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Galvanic exchange at layered doubled hydroxide/N-doped graphene as an *in-situ* method to fabricate powerful electrocatalysts for hydrogen evolution reaction

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ABSTRACT

Introducing a novel strategy for growing dispersed metal nanoparticles at reduced graphene oxide (rGO) and nitrogen-doped GO (rNGO), this work aimed to design Pt-free electrocatalysts for water splitting. For this purpose, gold nanoparticles were fabricated by the *in-situ* galvanic exchange of layered double hydroxide (LDH) metals on rGO and rNGO. The significant roles of the galvanic exchange method, LaNi-LDH, and the Au nanoparticles synthesized on the rGO/rNGO-LaNi-LDH surface (Au@rGO/rNGO-LaNi-LDH) were investigated via a variety of methods and certain novel properties such as nitrogen-metal bridge bonds between the metal component of Au@LDH and the nitrogen component of rNGO were established, which indicated the semi-nanorod morphology of the Au@rGO/rNGO-LaNi-LDH thus produced. Electrochemical studies were used to reveal an onset potential of only −80 mV *vs.* RHE at an exchange current density of about 10 mA cm^{-2} with a small Tafel slope of 60 mV dec^{-1} for the hydrogen generation reaction in a 0.5 mol L^{-1} H_2SO_4 solution. The isolated island architecture of rNGO/LaNi-LDH and rNGO/Au@LaNi-LDH were found to promise rich and active sites to be exposed, which allow for the effective interaction of the reactants (*e.g.*, protons) with these active sites.

1. Introduction

Concerns about the worldwide energy crisis and the associated environmental issues due to the burning of fossil fuels have stimulated the quest for sources of clean and renewable energy [1,2]. The search for green energy in recent years has drawn increasing attention to hydrogen as a promising source of energy in future [3,4]. Molecular hydrogen offers a good potential for green energy as it is an environmentally-friendly gas with a high energy content per unit mass. Furthermore, water does not produce greenhouse gasses or any other harmful chemicals when consumed to generate H_2 [5,6]. Water splitting is the technique used to generate H_2 by electrochemical and photochemical methods, in which an electrocatalyst (i.e., an electrochemical or a photochemical catalyst) plays the key role in the successful water splitting process. Study has revealed that a suitable electrocatalyst must have the following five properties [7,8]: 1) an atomic-scale size to increase the number of active sites, 2) a high aspect ratio to improve the catalytic performance per geometric area, 3) a porous structure to enhance the rapis mass transport of reagents, 4) an excellent electrical conductivity to facilitate electronic transfer, and 5) good physicochemical properties to yield a high-performance electrocatalyst activity [9,10]. The most efficient catalysts used for hydrogen generation are metals of the platinum group. However, noble metals such as platinum are not in abundance in the earth's crust, compared to other elements, to provide adequate supplies of the catalyst required for hydrogen evolution reaction at a scale comparable to the world energy demand [11]. Thus, research conducted to address electrocatalysts for hydrogen generation has been directed toward the application of molybdenum and tungsten sulfides for the hydrogen evolution reaction [12–14]. Both computational and experimental results have confirmed their hydrogen generation activity [15,16]. Transition metal sulfides are typical layered materials which have proved to be highly active and versatile electrocatalysts for the hydrogen evolution reaction in acidic solutions [17–20]. Another type of clear layered materials is

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the layered double hydroxides (LDH) with many such applications as electrocatalysts, photocatalysts, and intercalated catalysts [21–24]. One application of LDH, which we will use below to compare with transition metal sulfides, is its electrocatalytic application. It has, in fact, been widely used with a large of number of metals such as Ni and Co in electrocatalytic reactions [21].

The galvanic exchange, or replacement, reaction is a fundamental oxidation-reduction reaction which has drawn much attention as a pioneering method to design the legendary nanostructures. It is a spontaneous electrochemical reaction that can be monitored within a temporal target. Furthermore, it can produce varying compositions with different metallic nanostructures through combining different ratios of metals. The last but not least advantage is the unique morphology of the last exchanged nanostructure [25,26]. Xia and co-workers obtained hollow nanotubes of the Au-Ag alloy by titration of Ag nanowires using $HAuCl_4$ solution [25,26]. Moreover, efforts have been directed at producing nanoporous surfaces in Cu-Ni [27], synthesizing platinum nanofiber/nanotube junction structures by direct mixing of silver nanowire in a platinum solution [28], or forming hollow gold and platinum shell nanoparticles via the transmetallation reaction [29]. However, there still exist much more unknown materials in need of investigation despite many experimental works conducted to use the galvanic exchange reaction for the manufacturing of novel structures of interest.

