1. Introduction

Platinum (Pt) group nanomaterials attract growing interest due to their unique electronic properties, atomically ordered crystal structures and high catalytic activities\(^1\)–\(^3\) as well as their important applications as a counter electrode material for dye-sensitized solar cells (DSSC) and the hydrogen evolution reaction (HER). The shape, size, arrangement, phases and crystalline structures of Ge–Pt nanoparticles were determined, and the ability to be dispersed in nonpolar solvents enabled them to form a catalyst ink with a stable ejection for the spray coating technique. A series of electrochemical analyses confirmed the catalytic properties of Ge–Pt nanoparticles toward the \(\text{I}^-/\text{I}_3^-\) redox reaction system. The DSSC using GePt\(_3\) nanoparticles as the counter electrode exhibited excellent power conversion efficiency (PCE) of 8.04\% at 0.16 cm\(^2\), which was comparable to that of a DSSC using Pt as the counter electrode (8.0\%); it also exhibited an average PCE of 7.26\% even at a large working area (2 cm\(^2\)). In addition, the GePt\(_3\) catalyst exhibited excellent HER electrocatalytic performance with a large current density and a low Tafel slope, and it could stably operate at a working area of up to 5 cm\(^2\) with a low over potential (<0.06 V) to achieve 10 mA cm\(^{-2}\).

Pt usage while increasing the catalysts’ activities and long-term stability. It has been proved that improved activities normally result due to some synergetic effects including electronic and geometric effects, which originate from the lattice contraction and the downshift of the d-band center of Pt in the Pt compound.\(^19\)

Elemental germanium nanoparticle have been applied widely in fibre-optic systems, infrared optics, and as catalysts for the polymerization reaction as well as in solar cells and energy storage.\(^20\)–\(^23\) They can form diverse compounds or alloys with various elements. These germanium (Ge) compounds are used as highly reactive reagents (NaGe, KGe, GeBr\(_2\)), magnetic materials (FeGe, CoGe), optical and catalytic materials (Ge\(_3\)N\(_4\), GeS, GeSe) and non-volatile phase change materials for memory devices (GeTe, GeSbTe).\(^20\),\(^24\)–\(^26\) Moreover, the applications and the significance of silicon–germanium compounds as sensitive layers in integrated circuit (IC) are also well-known.\(^27\),\(^28\)

The Ge–Pt intermetallic compound system includes six phases: Ge\(_x\)Pt, GePt\(_2\), GePt\(_3\), Ge\(_2\)Pt, Ge\(_3\)Pt, and Ge\(_4\)Pt\(_2\).\(^29\) In this system, the electrophilic character of platinum can be increased by germanium, which acts as an electron-acceptor,\(^30\) resulting in the generation of unique catalytic properties. Recently, the investigation of the applications of Ge–Pt inter-
metallic compounds or Ge–Pt supported on carbon as electrocatalysts for CO oxidation and fine chemistry hydrogenation reactions have attracted great attention.\(^{31-33}\) In addition, previous reports show that Ge–Pt can prevent coke deposition on contiguous Pt surfaces in some of the naphtha reforming catalyst reactions.\(^{34}\) However, there is still a lack of studies on the catalytic properties of Ge–Pt intermetallic compounds at the nanoscale. We herein demonstrate the first example of a colloidal synthetic approach to obtain crystalline Ge\(_2\)Pt and GePt\(_3\) nanoparticles with well-defined shapes. During the synthesis, oleic acid (OA) or trioctylphosphine (TOP) ligands play an important role for single crystal formation,\(^{35,36}\) and the decomposition of Pt and Ge precursors in the nucleation step is critical to produce monodisperse nanoparticles.\(^{37}\) The as-synthesized well-dispersed nanoparticles can form a catalyst ink in a nonpolar solvent with a stable ejection for the spray coating technique. We experimentally show that the DSSC using GePt\(_3\) nanoparticles as the counter electrode exhibits an excellent power conversion efficiency (PCE) of 8.04% at 0.16 cm\(^2\), which is comparable to that of the DSSC using Pt as the counter electrode (8.0%); it also exhibits an average PCE of 7.26% even at a large working area (2 cm\(^2\)). Overall, our results show that the GePt\(_3\) nanoparticle-based DSSC cell can achieve a relatively low short-circuit current (∼27 mA) and an open-circuit voltage (∼0.7 V). On the other hand, when evaluated for the HER performance, GePt\(_3\) nanoparticles exhibit improved performance compared to conventional Pt (0.033 V at 0.07 cm\(^2\) and 0.024 V at 0.2 cm\(^2\)) and excellent long-term cycling stability in an acidic electrolyte. Finally, the HER area is enlarged to 5 cm\(^2\), and it can provide sufficient hydrogen to successfully operate a fuel cell system.

