Synthesis of nickel germanide (Ge\textsubscript{12}Ni\textsubscript{19}) nanoparticles for durable hydrogen evolution reaction in acid solutions†

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Designing advanced materials as electrochemical catalysts for the hydrogen evolution reaction (HER) has caught great attention owing to the growing demand for clean and renewable energy. Nickel (Ni)-based compounds and alloys are promising non-noble-metal electrocatalysts due to their low cost and high activity. However, in most cases, Ni-based compounds and alloys have low durability in acid electrolyte, which limits their application in the electrolytic processes. In this study, monoclinic Ge\textsubscript{12}Ni\textsubscript{19} nanoparticles were synthesized and exhibited high electrocatalytic activity and stability for the HER in acidic solution. Ge\textsubscript{12}Ni\textsubscript{19} nanoparticles achieve an overpotential of 190 mV at cathodic current density of 10 mA cm\textsuperscript{-2} and a Tafel slope of 88.5 mV per decade in 0.50 M H\textsubscript{2}SO\textsubscript{4} electrolyte. Moreover, the performance is maintained after a 10 000-cycle CV sweep (−0.3 to +0.1 V vs. RHE) or under a static overpotential of −0.7 V vs. RHE for 24 hours. The reported electrocatalytic performance of the Ge\textsubscript{12}Ni\textsubscript{19} nanoparticles sufficiently proves the excellent endurance at lower required overpotentials in acidic solution, enabling the broad applications of the Ni-based electrocatalysts. Finally, a large-area (5 cm\textsuperscript{2}) electrocatalyst for HER was demonstrated for the first time. The great efficiency of the energy conversion performance sufficiently represented the potential of Ge\textsubscript{12}Ni\textsubscript{19} nanoparticles as electrocatalysts in commercial fuel cells.

Introduction

Electrocatalytic hydrogen evolution reaction (HER) has been a highly attractive tool to generate hydrogen as the energy source due to its advantages of clean operation and renewability. Platinum alloys and compounds are the most efficient catalysts for HER, but there remain several challenges such as the cost and scarcity of platinum. Therefore, numerous studies have been carried out to develop noble-metal-free acid-stable catalysts for HER.

Nickel-based alloys and compounds, such as Ni–P, Ni–Mo, Ni–Co, not only exhibit high activity for HER, but also are cost-effective materials due to their abundance in earth. However, most Ni-based catalysts are not stable in acidic solutions due to Ni dissolution, making their electrolytic applications limited only to alkaline electrolytes. Several efforts have been made to improve the performance of Ni electrocatalysts for HER. Doping and alloying between metal elements has been widely studied, and their HER performance has been significantly improved via tuning of the electronic structures. For instance, McKone et al. synthesized unsupported Ni–Mo nanopowders as electrocatalyst for HER, and displayed stunning performance in active overpotential in acidic conditions at only 80 mV. However, the performance decreased after the electrocatalyst was operated for 7 hours. Furthermore, in 2016, Lu et al. presented Ni foam as a HER electrode with a stable activity in acidic electrolyte for 125 hours, but the overpotential required was as large as 210 mV.

Germanium (Ge)-based alloys and compounds have been commonly investigated in electronic applications, such as lithium ion batteries, solar cells and insulators, owing to their excellent electronic characteristics. In addition, Ge is known for its durability in acidic situations. In the early 1970s, Hart carried out a series of experiments to investigate the effects of acid solution concentration on Ge–Ni alloy’s corrosion. The study pointed out that in dilute acid solution, the corrosion would be reduced. In 1991, Shein et al. had compared the electrochemical performance of different eutectic metal–germanium alloys in acidic solution. The Ni–Ge alloys were not passivated in sulphuric acid. As a result, Ge alloys have been used as a catalyst promotor and passivator in electrochemical reactions reported previously. However, only a few reports have been devoted to the combination of Ge and Ni in the form of nanomaterials.
Therefore, HER-related applications of these types of materials have not been developed.

Herein, we demonstrate nickel germanide (Ge$_{12}$Ni$_{19}$) nanoparticles synthesized by decomposing germanium(IV) iodide (GeI$_4$) precursor and nickel(II) iodide (NiI$_2$) in the presence of a mixture of oleylamine (OLA), oleic acid (OA), and trioctylphosphine (TOP) under argon atmosphere at 260 °C. Notably, when examined as a HER electrocatalyst, the material showed extraordinary activity and durability for hydrogen evolution. The HER overpotential required for the Ge$_{12}$Ni$_{19}$ nanoparticles was as low as 190 mV at a cathodic current density of 10 mA cm$^{-2}$, resulting in a Tafel slope of 88.5 mV per decade. Moreover, the performance was maintained after a 10,000-cycle CV sweep (−0.3 to +0.1 V vs. RHE) or under a static overpotential of −0.7 V vs. RHE for 24 hours, which sufficiently proved the excellent endurance and reduced overpotential in acid solution.