In the present study, a novel synthetic strategy (i.e., the galvanic exchange reaction) was used to grow dispersed gold nanoparticles with the assistance of Lanthanum-Nickel Layered Double Hydroxide (LaNi-LDH) on the different media of graphitic plates of reduced graphene oxide (rGO) or nitrogen-doped reduced graphene oxide (rNGO). The synthesis of gold in the lanthanum-nickel layered double hydroxide/reduced graphene oxide (rNGO/Au@LaNi-LDH) and lanthanum-nickel layered double hydroxide/nitrogen-doped reduced graphene oxide (rGO/Au@LaNi-LDH) surfaces was achieved *via* a two-step method; i) loading different LDH percentages (by ultrasonic irradiation) on the surfaces of rNGO and rGO, and ii) using the simple galvanic exchange of LDH's metals (e.g., Ni) with gold in an acidic solution to form gold nanoparticles on the synthesized (rGO/Au@LaNi-LDH and rNGO/Au@LaNi-LDH) surfaces. The new nanomaterials (i.e., rGO/Au@LaNi-LDH and rNGO/Au@LaNi-LDH) provide several key advantages. Firstly, they are produced in a direct-step synthesis with no special instruments or harsh conditions required. Secondly, the Au nanoparticles are fabricated by *insitu* formation on rGO/LaNi-LDH and rNGO/LaNi-LDH environments. This allows for the aggregation of Au nanoparticles to be prevented. Finally, the excellently active metal-nitrogen interaction (M-N) provides a pathway for electron transfer. To the best of the authors' knowledge, this is the first report on the galvanic exchange of LDH metals employing nitrogen-metal/LDH interaction, LDH, and graphitic plates to disperse gold nanoparticles in order to improve upon the performance of LDH and N-doped graphene oxide used for the electrochemical hydrogen evolution. These extraordinary synthetic electrocatalysts are comparable, or even superior, to the different transition metal sulfides in such respects as onset potentials, Tafel slope, and current density.

2. Experimental

2.1. Reagents

Graphite, HNO_3, H_2SO_4, $Ni(NO_3)_2 \cdot 6H_2O$ and $La(NO_3)_3 \cdot 6H_2O$ were purchased from Merck. Nafion solution (5.0 wt% in lower aliphatic alcohols and water) and ammonium hydroxide solution were purchased from Aldrich. All other chemicals used in this investigation were of analytical grade and were purchased from Merck. Deionized water was used for the preparation of all of the solutions.

2.2. Apparatus

Fourier-transform infrared (FT-IR) spectra of the nanocomposites were investigated using a JASCO 680 (Japan) spectrophotometer over the wavenumber of 400–4000 cm^{-1}. Transmission electron microscopy (TEM) was performed using a Philips CM120. X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultra-high vacuum (UHV) set-up equipped with the concentric hemispherical analyzer and VG Microtech twin anode XR3E2 X-ray source was used as incident radiation. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area of the nanocomposites. Using the Barrett–Joyner–Halenda (BJH) model, the pore volumes, and pore-size distributions were derived from the adsorption branches of the isotherms, while the total pore volumes (V_t) were estimated from the adsorbed amount at a relative pressure P/P_0 of 0.989. Electrochemical measurements were performed in 0.5 mol L^{-1} H_2SO_4 solution at room temperature. The electrode potential was controlled by an Autolab electrochemical analyzer, Model PGSTAT 30 potentiostat/galvanostat (Eco–Chemie, The Netherlands). Data were acquired and processed (background correction) using the GPSE and FARA computrace software 4.9.007. A standard three-electrode cell, containing a platinum wire auxiliary electrode, a saturated Ag/AgCl reference electrode and the nanocomposites as working electrodes, was used.

2.3. Synthesis and preparation of graphene oxide and reduce graphene oxide

Modified Hummer's method was applied to synthesize graphene oxide (GO) from natural graphite powder [30]. Briefly, graphite powder (6.00 g, 325 meshes) was added into a solution containing 48 mL H_2SO_4 (98% w/w), 10.0 g of P_2O_5 and 10.0 g of $K_2S_2O_8$. The mixture was kept at 80 °C for 6 h. Then, the solution was diluted with 1.0 L of water, and it was left for 12 h. The mixture was filtrated and washed with 2.0 L of water. Afterward, 3.0 g of the pre-oxidized graphite was added to 240 mL conc. H_2SO_4 containing 30.0 g $KMnO_4$ under stirring and the temperature of the mixture was kept to be below 25 °C, using a water bath for 150 min. Then, the mixture was stirred at room temperature for 2 h, and it was diluted with 600 mL of water. Finally, 9.0 mL of 30% H_2O_2 was added to the above mixture. The mixture was filtered and washed with 1:10 HCl aqueous solution (2.0 L) to remove any metal ions. Then, it was repeatedly washed with water until the pH of the filtrate was neutral.

To prepare rGO, 30 mg GO was dispersed in water, and 150 mg $NaBH_4$ was added into the mixture in an ice bath for overnight. The mixture was filtered and washed with 100 mL water, and the solid sample was dried at room temperature.

2.4. Synthesis of nitrogen-doped reduced graphene oxide

Nitrogen-doped rGO was prepared using hydrothermal method. In a typical procedure, 70 mL of NH_4OH aqueous solution (30%) was added to 70 mg GO, which the reaction was kept at 40 °C with stirring for 1 h and sonicated for 30 min. Then, the reaction mixture was transferred into a 120 mL autoclave for hydrothermal reaction at 210–220 °C for 24 h. This hydrothermal step was also reduced NGO to rNGO. The resulted product was collected by centrifugation and washed with water and dried at room temperature.