2. Experimental section

2.1 Synthesis of platinum–germanium alloy nanoparticles

For the synthesis of GePt\(_3\), 0.1 mmol of platinum(II) iodide ([Pt\(_2\), 0.0464 g], 0.5 mL of OA and 6 mL of oleylamine (OLA) were added into a 50 mL three neck flask and connected to the Schlenk line system. The argon-filled three-neck flask was preheated for 30 minutes at 130 °C. Meanwhile, 0.035 mmol of germanium(IV) iodide (GeI\(_4\), 0.02 g), 0.25 mL of OA and 3 mL of OLA were added to a sample vial and sonicated until dissolution. The solution was then injected into the three-neck flask along with 0.5 mL of HMDS and reheated to 130 °C. The system was then heated up to 320 °C by 2 °C min\(^{-1}\) and cooled down instantly to room temperature with a cold water bath. The as-synthesized nanoparticles were then washed by adding 5 mL of toluene and 10 mL of ethanol followed by centrifugation at 8000 rpm for 5 min three times, and the byproduct and the unreacted precursors were discarded.

2.2 Characterization

The morphology and structure of the as-prepared nanoparticles were characterized by scanning electron microscopy (SEM, Hitachi SU8010). Transmission electron microscopy (TEM, Hitachi H-7100) was conducted for the further analysis of shape, size and crystalline phase. XRD data were obtained by a Rigaku Ultima IV X-ray diffractometer using a Cu radiation source (λ = 1.54 Å). An inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed on Agilent 7500ce (Agilent Technologies, Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) measurement was performed using ULVAC-PHI high resolution XPS equipped with monochromatized Al Kα (1486.6 eV) excitation.

2.3 DSSC counter electrode preparation

Typically, ∼30 mg of GePt\(_3\) or Ge\(_2\)Pt nanoparticles was dispersed in 10 ml toluene and sonicated for 30 min to prepare the catalyst ink. By spray coating, a thin layer of the electrocatalyst was deposited on the fluorine-doped tin oxide (FTO) glass substrate (SnO\(_2\): F glass, 8 Ω per square). Next, the resultant thin layer was sintered at 400 °C in an argon atmosphere for 2 hours by the chemical vapor deposition (CVD) method. For comparison, a standard Pt-based DSSC was also fabricated. For Pt counter electrode fabrication, a drop of plastisol (T/SP) solution was screen-printed onto FTO and incubated at 385 °C for 30 minutes.

2.4 DSSC assembly and measurements

A dye-adsorbed photoanode was fabricated using a screen-printed N719 dye-sensitized TiO\(_2\) film with thickness of 14–16 μm. The TiO\(_2\) film was then irradiated by UV light for 20 minutes and was soaked overnight in a mixed solution of acetonitrile and tert-butyl alcohol (1 : 1 (v/v)) containing 5 × 10\(^{-4}\) M N719 dye. Next, a spacer was inserted between the dye-adsorbed photoanode and the Ge–Pt or Pt-coated FTO counter electrode, and the films were firmly clamped together. The redox electrolyte (0.05 M I\(_2\), 0.1 M LiI, 0.6 M 1,2-dimethyl-1-3 propylimidazolium iodide (DMPII) and 0.5 M 4-tert-butyl-pyridine in acetonitrile) was injected into the interspace between the photoanode and the counter electrode through a predrilled hole. Finally, DSSCs were sealed with epoxy resin under heat. The Tafel polarization measurement was performed using an electro-chemical working system (Bio-Logic-science Instruments, VMP3) in a symmetrical cell with the scan range of 20–200 mV s\(^{-1}\). For cyclic voltammetry (CV)
measurements, Pt and Ag/Ag⁺ electrodes were applied as the counter and the reference electrodes. The resultant CV curves were recorded between 1.0 V and −1.0 V with a scan rate of 50 mV s⁻¹ in an acetonitrile-based electrolyte containing 10.0 mM LiI, 1.0 mM I₂ and 0.1 M LiClO₄. The performance of DSSC was then measured under simulated sunlight (AM 1.5 illumination). Electrochemical impedance spectroscopy was applied to determine the charge transfer resistance (Rct) under solar simulation in the range of 0.1–100 kHz.

