Supporting Information

Rh-Ag-Si ternary composite: highly active hydrogen evolution electrocatalysts over Pt-Ag-Si

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1. The calculated activation barriers of hydrogen diffusion

Table S1. The calculated activation barriers of hydrogen diffusion

Diffusion pathway of H atom	Activation barrier (eV)
From Rh atoms to the Ag(111) surface	0.46
From Pt atoms to the Ag(111) surface	0.53
Migration over the Ag(111) surface	0.12
From Ag(111) to the Si surface	0.26

2. XPS spectra

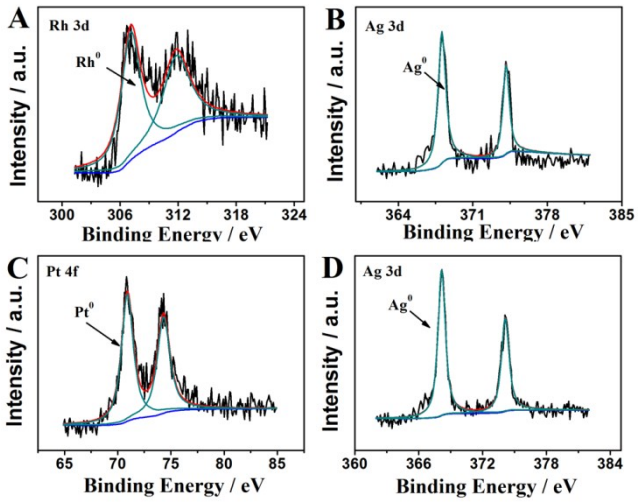

Figure S1. XPS spectra of (A) Rh 3d spectrum and (B) Ag 3d spectrum for Rh-Ag/SiNW nanocomposites; (C) Pt 4f spectrum and (D) Ag 3d spectrum for Pt-Ag/SiNW nanocomposites.

3. The SEM image of Rh-Ag/SiNW-2 nanocomposites

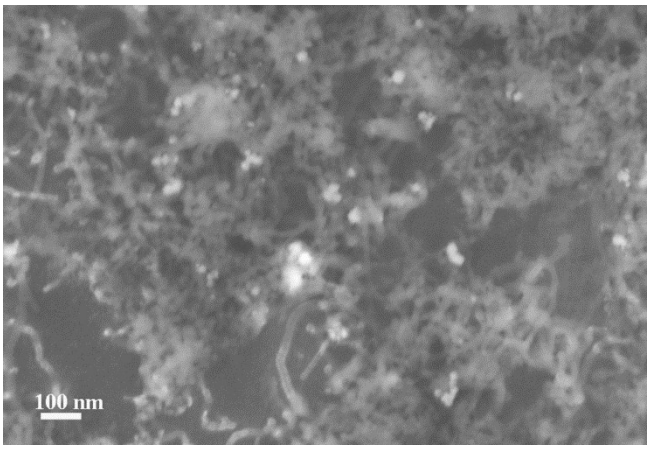

Figure S2. The SEM image of Rh-Ag/SiNW-2 nanocomposites.

4. The TEM images of Rh-Ag/SiNW nanocomposites

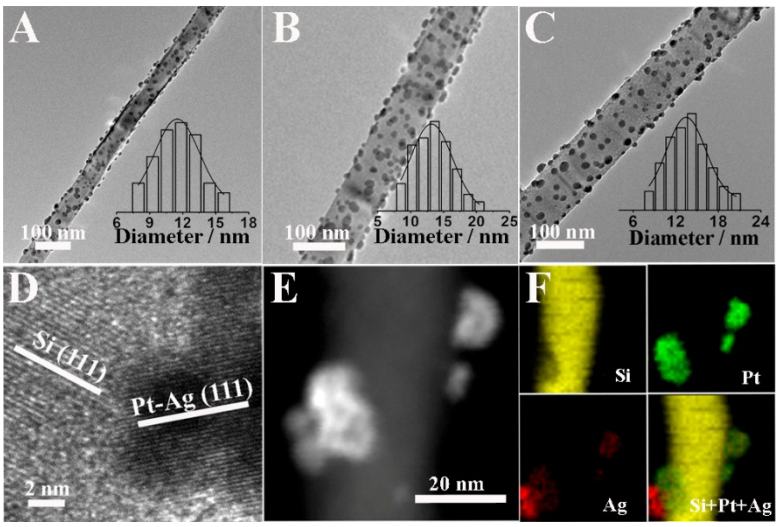

Figure S3. (A) The TEM images of Rh-Ag/SiNW-1, (B) Rh-Ag/SiNW-3 and (C) Pt-Ag/SiNW nanocomposites; (D) The HRTEM image showing crystal Pt-Ag nanoparticle; (E) HAADF-STEM image of Pt-Ag/SiNW catalysts, and (F) its corresponding EDS mapping showing the Si, Pt and Ag distributions. The inset is the size distribution of metal nanoparticles.

