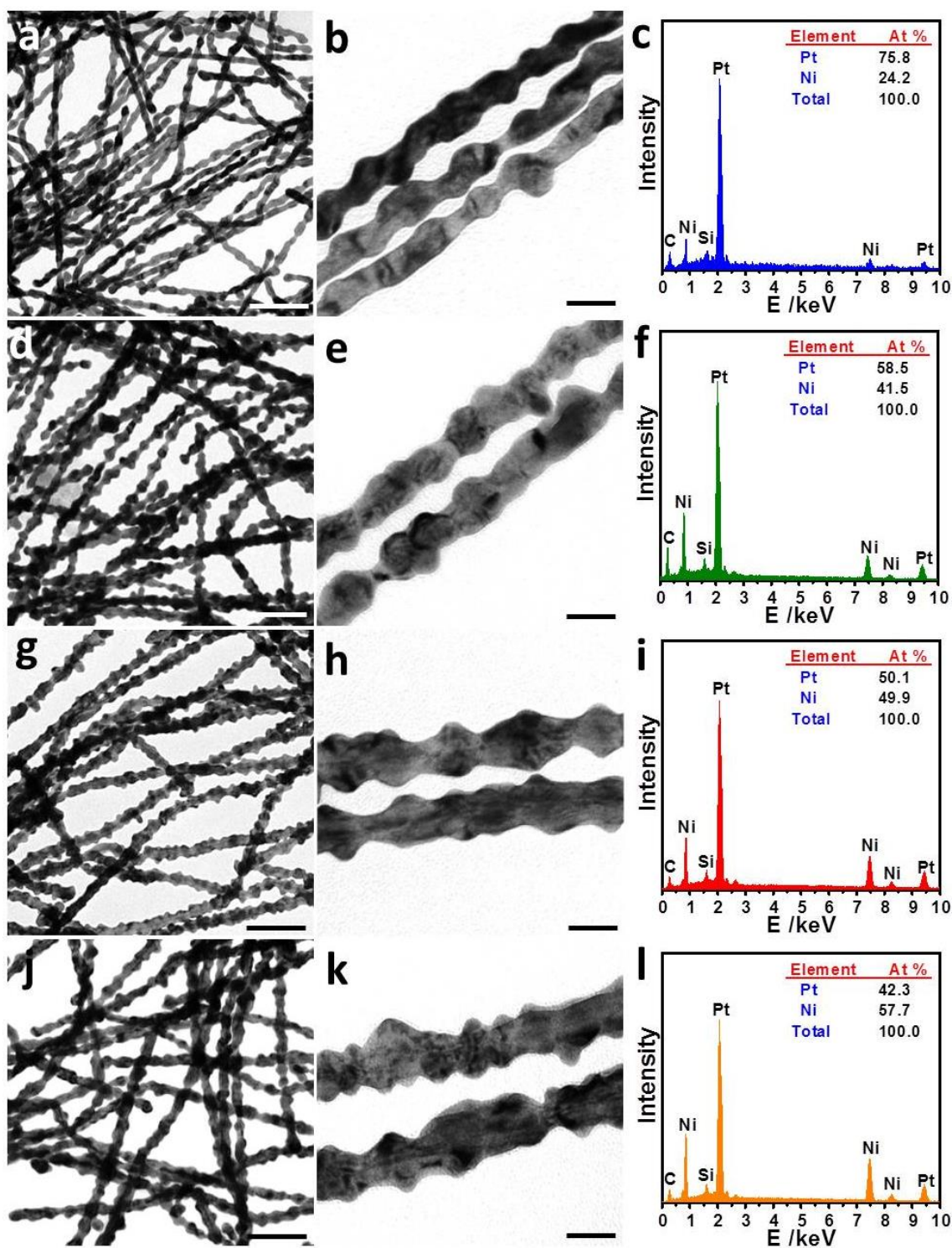
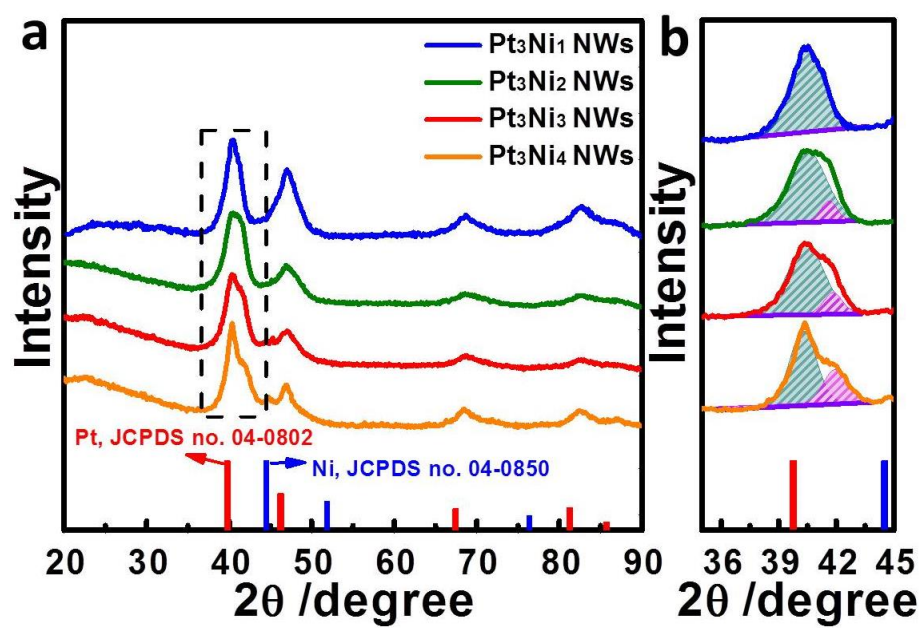


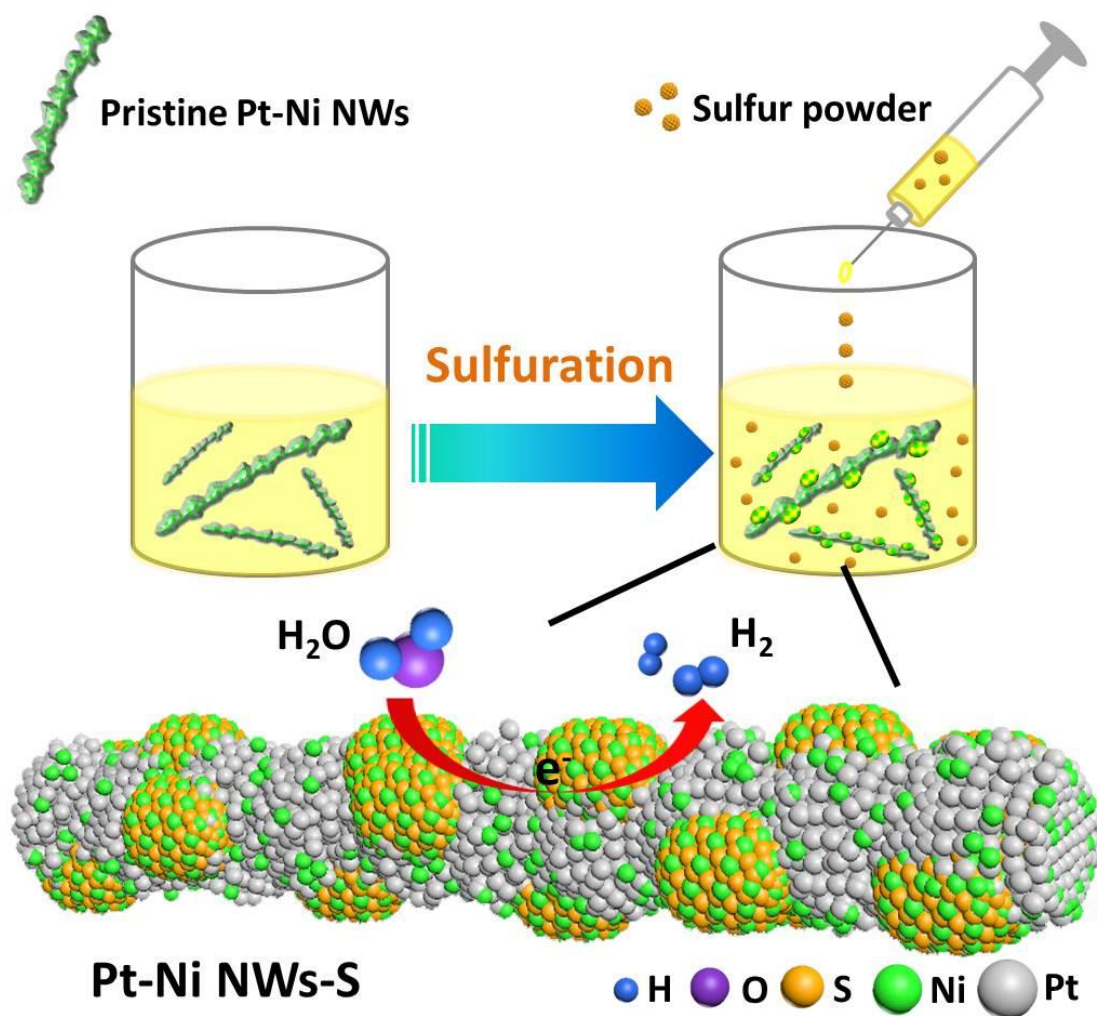


**Supplementary Figure 1.** TEM images of pristine (a, b) Pt<sub>3</sub>Ni<sub>1</sub> NWs, (d, e) Pt<sub>3</sub>