**Results and discussion**

**Synthesis and characterization of Ge$_{12}$Ni$_{19}$ nanoparticles**

Ge$_{12}$Ni$_{19}$ nanoparticles were synthesized by injecting GeI$_4$ solution into preheated NiI$_2$ and TOP solution at 260 °C in a 50 mL three-neck flask attached to a Schlenk line system under argon stream (Fig. 1). Ge$_{12}$Ni$_{19}$ nanoparticles were obtained after the uncovered precursor was removed by centrifugation. X-ray diffraction (XRD) patterns of the products were compared and interpreted with the standard database (shown in Fig. 2(a)). All fingerprint diffraction peaks were referred to an end-centered monoclinic structure and the space group $C_2$ with the following lattice parameters: $a = 11.63$ Å, $b = 6.715$ Å, $c = 10.048$ Å and $\beta = 90^\circ$ (JCPDS card no. 65-1256 [31]). The two main characteristic peaks for Ge$_{12}$Ni$_{19}$ appeared at 45.074° and 46.868°, which corresponded to (314)/(024) and (330) crystal facets of Ge$_{12}$Ni$_{19}$, respectively. The simulation of the end-centered monoclinic Ge$_{12}$Ni$_{19}$ crystal is shown in Fig. 2(b). Furthermore, X-ray photoelectron spectroscopy (XPS) analysis was also performed to investigate the surface states of the Ge$_{12}$Ni$_{19}$ nanoparticles. As shown in Fig. 2(c–e), the XPS spectrum indicated that the nanoparticles contained Ge and Ni elements. The Ge 3d and Ni 2p regions were labelled accordingly. All binding energies were corrected by referencing the C 1s peak (284.8 eV) (shown in Fig. 2(c)). The Ge 3d peak is located at 29.3 eV (shown in Fig. 2(d)). In addition to the Ge element, Fig. 2(d) reveals that exposure of Ge$_{12}$Ni$_{19}$ to air alters the surface, such that it partially consists of native GeO$_2$. The Ni 2p peaks are located at 852.6 and 869.9 eV with a peak separation of 17.3 eV, as shown in Fig. 2(e), representing the 2p$_{3/2}$ and 2p$_{1/2}$ states of Ni metal, respectively.

The detailed morphology and structure of the as-prepared Ge$_{12}$Ni$_{19}$ nanoparticles were evidenced by various electron microscopy analyses, including TEM and HRTEM. Observed from the low resolution TEM images (Fig. 3(a and b)), the size distribution histograms of the Ge$_{12}$Ni$_{19}$ nanoparticles present relatively narrow size distribution of the nanoparticles (inset in the Fig. 3(a)). The average diameter of the nanoparticles was 19 ± 5 nm, which was obtained based on statistical analysis over 250 Ge$_{12}$Ni$_{19}$ nanoparticles measured from the TEM images. In the HRTEM image (Fig. 3(c)), the interplanar spacing of 1.9 Å was correlated to the (330) plane. Furthermore, the fast Fourier transform (FFT) pattern of the nanoparticles (shown in Fig. 3(d)) provided the evidence that the (330) plane was the main growing plane of the nanoparticles, which agrees with the main peak at 46.868° in the XRD analysis.

A series of experiments were carried out to investigate the relationship of the effects of types and concentration of surfactant mixtures on the particle morphology. Fig. 4 shows the SEM images of Ge$_{12}$Ni$_{19}$ nanoparticles synthesized with different surfactant mixtures and proportions. Nanoparticles obtained from the surfactant mixtures (OLA, OA and TOP)
with higher OA concentrations had more polygonal morphology (Fig. 4(a) and (b)), whereas nanoparticles have spherical shapes from the reactions using lower OA concentrations (Fig. 4(c) and (d)). Moreover, for those surfactant mixtures with lower OA concentrations and also containing TOP (Fig. 4(c)–(f)), the products have more spherical morphology than those without TOP (Fig. 4(g and h)). Fig. 4(g) shows that the morphology is more oval at higher concentrations of the OLA surfactant. However, the interaction effect between surfactants OLA and OA lead to the sheet-shaped morphology (Fig. 4(h)). In brief conclusion, the concentration affects the growth rate of the crystal planes. Among all of the experiments, the best morphology of the Ge$_{12}$Ni$_{19}$ nanoparticles was formed in 6 mL OLA and 1 mL TOP, as shown in Fig. 4(d). The nanoparticles were monodispersed, uniform-sized, and nearly spherical.