As shown in Figures S3A and S3B, Rh-Ag nanoparticles are decorated on a SiNW, with average diameters of 11.5 and 13.2 nm for Rh-Ag/SiNW-1 and Rh-Ag/SiNW-3, respectively. For Pt-Ag/SiNW nanocomposites, Pt-Ag nanoparticles are decorated on the surface of a SiNW, with an average diameter of 12.3 nm (inset in Figure S3C). The spacing of 0.31 and 0.23 nm in the HRTEM image (Figure S3D) agree with the (111) plane of the cubic Si and Pt-Ag, respectively. Figure S3E shows the HAADF-STEM image of Pt-Ag/SiNW nanocomposites. The corresponding EDS mapping in Figure S3F exhibited the element distribution of silicon (yellow), sliver (red) and platinum (green) respectively, confirming Pt-Ag nanoparticles are successfully decorated on the

SiNWs.

5. The LSV and Tafel shope

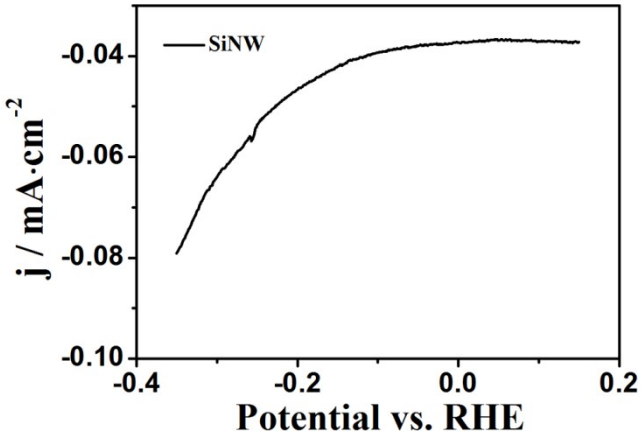

Figure S4. The LSV curve of SiNW in N_2-saturated 0.5 M H_2SO_4.

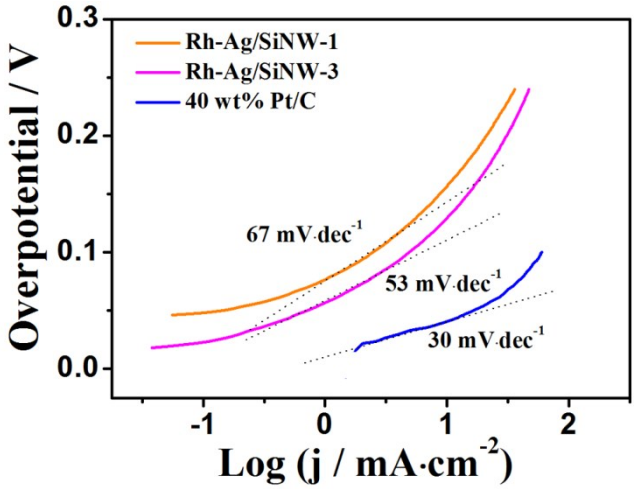

Figure S5. The Tafel slopes of Rh-Ag/SiNW-1, Rh-Ag/SiNW-3 and 40 wt% Pt/C catalysts.

6. The electrochemical impedance spectroscopy

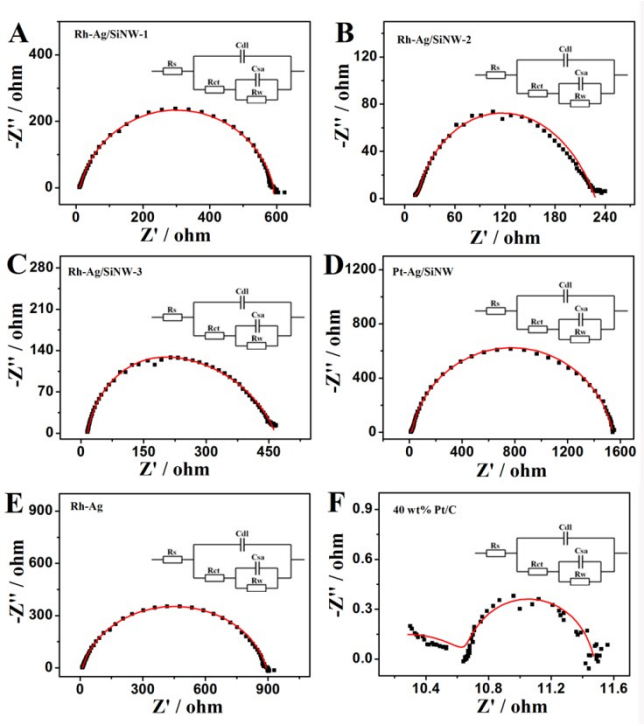

Figure S6. (A) Nyquist of Rh-Ag/SiNW-1 catalysts, (B) Rh-Ag/SiNW-2 catalysts, (C) Rh-Ag/SiNW-3, (D) Pt-Ag/SiNW, (E) Rh-Ag and (F) 40 wt% Pt/C at the overpotential of 65 mV. The inset is the equivalent circuit.