2.5 HER working electrode fabrication and measurements
A thin nanoparticle-based catalyst layer was deposited by the drop coating method for a small area, and the spray coating method was used for a large area. For the catalyst ink preparation, 0.020 g of the prepared Ge–Pt nanoparticles and a commercial Pt catalyst were dispersed in 5 mL of a mixed solvent containing tetrahydrofuran (THF), 2-propanol, and 5% Nafion (volume ratio was 3 : 1 : 0.1) and sonicated for 30 min. The working electrode was prepared by depositing 0.2 mg cm⁻² of the catalyst ink on a glassy carbon electrode or a rotating disk electrode (RDE, Pine Instruments, d = 0.5 cm) and drying at room temperature. All electrochemical experiments were carried out on the VMP3 electrochemical workstation with a conventional three electrode system at room temperature. A platinum wire was used as the counter electrode, and a reversible hydrogen electrode (RHE, ALS) was employed as the reference electrode. Also, 0.5 M highly pure H₂-saturated H₂SO₄ aqueous solution was used as the supporting electrolyte for all the experiments. The LSV curves were recorded in the range from 0.3 V to −0.3 V at a scan rate of 5 mV s⁻¹, and the long-term durability test data were recorded at a stable voltage of −0.1 V vs. RHE over 12 h in 0.5 M H₂SO₄ with the electrode rotation of 2800 rpm. For the cycling durability test, ~30 cycles were performed in 0.5 M H₂SO₄ solution before the measurement to remove the residual surfactants in the voltage range from −0.3 to 0.2 V vs. RHE at 120 mV s⁻¹ scan rate. The resultant CV curves were recorded between −0.3 and 0.2 V vs. RHE at 120 mV s⁻¹ scan rate with the electrode rotation of 2800 rpm for 10 000 cycles.