**Hydrogen evolution reaction (HER)**

The electrocatalytic activity of Ge$_{12}$Ni$_{19}$ nanoparticles for HER was examined in a standard electrochemical configuration in 0.50 M H$_2$SO$_4$ with the working electrode prepared by drop-coating the Ge$_{12}$Ni$_{19}$ nanoink onto a 0.196 cm$^2$ rotating disk electrode with a mass loading of $\sim$4 mg cm$^{-1}$ (results are shown in Fig. 5). Nanoparticles with a high degree of ligand coverage may affect the electrocatalytic activity of the hydrogen evolution reaction (HER). We used different types of washing solvents to obtain nanoparticles with various degrees of ligand removal and compared their HER performances. Fig. S1† shows the morphologies of the Ge$_{12}$Ni$_{19}$ nanoparticles sonicated in different solvents and at various time periods after the synthesis in a three-neck flask. In this step, the solvent was used to remove by-products and the ligand cladding over the nanoparticles.$^{6,33}$ As shown in Fig. 5(a), the nanoparticle performances for hydrogen evolution after washing with different solvents are compared. The polarization curves of Ge$_{12}$Ni$_{19}$ nanoparticles washed with four different solvents: toluene, acetic acid, saturated sodium borohydride (NaBH$_4$) in tetrahydrofuran (THF), and THF are shown in Fig. 5(a); the overpotential to achieve a catalytic current density of 10 mA cm$^{-2}$ were $-237$, $-226$, $-242$ and $-190$ mV vs. reversible hydrogen.
potential (RHE), respectively. In addition, the electrochemical performance of commercial 20 wt% platinum on carbon was also compared. In comparison, Ge12Ni19 nanoparticles after a sonicated wash in THF had the lowest overpotential. Moreover, different sonication times were also tested. Even though the sonication time had been extended, the ligand cladding over the nanoparticles washed by toluene, acetic acid and satd. NaBH4 in THF remained the same (Fig. S1(d)−(f)). In contrast, the nanoparticles washed by THF (Fig. S1(a)−(c)) aggregated more significantly as the sonication time was extended. This result might be because the ligand cladding on the nanoparticles was removed.

Combining the two HER experimental results, we conclude that the lower the ligand cladding on the nanoparticles, the lower would be the electrocatalytic overpotential. This phenomenon might occur because organic ligands have poor conductivity, higher energy band gap and would a

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Fig. 5 (a) Comparison of polarization data and (b) Tafel plots of polarization curves for 20 wt% Pt/C and Ge12Ni19 nanoparticles treated with different solvents: toluene, acetic acid, saturated NaBH4 in THF, and THF. (c) Polarization data for THF-treated Ge12Ni19 sample nanoparticles between 0.3 and 0.1 V versus RHE, showing negligible current density loss even after 10 000 CV cycles. The inset is an enlargement of the area. (d) Time dependence of the current density under a static over-potential of −0.7 V. The inset is an enlargement of the area. All electrochemical studies were performed in 0.5 M H2SO4 at room temperature.

is the Tafel slope). The Tafel slopes for Ge12Ni19 nanoparticles treated with toluene, acetic acid, saturated sodium borohydride (NaBH4) in tetrahydrofuran and tetrahydrofuran (THF) were 138, 123.8, 112.2 and 88.5 mV per decade, respectively. The slope of Ge12Ni19 nanoparticles treated with tetrahydrofuran was lower than that of Ge12Ni19 nanoparticles treated with other solvents, thus exhibiting a rapid increase in HER rate with lower overpotential that is more beneficial for electrocatalytic applications. Generally, there are three principle mechanisms for hydrogen evolution: the Volmer, the Heyrovsky and the Tafel. Regardless of which mechanism generates hydrogen gas, the adsorbed hydrogen intermediate in the Volmer step is necessary. A comparison of Tafel slopes between the Heyrovsky and the Tafel step has been reported.41,44 The distinction between the slopes is in the voltage range; the slope of the Heyrovsky mechanism is from −42 to −118 mV and that of the Tafel mechanism is from −29 to ∞ (limiting current) mV. Consequently, the HER mechanism of our catalyst might follow a Volmer−Heyrovsky reaction, where electrochemical desorption is the rate-determining step.

