential sweeping. In these curves, the passive layer which consists of an \(\alpha\)-Ni(OH)\(_2\) amorphous layer is formed, as indicated by the current peak Ni\(_1\) at the potential about \(-0.75\) V vs. SCE during the first positive potential scan (Fig. 2b). In the potential domain of the plateau (X\(_1\), potential about 0 V vs. SCE), the amount of nickel oxide increases and there is simultaneous transformation of \(\alpha\)-Ni(OH)\(_2\) into a less hydrated and crystallized \(\beta\)-Ni(OH)\(_2\). At a potential higher than that of the oxidation peak X\(_1\), \(\beta\)-Ni(OH)\(_2\) is oxidized into \(\beta\)-NiOOH and the transformation is complete at potential about 0.48 V vs. SCE (marked peak Ni\(_2\)). During the decreasing potential scan, the reverse reduction reaction from \(\beta\)-NiOOH to \(\beta\)-Ni(OH)\(_2\) is observed at potential about 0.25 V vs. SCE corresponding to

![Graph showing cyclic voltammetry characterization](image-url)
Fig. 2 – Cyclic voltammograms of MECN (down) and Pd/MECN (upper) in potential region between −1.4 and 0.6 V vs. SCE (a) and related negative potential region between −1.4 and 0 V vs. SCE (b) at scanning rate 10 mV s⁻¹. (c) Cyclic voltammograms of Pd/NICMECN and Pd/NGMECN in potential region between −1.4 and 0.6 V vs. SCE at scanning rate 10 mV s⁻¹ (d) HER polarization curves of Pd/MECN, Pd/NICMECN and Pd/NGMECN electrodes at a scanning rate of 10 mV s⁻¹ and the corresponding Tafel plots (inset).
the cathodic peak Ni$_3$. When the potential scan is reversed at $-0.2$ V vs. SCE, a reduced process of $\beta$-Ni(OH)$_2$ is observed at the potential about $-1.1$ V vs. SCE corresponding to the cathodic peak X$_2$.

After electroplating Pd, the clearly wide peak appears at the potential about $-0.65$ V vs. SCE corresponding to the oxidation process of adsorbed hydrogen on surface of Pd nanoparticles (marked as peak Pd$_1$). The oxide state of palladium (PdO) appears at the potential domain of the plateau ($X_1$), which overlapping with the electrochemical transformation process of $\alpha$-Ni(OH)$_2$ into $\beta$-Ni(OH)$_2$. There are only peaks of oxidation and reduction processes corresponding to the surface reaction of pure nickel metal at a potential higher than that of the oxidation peak X$_1$, i.e. the generation and reduction processes of NiOOH. During the decreasing potential scan, the reverse reduction reaction from PdO to Pd is observed at potential about $-0.36$ V vs. SCE corresponding to the cathodic peak Pd$_2$. The hydrogen absorption process on the surface of Pd nanoparticles appear at the potential about $-1.0$ V vs. SCE corresponding to the cathodic peak X$_2$, which overlapping with the reduced process of $\beta$-Ni(OH)$_2$.

For case of the upper limit potential 0 V vs. SCE, it can also be noticed that there are two anodic peaks in CV curves for Pd deposited MECN. Comparing to the CV curve of MECN, it could be judged that the two peaks are corresponds to the formation of passive $\alpha$-Ni(OH)$_2$ amorphous layer (peak Ni$_3$, at potential $-0.65$ V vs. SCE) and the oxidation process of adsorbed hydrogen on the surface of Pd nanoparticles (peak Pd$_1$, at potential $-0.4$ V vs. SCE). The reduction peak of PdO disappears during the decreasing potential scan due to the absence of oxidation state of Pd under such limited upper potential. It also can be noticed that cathodic peak intensity of X$_2$ decreases after deposition process of Pd on Ni particle for both cases of upper limit potential 0 and 0.6 V vs. SCE. It may be the competition mechanism of the hydrogen adsorbed on Pd and Ni nanoparticles to form the wide and unclear cathodic peak.