Ni<sub>2</sub> NWs, (g, h) Pt<sub>3</sub>Ni<sub>3</sub> NWs and (j, k) Pt<sub>3</sub>Ni<sub>4</sub> NWs. SEM-EDS patterns of pristine (c) Pt<sub>3</sub>Ni<sub>1</sub> NWs, (f) Pt<sub>3</sub>Ni<sub>2</sub> NWs, (i) Pt<sub>3</sub>Ni<sub>3</sub> NWs and (l) Pt<sub>3</sub>Ni<sub>4</sub> NWs. The scale bars in a, d, g and j are 100 nm. The scale bars in b, e, h and k are 20 nm.

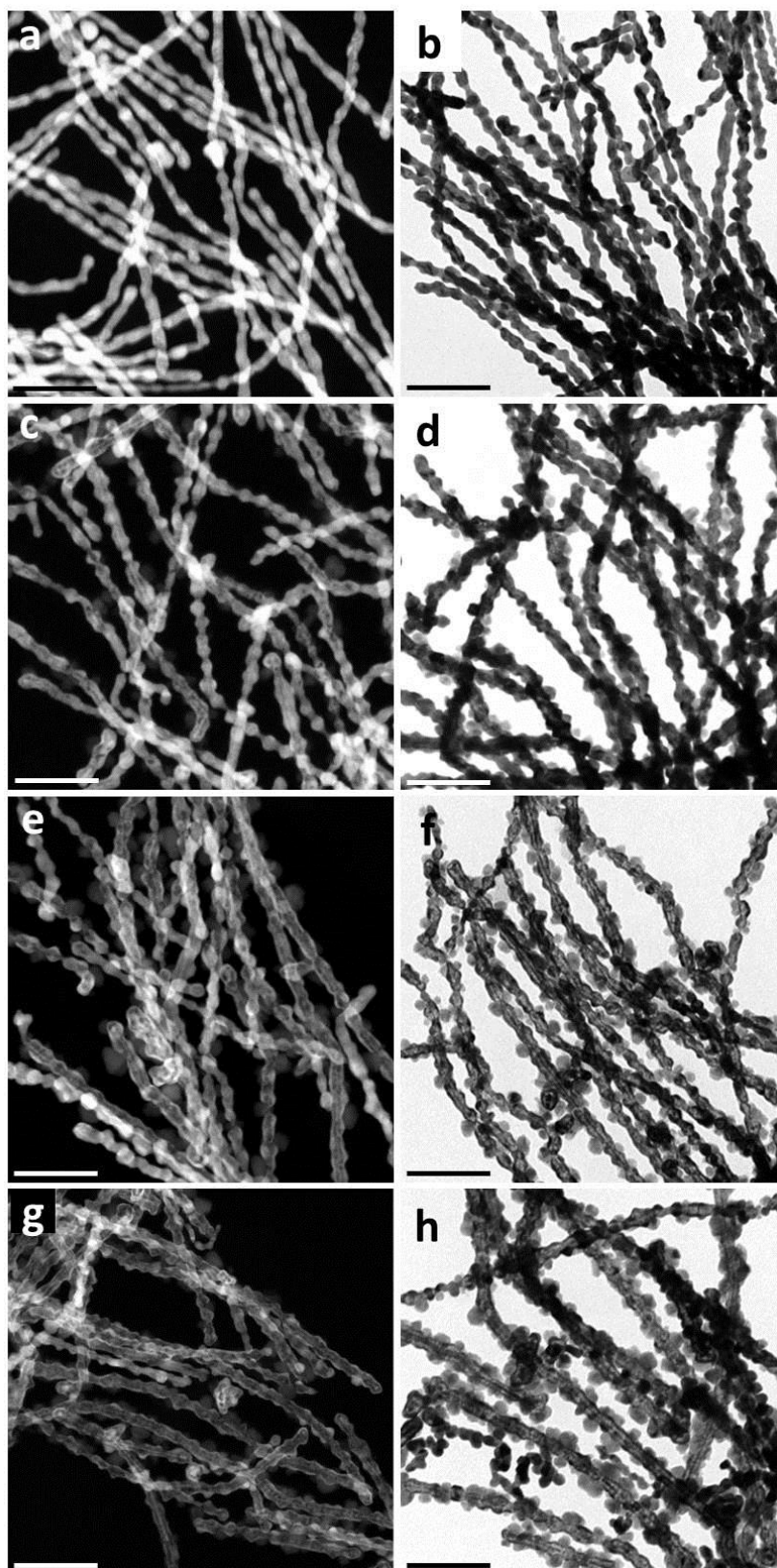


**Supplementary Figure 2.