Furthermore, the stability of the Ge12Ni19 nanoparticles was evaluated with continuous cyclic voltammetric (CV) sweeps between −0.3 and +0.1 V vs. the reversible hydrogen electrode potential, RHE) applied to the Ge12Ni19 working electrodes (Fig. 5(c)). After the 1000-cycle and 10 000-cycle CV sweeps, the polarization curves were surprisingly superimposed. The inset of Fig. 5(c) displays the enlargement of an area, revealing that the overpotential required to achieve current densities of 10 mA cm−2 is nearly the same (from −0.191 to −0.189 mV).

The long-term stability of the Ge12Ni19 nanoparticles catalyst was tested by chronoamperometry measurements with a high catalyst loading of ~4 mg cm−2 on an RDE. A continuous HER process was performed at a constant overpotential of −0.7 V vs. RHE in 0.50 M H2SO4 for one day (Fig. 5(d)). The impressive improvement may be due to the activation through gradual electrolyte wetting or cleaning of the Ge12Ni19 nanoparticles catalyst, which exposed more active sites. The exceptional long-term durability of Ge12Ni19 nanoparticles catalysts suggests the prospect for implementing this new catalyst into realistic hydrogen evolution electrodes. When hydrogen gas was continuously generated, the hydrogen bubbles were released on the electrode surface, corresponding to the noise in the data (shown in the inset Fig. 5(d)). The current density was maintained and even increased after the 24 hours-operation, sufficiently showing the excellent stability and endurance of the Ge12Ni19 nanoparticles as electrocatalysts in acid solution. The comparison of the hydrogen evolution activity and stability data for this and other recently reported catalysts are summarized in Table 1.4,6,12,13,45−47 In Table 1, we compared the performance of our as-prepared catalyst with those of Ni-based catalysts, such as Ni3P nanoparticles, NiP1.93Se0.07 nanoparticles, Ni−Mo powder, Ni−Mo−S nanosheets and Ni foam. Our as-prepared Ge12Ni19 nanoparticles are more stable than Ni3P, Ni−Mo−S, Ni−Mo and NiP1.93Se0.07, thus demonstrating improved durability in acid solution. Even though Ni3P nanoparticles47 have better performance in terms of both
overpotential and durability and Ni foam\textsuperscript{13} has better durability, our as-prepared catalyst has advantages in of high-yield synthesis, monodispersion, superior average diameter, and easier preparation compared to Ni foam.

Moreover, the Ge\textsubscript{12}Ni\textsubscript{19} nanoparticles-based catalyst was used on a large-area surface for hydrogen evolution. The large area for HER was generated by spray-coating Ge\textsubscript{12}Ni\textsubscript{19} nanoparticles onto a 5 cm\textsuperscript{2} glass carbon electrode (shown in Fig. 6(a), the background is a 1 cm grid paper). It can be seen that Ge\textsubscript{12}Ni\textsubscript{19} nanoparticles form a dense coating layer on the electrode surface. The combination system, also shown in Fig. 6(b), directly delivered hydrogen gas into the fuel cell for generating electric power when the HER process was continuously operated. Simultaneously, a fan could be rotated uninterrupted when the hydrogen gas was steadily supplied.

Fig. 6(c) shows the chronoamperometry measurements of the 5 cm\textsuperscript{2} glass carbon electrode performed at a constant overpotential of $-0.4$ V vs. RHE in 0.50 M H\textsubscript{2}SO\textsubscript{4} for 12 hours. The digital picture (inset of Fig. 6(c)) of the Ge\textsubscript{12}Ni\textsubscript{19} nanoparticle-coated electrode shows vigorous hydrogen evolution under operation, whereas the current density decrement might be due to the adhesion of hydrogen bubbles on the electrode surface that leads to transportation resistance of the reacting species. The electrolysis efficiency for the large-area hydrogen evolution (the calculation was shown in Table S1\textsuperscript{†}) was 61.7\%, showing the great efficiency of the conversion between current input and the hydrogen energy output.