3. Results and discussion
The colloidal synthesis process of Ge₂Pt and GePt₃ nanoparticles is depicted in Fig. 1(a). Iodide compounds were used for both germanium and platinum precursors, whereas OLA and OA were applied as the synthetic mixture or reducing (capping) agents. Fig. S1† shows the equilibrium diagram of the Ge–Pt system, indicating that the Ge–Pt compound could particularly form six types of phases.²⁹ Typical powdered X-ray diffraction (XRD) was applied as a bulk analysis technique to ensure compositional homogeneity of the GePt₃ nanoparticles. Fig. 2(a) shows the major reflections at 2θ values corresponding to (220), (113), (222), (400), (313) and (440) planes of an orthorhombic structure. Most peaks could be well indexed and matched well with the previously reported GePt₃ case (JCPDS no. 89-3026). Fig. 2(b) shows the simulated structural demonstration of crystalline monoclinic GePt₃ with the lattice constants of a = 7.92 Å, b = 7.77 Å, and c = 5.52 Å. The detailed morphology and structure of GePt₃ nanoparticles were further investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 2(c) and (d) show the representative SEM image and the relative low magnification TEM result of the as-synthesized GePt₃ nanoparticles. GePt₃ nanoparticles formed spherical clusters with an average particle size of 55.4 ± 3.8 nm (Fig. 2(d), inset). The corresponding selected area electron diffraction (SAED) pattern (Fig. 2(e)) showed rings that matched the peaks of the XRD pattern, which verified the face-centered monoclinic (FCM)-type crystalline structure of GePt₃. Interestingly, when an individual GePt₃ nanocrystal was observed under TEM, the morphology showed a popcorn shape with uneven surfaces (Fig. 2(f)) (for more details on GePt₃ morphology, please refer to Fig. S2†). High-resolution transmission electron microscopy (HRTEM) images (Fig. 2(g–j)) showed two directions with the associated fast Fourier transform (FFT) of GePt₃ nanocrystals along the zone axis of [100] and [001] directions; the lattice fringes of the nanoparticles referring to GePt₃ lattice images indicated the (002) and (220) planes with the corresponding interplanar spacings of 0.39 nm and 0.28 nm. Also, from the HRTEM analysis, nanodendrites forming convex–concave surface structures covering GePt₃ nanoparticles could be clearly observed. It is believed that these structures may be due to a large number of stacking faults or convex atoms with low coordination numbers exposed on the surface, providing a high number of active sites.³⁸,³⁹ Notably, the fragmental surfaces in HRTEM images (Fig. 2(g–j)) were assigned to exposed multiple facets including (220), (040), and (002) that resulted from high-density atomic steps, kinks, edges and dangling bonds, which exhibited higher catalytic activity, as reported by previous studies.⁴⁰–⁴⁴ Ge₂Pt nanocrystals were synthesized by adding a small amount of the reducing (capping) agent trietylphosphine (TOP) and altering the final reaction temperature to 320 °C. Under XRD analysis, the diffraction peaks including (110), (200), (011), (220), (211) and (121) could be clearly observed.
which matched well with that of the monoclinic structure of previously reported bulk Ge$_2$Pt (JCPDS no. 89-3029). Fig. 3(b) shows the simulated structure of orthorhombic Ge$_2$Pt with the lattice parameters of $a = 6.19$ Å, $b = 5.77$ Å, and $c = 2.91$ Å. TEM analysis results with different levels of magnifications successfully demonstrated classic spherical morphology, monodispersity and self-arrangement behavior of Ge$_2$Pt nanoparticles (Fig. 3(c) and (d)) (please refer to Fig. S3† for more details on SEM and TEM analyses). Ge$_2$Pt nanoparticles with an average particle size of 7.3 nm (Fig. 3(c), inset) and their uniform morphology could be controlled. It is possible that the capping or reducing agent applied during the synthesis reaction caused the different shapes of the nanoparticles. For the synthesis of GePt$_3$, OA was applied since OLA readily desorbs from the nanoparticle surface owing to it being a relatively weak ligand; thus, GePt$_3$ nanoparticles were prone to agglomeration during reactions at high temperature, resulting in the formation of irregular-shaped (popcorn-shaped) particles. On the other hand, this also indicated that the nanoparticles formed in the presence of TOP were spherical in shape, and their size decreased with an increase in the TOP/precursor ratio. Please note that sufficient TOP was added as the capping agent during the synthesis process of Ge$_2$Pt. This trend was quite consistent with the results of TOP addition as it is a very effective additive for controlling the size and shape (small, spherical) of Ge$_2$Pt nanoparticles. The detailed crystal-line structure of Ge$_2$Pt nanoparticles was further analyzed by HRTEM (Fig. 3(e) and (f)), and the associated FFT of the nanoparticles confirmed the as-synthesized product. The $d$-spacing between two lattice fringes was calculated to be 0.29 nm from the HRTEM images, which clearly indicated the presence of
the (011) plane with [100] zone axes of ordered Ge$_2$Pt nanoparticles. Energy dispersive spectroscopy (EDS) analysis under TEM analysis further confirmed the stoichiometry of the as-synthesized nanoparticles. As shown in Fig. S4† the elemental ratio of Ge : Pt was close to 1 : 3 for GePt$_3$, and the elemental ratio of Ge : Pt was about 2 : 1 for Ge$_2$Pt.

X-ray photoelectron spectroscopy (XPS) was used to investigate the nature of bonding, electronic structure and the chemical environment of constituent elements on the surface of Ge–Pt compounds. Peak energies were calibrated to adventitious carbon’s C 1s peak centered at 284.8 eV (Fig. S5†). The Ge 3d$_{5/2}$ peaks were at about 30.1 and 29.6 eV for GePt$_3$ and Ge$_2$Pt, respectively (Fig. 4(a) and (c)), which slightly upshifted compared to that of the conventional Ge powder (29.3 eV), indicating the presence of a bimetallic compound and the modification of electronic structures due to alloying of Ge with Pt. The presence of a significant amount of GeO$_2$ in Ge$_2$Pt was not surprising and seemed to be unavoidable due to the gradual oxidation of Ge or oxidized germanium chemisorbed on Pt during air exposure. As shown in Fig. 4(b) and (d), after the formation of the Ge–Pt alloy, the Pt 4f binding energy of Pt–Ge clearly blue-shifted compared to that of conventional Pt. The peaks of Pt 4f$_{7/2}$ and Pt 4f$_{5/2}$ in the spectrum of Pt were located at 71.2 and 74.5 eV for GePt$_3$ and at 71.1 and 74.4 eV for Ge$_2$Pt, respectively.