The CV curves acquired from Pd/NiCMECN and Pd/NGMECN in the potential range of $-1.2$ to $-0.7$ V vs. SCE at scanning rate $10$ mV s$^{-1}$ are shown in Fig. 2c. Similar cyclic voltammograms and oxidation–reduction behavior are observed from these samples in this potential region. The same symbols are used to mark the oxidation–reduction processes for Ni and Pd nanoparticles. Even they are show the almost same oxidation process of adsorbed hydrogen on surface of Pd nanoparticles (marked as peak Pd$_1$), the oxidation process of Ni(OH)$_2$ are overlap with the water oxidation current peak when the potential positive than about 0.45 V vs. SEC for Pd/NiCMECN. With the aid of anneal process, inner layer carbon atoms pass rapidly through the hole between the mobile nickel atoms, to form the graphene layer on the surface [42]. As the nanographene formed on the surface of Ni nanoparticles, the oxidation–reduction peaks for Ni nanoparticles appear (marked as peak Ni$_3$ and Ni$_4$). At the same time, the large current peaks of oxidation–reduction processes for Pd nanoparticles appear (marked as Pd$_1$). That is to say, the formation of nanographene on the surface of Ni nanoparticles can improve the electrochemical redox process for Pd nanoparticles even on the surface layer, as show the schematic images in Fig. 1(V–VII).

To explore the catalysts in water splitting, the electrocatalytic HER performance of all of the samples was assessed in 1 M KOH using Linear Sweep Voltammetry (LSV) at a scanning rate of 10 mV s$^{-1}$, as shown in Fig. 2d, and inset is the related Tafel plot. To consider the electrochemical test are done in 1 mol L$^{-1}$ KOH solution (pH ~14), the zero of overpotential can be determined at 1.067 V vs. SEC [43], and the data of LSV and Tafel are shown in reversible hydrogen electrode (RHE) potential for simplicity. The cathodic current density is an important criterion in evaluating the HER activity of catalysts. With regard to Pd/NiCMECN and Pd/NGMECN, only overpotential $-43$ mV is required to generate a cathodic current density of 10 mA cm$^{-2}$, which is much smaller than the value required for Pd/MECN (overpotential $-93$ mV). For large cathodic current density, such as 100 mA cm$^{-2}$, the overpotential $-253$ mV is required for Pd/NGMECN, which is much smaller than the values required for Pd/NiCMECN (overpotential $-350$ mV) and Pd/MECN (overpotential $-428$ mV). It also indicates that it is suitable to apply to the HER condition of high current density for Pd/NGMECN. The linear regions in the LSV curves are fitted to the Tafel equation to obtain the corresponding Tafel slopes. The Tafel slope of the Pd/NGMECN (42.2 mV dec$^{-1}$) is smaller than those of the other electrocatalysts for Pd/NiCMECN (50 mV dec$^{-1}$) and Pd/MECN (90 mV dec$^{-1}$). The Tafel slope also reveals better HER performance for Pd/NGMECN, in good agreement with the LSV data. Similar information was obtained in literatures. Such as, the overpotential 124 mV and Tafel slope 70 mV dec$^{-1}$ were found at 100 mA cm$^{-2}$ for Pd-modified CoSnZn on a graphite substrate in 1.0 M KOH at room temperature [31]. In another study [32], Tafel slope 45 mV dec$^{-1}$ was found for Pd/graphene on a glassy carbon electrode in 0.5 M H$_2$SO$_4$ solution, and the overpotential 200 mA could be found at 100 mA cm$^{-2}$. An overpotential of 187 mV is required for PdNi alloy nanoparticles on carbon nanofiber in the HER over the catalyst to arrive 10 mA cm$^{-2}$ under 1 M KOH electrolyte [33].

In order to explain the improving HER properties, the CV curves acquired from Pd/MECN, Pd/NiCMECN, and Pd/NGMECN in the potential range of $-1.5$ to $-0.5$ V vs. SEC at scanning rates between 10 and 100 mV s$^{-1}$ are shown in Fig. 3a–c, respectively. It can be noticed that it would be a good choice to avoid the oxidation–reduction behavior of Pd nanoparticles through selecting the upper limit potential 0 V vs. SCE. Similar cyclic voltammograms and oxidation–reduction behavior are observed from these samples in this potential region. As discussion before, two anodic peaks are corresponds to the formation of passive $\alpha$-Ni(OH)$_2$ amorphous layer (peak Ni$_3$) and the oxidation process of adsorbed hydrogen on the surface of Pd nanoparticles (peak Pd$_1$). The reduction peak of PdO disappears under different sweep rates (from 10 to 100 mV s$^{-1}$) during the decreasing potential scan due to the absence of oxidation state of Pd under such limited upper potential. It also can be noticed that cathodic peaks X$_2$ appear for Pd/MECN, and the intensities of cathodic peaks X$_2$ increase for Pd/NiCMECN and Pd/NGMECN comparing to the Pd/MECN for case of upper limit potential 0 V vs. SCE, even the clearly cathodic peaks appear for Pd/NGMECN. To consider that the cathodic peak X$_2$ correspond to the two electrochemical processes, including of hydrogen absorption process on the
The current densities of anodic peak Pd1 (j, in the unit of A cm$^{-2}$) change with the sweep rates v (V s$^{-1}$) is shown in Fig. 3d as the plot of log (j) versus log (v). The solid line with slope of 1 is shown for comparison. With regard to the Pd/NGMECN electrode, the current densities of the anodic peaks increase with a slope of about 1.0 for all sweep rates from 10 to 100 mV s$^{-1}$ and it indicates that the oxidation of adsorbed hydrogen on the Pd surface is surface-controlled process [44,45]. Then the low slopes appear for Pd/MECN and Pd/NiCMECN (only slopes of about 0.8 and 0.7, respectively) and it may be due to the high ohmic contribution of the metal layer limits the rate capability.

