Supporting Information

Synthesis of Germanium-Platinum Nanoparticles as High-Performance Catalysts for Spray-Deposited Large-Area Dye-sensitized Solar Cells (DSSC) and Hydrogen Evolution Reaction (HER)

Suh-Ciuan Lim, ‡^a Ming-Cheng Hsiao,‡^a Ming-De Lu,^b Yung-Liang Tung,^b and Hsing-

Yu Tuan*a

^aDepartment of Chemical Engineering, National Tsing Hua University, 101, Section 2,

Kuang-Fu Road, Hsinchu, Taiwan 30013, ROC.

^bGreen Energy & Environment Research Laboratories, Industrial Technology Research

Institute, 195, Sec. 4, Chung Hsing Rd., Chutung, Hsinchu, Taiwan 31040, ROC.

*Corresponding author

Email address: hytuan@che.nthu.edu.tw

[‡]These authors contributed equally to this work.

Experimental Section

Chemicals

All chemicals were used as receive, including platinum (II) iodide (PtI₂, 98%, Alfa, CAS-NO.7790-39-8), germanium (IV) iodide (GeI₄, 99.99%, Aldrich, CAS-NO. 13450 -95-8), tri-octylphosphine (TOP, [CH₃(CH₂)₇]₃, 90%,Aldrich, CAS-NO. 4731-53-7), oleic acid (OA, 90%, Aldrich, CAS-NO.112-80-1), oleylamine (OLA, 70%, Aldrich CAS-NO.112-90-3), hexamethyldisilazane (HMDS, 98%, Acros, CAS-NO. 999-97-3), toluene, ethanol (ACS reagent grade, >99.5%, Aldrich), Nafion® 117 solution (Aldrich CAS-NO.31175-20-9), tetrahydrofunan (Aldrich, 99.9%, CAS-NO. 109-99-9), sulfur acid (ACS reagent grade, 95~98%, J.T.Baker, CAS-NO. 7664-93-9), platinum 20% on carbon (Johnson Matthey Fuel Cells, PC: 599002).



Fig. S1 Pt-Ge phase diagrams.²⁹



Fig. S2 The GePt₃ nanoparticles (a-b) SEM image (c-d) TEM image



Fig. S3 The Ge₂Pt nanoparticles (a) SEM image (b-d) TEM image



Fig. S4 Energy dispersive spectroscopy (EDS) analysis under TEM (a) $GePt_3$ nanoparticles (b) Ge_2Pt nanoparticles.



Fig. S5 XPS spectra C1s calibration of (a) GePt₃ (b) Ge₂Pt



Fig. S6 (a) 0.4*0.4 cm² of DSSC (GePt₃ as counter-electrode) (b) 0.4*0.4 cm² of DSSC (Pt as counter-electrode)



Fig. S7 The top view SEM image of $GePt_3$ on FTO



Fig. S8 (a) Tafel polarization curves of I^-/I_3^- symmetrical cells of Pt, GePt₃/FTO and GePt₂/FTO substrate, (b-d) Tafel-fitting for three different counter-electrodes, the insets show the symmetrical dummy cells.



Fig. S9 Equipment for demonstration: series-connected GePt₃-based DSSCs



Fig. S10 Comparison of the specific HER activities for the catalysts and mass activities at -0.1 V *vs.* RHE.