Fig. S6† shows the assembled DSSCs with two different reaction areas in this study. The band structure of a Ge$_2$Pt or GePt$_3$ counter electrode-based DSSC is described in Fig. 5(a), and the measured work functions of GePt$_3$ and Ge$_2$Pt thin films were 4.51 eV and 4.38 eV, respectively; both these values were close to the previously reported value for graphene layer (4.5 eV). To experimentally investigate the catalytic activities of the counter electrodes, we applied cyclic voltammetry (CV) analysis at a scan rate of 50 mV s$^{-1}$ in acetonitrile-based electrolyte containing 10 mM LiI, 1.0 mM I$_2$ and 0.1 M LiClO$_4$. Fig. 5(b) shows two pairs of prominent redox peaks, where peaks $\alpha$ and $\beta$ represent two oxidation steps corresponding to eqn (1) and (2).

$$3I^- \rightarrow I_3^- + 2e^- \quad (1)$$
$$2I_3^- \rightarrow 3I_2 + 2e^- \quad (2)$$

Eqn (1) and (2) show the oxidation reaction of iodide to tri-iodide (peak $\alpha$) and the oxidation reaction of tri-iodide to iodine (peak $\beta$). In reverse reactions, peaks $\alpha'$ and $\beta'$ represent two reduction steps corresponding to eqn (3) and (4).

$$3I_2^- \rightarrow 2e^- \rightarrow 2I_3^- \quad (3)$$

![Fig. 4](image)

**Fig. 4** XPS spectra of GePt$_3$ (a) Ge 3d (b) Pt 4f and Ge$_2$Pt (c) Ge 3d (d) Pt 4f.

![Fig. 5](image)

**Fig. 5** (a) Band structure of a Ge$_2$Pt or GePt$_3$ counter electrode-based DSSC. (b) Cyclic voltagograms of Pt wafer, GePt$_3$-coated FTO, and Ge$_2$Pt-coated FTO substrate for the I$_2$/I$^-_3$ system. (c) Tafel polarization curves of I$^-$/I$_3^-$ symmetrical cells of Pt, GePt$_3$/FTO and Ge$_2$Pt/FTO substrates. (d) $J$–$V$ curves of the 0.16 cm$^2$ DSSC with Pt, GePt$_3$-coated FTO, and Ge$_2$Pt-coated FTO. (e–f) Nyquist plots of the 0.16 cm$^2$ DSSC with Pt and GePt$_3$-coated FTO.
Eqn (3) and (4) show the reduction reaction of iodine to triiodide (peak $\beta'$) and the reduction reaction of tri-iodide to iodide (peak $\alpha'$). Next, we employed the Tafel polarization measurement to estimate interfacial charge-transfer properties on the electrode surface. The measured Tafel curves of Pt, GePt$_3$ and Ge$_2$Pt electrodes by symmetrical dummy cells are shown in Fig. 5(c); the relative $R_{ct}$ values can be obtained from eqn (5):$^{58}$

$$J_0 = \frac{RT}{nF R_{ct}}$$

In the above equation, $R$ represents the gas constant, $T$ represents the temperature, $n$ represents the total number of electrons involved in the reaction, $F$ represents the Faraday’s constant, $J_0$ represents the exchange current density and $R_{ct}$ is the direct measurement of the electron exchange ability between the electrode and the electrolyte.$^{59,60}$ also, $J_0$ is inversely proportional to $R_{ct}$ (Fig. S8†). Next, we applied the nanoparticles to DSSC devices as the cathode with a working area of 0.16 cm$^2$. Fig. 5(d) shows the photocurrent density–voltage ($J$–$V$) curves of Pt, GePt$_3$/FTO and Ge$_2$Pt/FTO when applied as the counter electrodes of DSSC. All photovoltaic parameters of DSSCs are summarized in Table 1, and the results indicated that the GePt$_3$/FTO counter electrode exhibited an average power-conversion efficiency (PCE) of 8.04%, which was comparable to that of the DSSC using Pt as the counter electrode (8.0%). This demonstrated that the reactions of $I_3^−/I^−$ redox pairs could be enhanced by using GePt$_3$ as the counter electrode. In addition, the good performance might be due to the higher Pt molecular ratio in GePt$_3$ nanoparticles. In addition, our data showed that $R_{ct}$ of the GePt$_3$/FTO counter electrode was slightly higher than that of Pt (Fig. 5(e and f)). The open circuit voltages ($V_{oc}$) of Pt, GePt$_3$/FTO, or Ge$_2$Pt/FTO-based DSSCs were around 0.68 to 0.70 V; please note that the DSSC using GePt$_3$ as the counter electrode exhibited a lower fill factor (FF) and higher $R_{ct}$ than Pt since its short-circuit current density was slightly lower.