** PXRD patterns of pristine Pt<sub>3</sub>Ni<sub>1</sub> NWs, Pt<sub>3</sub>Ni<sub>2</sub> NWs, Pt<sub>3</sub>Ni<sub>3</sub> NWs and Pt<sub>3</sub>Ni<sub>4</sub> NWs.

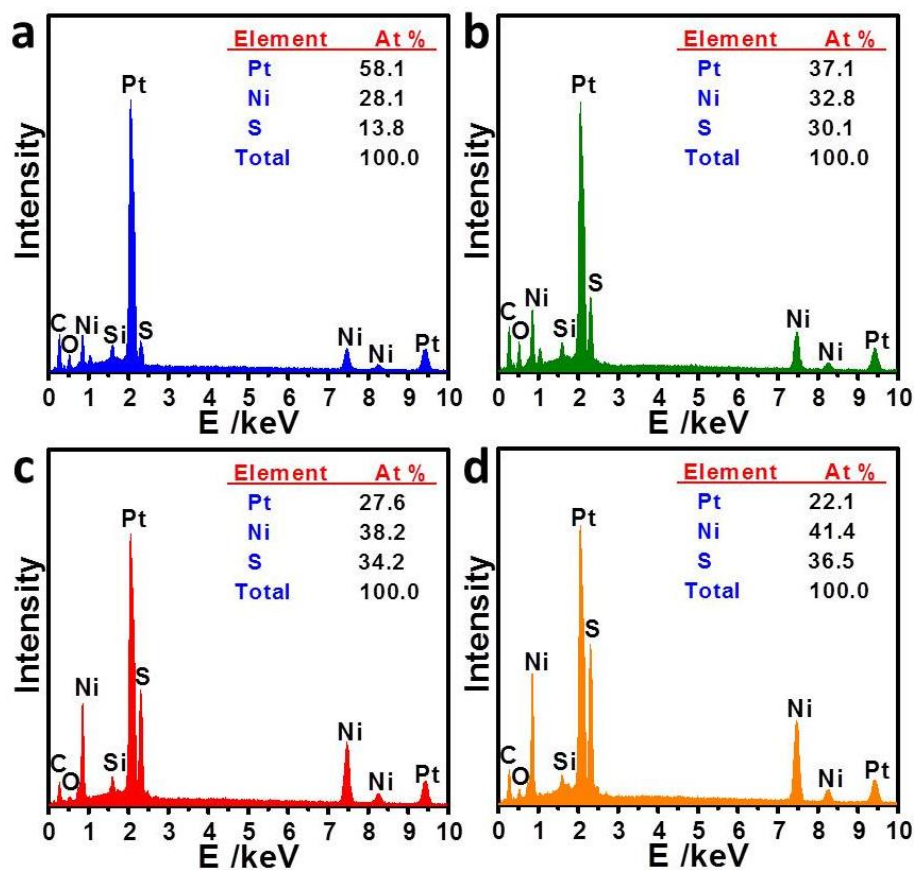
(b) The fitted peak curves from the dashed region marked in (a).