**Impedance measurements**

In order to systemically study the electrochemical characteristics of Pd deposited different electrodes, electrochemical impedance spectra (EIS) are acquired in the frequency range from 100,000 to 0.1 Hz with a potential amplitude of 5 mV at the open circuit potential (OCP). The impedance diagrams are shown in Fig. 4a–c as plots of Nyquist and Bode planes. The inset in Fig. 4a depicts the high-frequency domain. The experimental (dotted) and fitted (line) data are shown after complex nonlinear least square (CNLS) fitting and the fitting parameters are also listed in Table 1. SEM reveals that the nickel, Ni–C alloy or nano-graphene formed on the MECN is composed of about 10–20 nm particles (Fig. 1 (II-IV)) and the corresponding equivalent circuit (EC) shown in inset of Fig. 4b [46,47]. The parallel parameters of constant phase element (CPE) and resistance R represent the electrochemical process
of the 3D electrode due to the distribution effects and porosity [47]. The CPE equation is:

$$Z_{\text{CPE}} = \frac{1}{CPE - T(j\omega)^{CPE-P}}.$$  \hspace{1cm} (2)

where CPE-P and CPE-T are the fitting parameters. When CPE-P is between 0 and 0.5, CPE tends to show the resistance characteristics but if CPE-P is between 0.5 and 1, it tends to show the capacitance characteristics. In the equivalent circuit as shown in Fig. 4b inset, $R_s$ is the solution series resistance.

The two parallel EC can be assigned to the electrochemical processes at the interfaces between electrodes and electrolyte. The parallel parameters of CPE1 and $R_1$ represent the constant phase element and charge transfer resistance, respectively, for the electrochemical process at the interface between NG (or Ni or NiC) and electrolyte. CPE2 is the constant phase element and $R_2$ is the charge transfer resistance of the double layer at the Pd nanoparticles/electrolyte interface. There is good consistency between the experimental and fitted data in the appropriate interface physical pictures and equivalent circuits and the corresponding fitted parameters also convey some physical meanings, and the fitting data are listed in Table 1. The small discrepancy between the experimental and fitted results at low frequencies may stem from the 3D architecture due to its complex mass transformation.

It shows that the stability of the NiCMECN electrodes increases in KOH solution in association with increasing charge transfer resistance $R_1$ ($50.41 \Omega \text{cm}^2$) comparing to the MECN electrode ($28.78 \Omega \text{cm}^2$) due to the compacted surface Ni–C alloy and the high conductivity. The charge transfer resistance increases to $R_1 \approx 84.46 \Omega \text{cm}^2$ after the nanographene formed on the Ni nanoparticles surface and indicates the improved stability of the NGMECN electrodes in KOH solution. After Ni–C alloy formed on the surface of Ni nanoparticles, the