Both Ge$_2$Pt and GePt$_3$ nanoparticles were well dispersed in nonpolar solvents, forming catalyst inks that can be applied for stable ejections (Fig. 6(a)).$^{61}$ For the nanoparticle films, sintering process is important for the removal of surfactants from nanoparticles. After annealing for 2 hours in an argon atmosphere at 400 °C, both GePt$_3$ and Ge$_2$Pt nanocrystals could form a thin layer when applied onto suitable substrates. Fig. 6(b) shows the process of spray coating an FTO substrate to assemble DSSCs with a reactive area of 2 cm$^2$. (c) Corresponding FTOs after spray coating. (d) Cross-sectional SEM image of GePt$_3$ on FTO.

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<table>
<thead>
<tr>
<th>Table 1</th>
<th>Photovoltaic performances of 0.16 cm$^2$ DSSCs with Pt, GePt$_3$/FTO, and Ge$_2$Pt/FTO counter electrodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{oc}$ (V)</td>
<td>$J_{sc}$ (mA cm$^{-2}$)</td>
</tr>
<tr>
<td>Pt-1</td>
<td>0.68</td>
</tr>
<tr>
<td>Pt-2</td>
<td>0.69</td>
</tr>
<tr>
<td>GePt$_3$/FTO-1</td>
<td>0.70</td>
</tr>
<tr>
<td>GePt$_3$/FTO-2</td>
<td>0.72</td>
</tr>
<tr>
<td>Ge$_2$Pt/FTO-3</td>
<td>0.69</td>
</tr>
<tr>
<td>Ge$_2$Pt/FTO</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Fig. 7 (a) $J$–$V$ curves of 2 cm$^2$ DSSCs with Pt and GePt$_3$-coated FTO. (b–c) Nyquist plots of 2 cm$^2$ DSSCs with Pt and GePt$_3$-coated FTO. (d) Schematic diagram of series-connected DSSCs. (e–f) Demonstration of a GePt$_3$-based series-connected DSSC application.
Nanoscale Paper

DSSC devices with 2 cm² counter electrodes are summarized in Table 2. It was found that the DSSC using Pt as the counter electrode still exhibited a relatively high average PCE (7.26%). The decreasing photovoltaic parameters in DSSCs could be due to the increasing working area. Fig. 7(b) and (c) and Table 2 show that similar series resistance \( R_s \) results were found for the DSSC using Pt as the counter electrode and the DSSC using GePt₃ as the counter electrode (0.51 and 0.53 Ω). Next, the DSSCs using GePt₃ as the counter electrode were tested by applying onto certain electronic devices (Fig. 7(e) and (f)). The GePt₃-based DSSC with a reactive area of 2 cm² could generate a short current of ~27 mA. However, the open-circuit voltage of each cell (~0.6 V) was too low to drive an electronic device; therefore, four DSSCs were connected in series to achieve an open-circuit voltage of 2.4 V (Fig. 7(d)). As an example of demonstration, GePt₃-based DSSCs were series-connected to a light-emitting diode (LED) board containing ~70 yellow and red LED bulbs. It successfully lit the LED bulbs without fading for a certain time (Fig. 7(e) and Fig. S9(a), Movie S1†). The GePt₃-based DSSC array was then further applied to an electric fan. As long as the illumination kept the DSSC array functioning, the electric fan kept spinning (Fig. 7(f) and Fig. S9(b), Movie S2†). A higher current could be produced by the parallel connection of GePt₃-based DSSCs of larger reaction area. Thus, it is believed that a module containing 25 or above series-connected cells has the potential to increase the open-circuit voltage to 12 V, which can possibly drive an automobile in the future.