The catalytic kinetics of HER was measured by electrochemical impedance spectroscopy (EIS) approach. The Nyquist plots of the various catalysts were measured in the frequency ranging from 100 kHz to 0.1 Hz in N_2-saturated 0.5 M H_2SO_4 solution (Figure S6). The impedance spectra for all modified electrodes studied consisted of following components: (i) a higher-frequency process represented the double-layer capacitance and (ii) a lower-frequency component associated with the H species coverage, and the equivalent circuit was applied to conform to impedance spectra (inset of Figure S6). The R_s is the solution resistance, R_{ct} the resistance of the charge-transfer step, C_{dl} the double layer capacitance, R_{sa} resistance of surface adsorption and C_{sa}

capacitance of surface adsorption. C_{dl} and S_{real} were calculated according to the following equations:[S1, S2]

$$C_{dl} = (Y_{01}/(R_s^{-1} + (R_{ct} + R_{sa})^{-1})^{1-n1})^{\frac{1}{n1}};$$

$$S_{real} = \frac{C_{dl}}{k}, k = 20\mu F \cdot cm^{-2}.$$

7. The pH effect on Rh-Ag/SiNW catalysts for HER

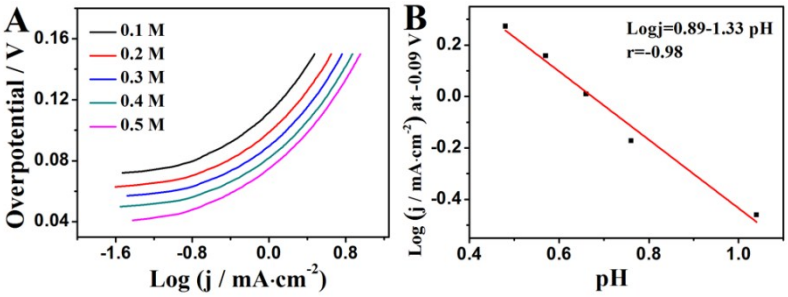

Figure S7. (A) Tafel curves of Rh-Ag/SiNW-2 catalysts for HER measured in different concentration of H_2SO_4; and (B) the plot of Log *j* at -0.09 V (vs. RHE) versus pH.

7. The stability of catalysts

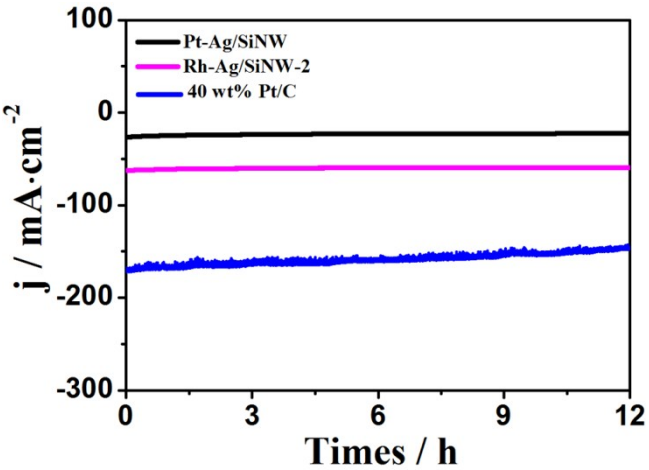

Figure S8. The stability of Pt-Ag/SiNW, Rh-Ag/SiNW-2 and 40 wt% Pt/C catalysts.

The stability of Pt-Ag/SiNW, Rh-Ag/SiNW-2 and 40 wt% Pt/C catalysts were carried

out by *i-t* curves at -0.25 V in N_2-saturated 0.5 M H_2SO_4 at room temperature (Figure S8). The results show that Rh-Ag/SiNW-2 has good stability.

References

S1 I. Herraiz-Cardona, E. Ortega and V. Pérez-Herranz, *Electrochim. Acta*, 2011, **56**, 1308-1315.

S2 A. Lasia, *Springer Science-Business Media*, New York, 2014, pp. 220-221.