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*R_s is the solution series resistances in $\Omega$, $R_1$ and $R_2$ are the charge transfer resistances in $\Omega \text{ cm}^2$, CPE-T and CPE-P parameters represent the constant phase element, CPE-T in $\text{F cm}^2$.\textsuperscript{2}.*
Fig. 5 — Modulus (a), Phase degree (b), differential capacitance (c) plots of Pd/MECN, Pd/NiMECN and Pd/NGMECN electrodes at frequency 1 Hz.
electrochemical process may be mainly the adsorption/desorption process on the double layer at the Pd nanoparticle/electrolyte interface in association with increasing CPE2-P parameter (0.90), compared to the Pd/MECN electrode (0.84). Even the double layer capacitance properties appear at the interface between Pd nanoparticle and electrolyte after the nanographene formed on the Ni surface, corresponding to unity CPE2-P parameter (0.98) for Pd/NGMECN electrode. In this case, the double layer capacitance can reach about 0.026 F cm 2. Corresponding to the adsorption/desorption processes at the double layer, the charge transfer resistances R2 is related to the kinetics of the electrochemical reaction across the double layer, the smaller value and the faster reaction rate [48]. The surface nanographene on the Ni surface can decrease the charge transfer resistances R2 (58.31 Ω cm2), compared to Ni−C alloy coating Ni electrode (83.37 Ω cm2) and only Ni electrode (188.4 Ω cm2). It may be the high-conductivity of surface layer (such as NiC alloy and graphene) can make the electron pass through electrode quickly and to hinder the redox process for the next layer and protect total electrode [49]. It indicates that the surface nanographene on the Ni nanoparticles can protect the metal electrode and also improve the adsorption/desorption reaction rate at the double layer structure on the interface between Pd nanoparticles and electrolyzer.

The surface electrochemical properties of the metal electrode can be investigated by semiconductor electrochemistry [50], especially the adsorption/desorption process on the electrode surface at the low frequency case (long time) [51]. A Schottky barrier is present at the metal electrode/electrolyte interface with a potential drop and the differential space charge capacitance (CSC) can be obtained by alternating the voltage in the impedance techniques according to the following equation [50].

\[
C_{SC} = \frac{1}{2\pi f \text{Im}(Z)/A}
\]  

(3)

where A is the apparent electrode area, Im(Z) is the imaginary part of the impedance data, and f the frequency (1 Hz in our case). For the different samples in KOH solution, the modulus impedances |Z| and phase degrees versus operating potentials and corresponding differential capacitances are shown in Fig. 5a−c. It shows that the modulus |Z| of impedance data of the Pd/MECN, Pd/NGMECN, and Pd/NGMECN samples show a similar trend in the voltage region between −1.2 V and 0 V vs. Sce, and the smallest average impedance values shows for Pd/NGMECN sample. It can also be noticed the values of impedance data show clearly drops at potential about −0.5 V vs. Sce for three samples (marked by arrow), especially for Pd/NGMECN and Pd/NGMECN samples. For phase degrees of impedance data, there are also the maxima values (approaching zero) at the potential about −0.5 V vs. Sce (marked by arrow). In this case, the differential capacitances CSC obtained from Eq. (3) show peaks at the same potential, as shown in Fig. 5c. It suggests that the adsorption/desorption phenomena would be appeared at the certain operation potential and increase the differential capacitance (decrease the resistant and increase phase degree) property of electrode. Comparing to the CV curves in Fig. 2a−b, it can judge that the peak of differential capacitance is corresponding to the process of H+ adsorption and oxidation. The area of the differential capacitance peaks is related to the stored charge density Q (C/cm2) by the definition of differential capacitance [52]:

\[
C_f = \frac{dQ}{dV} \text{ or } Q = \int C_f dV
\]  

(4)

and the integration area of peaks are about 0.12 C cm−2 for Pd/NiCMECN, and about 0.14 C cm−2 for Pd/NGMECN, corresponding to the area up the dashed lines are shown in Fig. 5c. It indicates that the introduced of graphene on the surface of Ni nanoparticles can effectively improve the adsorption and oxidation process of H+ ions on Pd surface.

**Conclusion**

Palladium nanoparticles were electrodeposited on nanographene coated macroporous electrically conductive network (MECN), and the electrochemical hydrogen evolution properties in KOH solution were evaluated by cyclic voltammetry, Tafel plots, and electrochemical impedance spectroscopy. As a result of the 2D structure and high electrical conductivity, the nanographene-coated MECN electrode shows high conductivity and stability in KOH solution. Through analysis the electrochemical data, it shows that the surface nanographene on Ni nanoparticles can improve H+ ion adsorption/desorption on the Pd nanoparticles and oxidation reaction rate for H2O. It can also decrease charge transfer resistance for H2O reduction reaction across the double layer on Pd surface. After introduction of nanographene on the surface of 3D Ni electrode, the improving electrochemical properties can enhance electrocatalytic hydrogen evolution for deposited Pd nanoparticles, which shown the overpotential 43 mV and Tafel slope 42.2 mV dec−1 at 10 mA cm−2 for Pd/NGMECN in 1.0 M KOH. The experimental results provide fundamental understanding of 3D nanographene electrode structure and suggest promising application in 3D electrochemical energy conversion devices for nano-graphene-coated MECN electrodes.

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