Similar to solar energy, hydrogen energy is also known as an important renewable energy source. We also conducted more experiments to evaluate the application of Ge-Pt nanoparticles as the catalyst of the working electrode for the hydrogen evolution reaction (HER). HER is the cathodic half reaction (2H₂O → 2H₂ + O₂) and it is one of the most well-studied electrochemical reactions. The electrocatalytic HER activity of the as-synthesized GePt₃ nanoparticles deposited on a glassy carbon electrode was investigated in 0.5 M H₂SO₄ electrolyte \( (2\text{H}_\text{aq}^+ + 2\text{e}^- \rightarrow \text{H}_2) \) using a typical three-electrode system at room temperature. In a solar water splitting system, the HER current density of 10 mA cm²⁻² cathode is assumed as a significant performance index as it is the current density expected for a 12.3% efficient solar water-splitting device. From this perspective, for the linear sweep voltammetry (LSV) measurement, we compared the HER activities of GePt₃ and Ge₂Pt with that of commercial 20 wt% Pt/C, and the results are summarized as Fig. 8(a). However, Ge₂Pt nanoparticles resulted in a very poor HER catalytic activity or they were merely non-reactive. Subsequently, a series of HER activity tests based on GePt₃ were conducted at different HER reactive areas, and the resultant HER activities of GePt₃ nanoparticles were comparable to those of Pt/C at a current density of 10 mA cm⁻² (Table 3). As shown in Table 3, HER of the GePt₃ electrode at a larger area (5 cm²) required a higher overpotential (0.081 V) to achieve a current density of 10 mA cm⁻². We tried to improve the performance of the catalyst by activating it with a stable potential of 0.1 V for 10 minutes to remove the possible surface contaminants, and the HER activity at 5 cm² was reevaluated. As expected, the result improved with an overpotential reduction from 0.081 V to 0.053 V. To probe the HER kinetics, Tafel slopes were calculated. As depicted in Fig. 8(b), the Tafel slopes were 51.1 mV per decade for Pt/C and 40.7 mV per

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### Table 2 Photovoltaic performances of 2 cm² DSSCs with Pt and GePt₃/FTO counter electrodes

<table>
<thead>
<tr>
<th>Electrode</th>
<th>( V_{oc} ) (V)</th>
<th>( J_{sc} ) (mA cm⁻²)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>( R_s ) (Ω)</th>
<th>( R_{ct} ) (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>0.752</td>
<td>14.29</td>
<td>0.736</td>
<td>7.9</td>
<td>0.53</td>
<td>0.17</td>
</tr>
<tr>
<td>Pt</td>
<td>0.757</td>
<td>14.36</td>
<td>0.735</td>
<td>7.64</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>GePt₃/FTO-1</td>
<td>0.743</td>
<td>13.46</td>
<td>0.702</td>
<td>7.06</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>GePt₃/FTO-2</td>
<td>0.742</td>
<td>13.66</td>
<td>0.713</td>
<td>7.23</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>GePt₃/FTO-3</td>
<td>0.746</td>
<td>13.58</td>
<td>0.727</td>
<td>7.37</td>
<td>0.51</td>
<td>0.12</td>
</tr>
<tr>
<td>GePt₃/FTO-4</td>
<td>0.738</td>
<td>13.49</td>
<td>0.742</td>
<td>7.38</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

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### Table 3 Electrochemical performances of 0.07, 0.2, 5 cm² areas with Pt/C and GePt₃ working electrode, showing the overpotential result for –10 mA cm⁻² when applied for hydrogen evolution

<table>
<thead>
<tr>
<th>Area (cm²)</th>
<th>0.07 cm²</th>
<th>0.2 cm²</th>
<th>5 cm²</th>
<th>5 cm²-activated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>0.032</td>
<td>0.025</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>GePt₃</td>
<td>0.033</td>
<td>0.024</td>
<td>0.081</td>
<td>0.053</td>
</tr>
</tbody>
</table>

