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

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## ARTICLE INFO

## ABSTRACT

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 $H^+$ ion adsorption/desorption and reaction rate.

## Introduction

Hydrogen energy is one of the potential candidates for replacing fossil fuels in the future to minimize the $CO_2$ 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

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then hydrogen gas [5–7]. The HER, which explores the mechanism of multi-electron transfer processes in electro-catalysis, 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 catalyst as, 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 nano-graphene 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 (OER), 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 electro-catalysis properties and to get deep understanding of the function of surface nanographene. It is also necessary to understand the electrochemical properties of the 3D nano-graphene 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 ($PdCl_2$), ethylene diaminetetraacetic acid (EDTA), Nickel chloride hexahydrate ($NiCl_2·6H_2O$) and ammonium chloride ($NH_4Cl$) were purchased from Aladdin Reagent and triethylene glycol ($C_6H_{14}O_4$), sodium hypophosphite monohydrate ($NaH_2PO_2·H_2O$), 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. The importance 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 electro-chemical 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 MECNs 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 MECNs (labeled as NGMECN). More details about the