Conclusions

In summary, Ge\textsubscript{12}Ni\textsubscript{19} nanoparticles were synthesized with an average diameter of 19 nm at 260 °C. The as-synthesized Ge\textsubscript{12}Ni\textsubscript{19} nanoparticles exhibit a distinguished overpotential of $-190$ mV at current density of 10 mA cm\textsuperscript{-2} vs. reversible hydrogen electrode (RHE) as HER electrocatalyst, with a Tafel slope of 88.5 mV per decade. In addition, they also demonstrated excellent stability in an acid electrolyte environment. Subsequently, the electrocatalyst on a 5 cm\textsuperscript{2} area electrode for HER had a constant overpotential of $-0.4$ V vs. RHE in 0.50 M H\textsubscript{2}SO\textsubscript{4} for 12 hours. These results show that Ge\textsubscript{12}Ni\textsubscript{19} nanoparticles are appealing for Ni-based electrocatalysts in acid electrolytes, making the application of Ni-based electrocatalysts less limited in the future.

Experimental

Chemicals

All chemicals are commercially analytical grade reagents. Germanium(IV) iodide (GeI\textsubscript{4}; 99.99\%), nickel(II) iodide (NiI\textsubscript{2}; powder), trioctylphosphine (TOP; 90\%), oleylamine (OLA; 70\%), oleic acid (OA; 90\%), hexamethyldisilazane (HMDS; $\geq$99\%), toluene (99\%), ethanol (99.99\%), sodium borohydride (NaBH\textsubscript{4}; $\geq$98.0\%) and tetrahydrofuran (THF; anhydrous, $\geq$99.9\%) were purchased from Sigma-Aldrich corporation.

Synthesis of Ge\textsubscript{12}Ni\textsubscript{19} Nanoparticles

Ge\textsubscript{12}Ni\textsubscript{19} nanoparticles were synthesized in a 50 mL three-neck flask connected to the Schlenk line system under an argon
atmosphere. First, 45 mg of NiI₂, 6 mL of OLA, and 1 mL of TOP were loaded into a 50 mL three-neck flask. The flask was purged with argon from the Schlenk system and preheated at 130 °C for 30 min with continuous stirring. Next, the stock solution was prepared by adding 60 mg of GeI₄, 10 mL OLA purged with argon from the Schlenksystem and preheated at 140 °C. The TOP were loaded into a 50 mL three-neck flask. The flask was heated to 140 °C. Then, we heated the reaction to 260 °C at a rate of 2 °C min⁻¹. After the temperature was steady at 260 °C for 45 minutes, the flask was quenched by a cold water bath instantly to room temperature in order to stop the reaction. In order to discard the by-products and unreacted precursors, the nanoparticles were sonicated in THF for 1 hour and then washed by centrifugation at 8000 rpm for 5 min with approximately 1:2 v/v toluene and ethanol several times (shown in Fig. 1).

**HER working electrode fabrication**

A thin layer of Ge₁₂Ni₁₉ nanoparticles was deposited by drop coating method to a small area and spray coating to a large area. The nanoink was prepared from nanoparticles dispersed in toluene. Typically, 45 mg of catalyst was dispersed in 1 mL toluene by sonicating for an hour to form a homogeneous nanoink. Then, 20 μL of the nanoink (containing 0.8 mg of catalyst) was poured onto glassy carbon electrodes (loading 2 mg cm⁻²), and sprayed onto a glassy carbon plate (loading 2 mg on 5 cm²).

**Electrochemical characterization**

The electrochemical measurements were performed on a three-electrode system using a rotating disk electrode (RDE formed on the catalyst's surface, 5 mm diameter, 0.196 cm²) with a Biologic potentiostat (VMP3 with Ec-lab software). In order to eradicate the diffusion effect of the reacting species and remove the gas product (H₂) formed on the catalyst's surface, the RDE was rotated at 3200 rpm during the tests. Linear sweep voltammetry (LSV) with a scan rate of 10 mV s⁻¹ was conducted in 0.50 M H₂SO₄ using a reverse hydrogen electrode (RHE, ALS) as the reference electrode, a platinum wire as the counter electrode, and the glassy carbon electrode with various catalysts as the working electrode. All of the potentials were calibrated to RHE. Cyclic voltammetry (CV) was conducted between −0.3 and 0.1 V vs. RHE at 100 mV s⁻¹ to investigate the cycling stability. Prior to each polarization and CV test, the catalyst-coated electrode was pre-treated in the same 0.50 M H₂SO₄ using a 10 000 cycle fast scan between +0.1 and −0.3 V vs. RHE at 100 mV s⁻¹ to yield a stable current–voltage curve by removing possible surface contaminants on the catalyst.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**