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decade for GePt₃ at 0.07 cm². The HER area was then enlarged to 0.2 cm², and the resultant Tafel slopes were 50.0 mV per decade for Pt/C and 38.9 mV per decade for GePt₃. It was remarkable that the activated GePt₃ electrocatalyst could still yield a Tafel slope of 37 mV per decade even at a large HER reactive area (5 cm²), indicating significant electrocatalytic activity towards HER with the Volmer–Heyrovsky mechanism.⁶³

Pt-Related compounds can serve as electrocatalysts in alkaline or acidic electrolytes.⁶⁴–⁶⁶ In addition to overpotential, stability is one of the most important factors to estimate an electrocatalyst.⁶⁷ Next, we evaluated the electrochemical durability of GePt₃ via a cycling test by running continuous CVs between 0.2 and −0.3 V (vs. RHE) at a scan rate of 120 mV s⁻¹ for 10 000 cycles (Fig. 8(c)); the overlapping curves implied that there was no decrease in the performance after 10 000 cycles. Additionally, as clarified in Fig. 8(d), the chronoamperometry measurement showed that the GePt₃ electrocatalyst maintained a stable current density at −0.1 V vs. RHE in 0.5 M H₂SO₄ solution for 12 hours. The current density for hydrogen evolution reaction was −56 mA cm⁻², and it remained almost constant throughout the testing period. To further illustrate the intrinsic catalytic activity of GePt₃, its specific HER activity and the mass activity at −0.1 V vs. RHE were compared with those of commercial Pt black and Pt/C catalysts (Fig. S10†). The total Pt content in the GePt₃ electrocatalyst was about 76.4 wt%, which was quantitatively measured by the inductively coupled plasma mass spectrometry (ICP-MS) technique. It showed that the corresponding specific activity of GePt₃ was 56.2 mA cm⁻², which was larger than those of Pt black (52.7 mA cm⁻²) and Pt/C (46.9 mA cm⁻²). Similarly, the mass activity of GePt₃ was 367.8 mA mg⁻¹, which was also higher than that of Pt black (263.8 mA mg⁻¹). Notably, the carbon-supported Pt (Pt/C) was able to achieve a relatively high mass activity (1172.5 mA mg⁻¹), indicating that it is possible to dramatically reduce the Pt usage and enhance the HER mass activity of the as-synthesized GePt₃ catalyst as long as it is applied with an appropriate support material.

Our experimental results indicated that GePt₃ can serve as an excellent electrocatalyst in an acidic solution. Next, we applied the water displacement method to confirm the continuous production of hydrogen during the reaction. The resultant volume ratio of collected hydrogen and oxygen was 2 to 1, yielding the volume ratio of hydrogen and oxygen in a water splitting system (Fig. 8(e)). Finally, the hydrogen gas produced from the HER system was applied directly to a fuel cell system to drive an electric fan (Fig. 8(f) and Movie S3†). During the demonstration, a constant voltage (0.3 V) was applied to the HER system and it could provide sufficient hydrogen to continuously function the fuel cell.

4. Conclusions
In summary, we developed facile colloidal synthesis of GePt₃ and Ge–Pt nanoparticle-based counter electrodes with reactive areas of 0.16 and 2 cm² resulted in average PCEs of 8.04% and 7.26%, which were comparable to that of Pt electrodes. We successfully achieved the demonstrations of GePt₃-based series-connected DSSC applications by driving an electric fan and illuminating an LED array. Further work to explore DSSC modules of advanced design for a higher voltage and a higher current output for a wide range of applications is currently underway. Also, the drop coating method and spray coating method were applied to deposit the as-synthesized nanoparticles onto different substrates as working electrodes for the HER water splitting system. The LSV measurements demonstrated an extremely low value of overpotential (<0.06 V) even at a larger reactive area (5 cm²). Next, the GePt₃-based electrode was applied to a series of tests including cycling durability tests and a fuel cell system demonstration, and the test results verified the prominent stability of the catalyst even after continuously reacting for 10 000 cycles or 12 hours. For the demonstration of the fuel cell system, hydrogen was continuously produced and collected and it could successfully drive an electric fan. All in all, this highly reactive and stable Ge–Pt nanoparticle-based catalyst could serve as a high-performance counter electrode for photoelectric conversions and as a promising candidate material to enable the widespread deployment of cost-effective systems for electrochemical hydrogen production.

Conflicts of interest
There are no conflicts to declare.

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