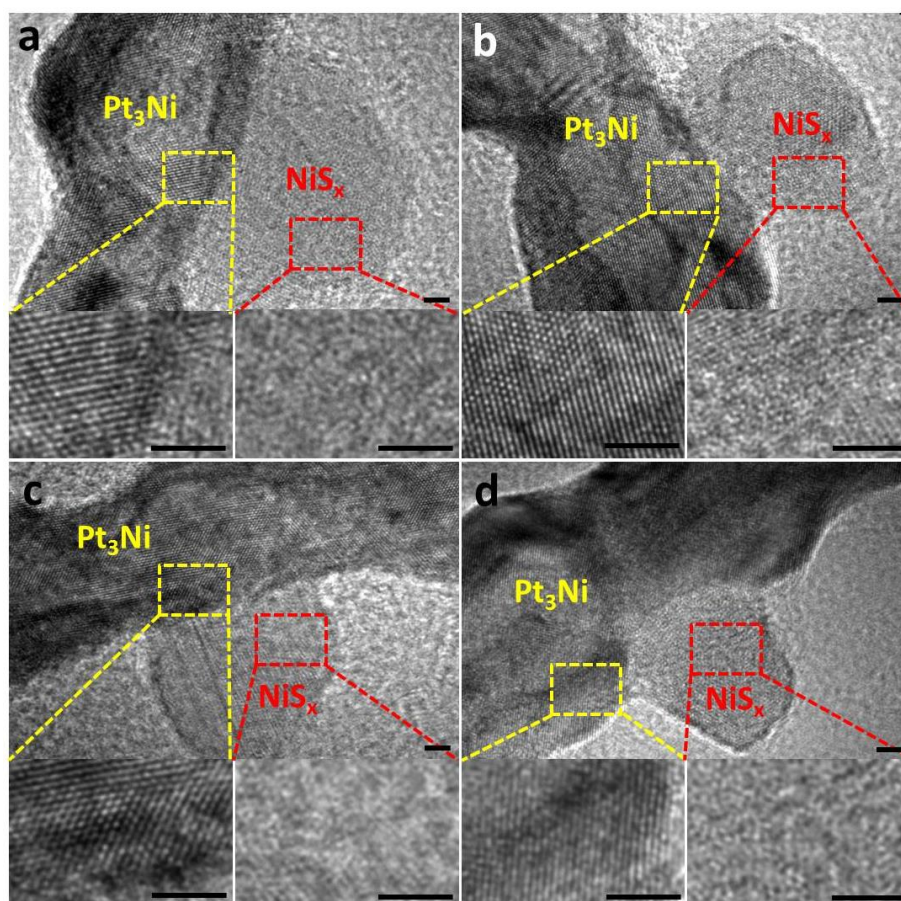
**Supplementary Figure 3.** Schematic illustration on the sulfuration of the composition-segregated Pt-Ni NWs. The sulfuration was performed by adding sulfur powder into the pristine Pt-Ni NWs to achieve the Pt-Ni NWs-S with heterostructures.



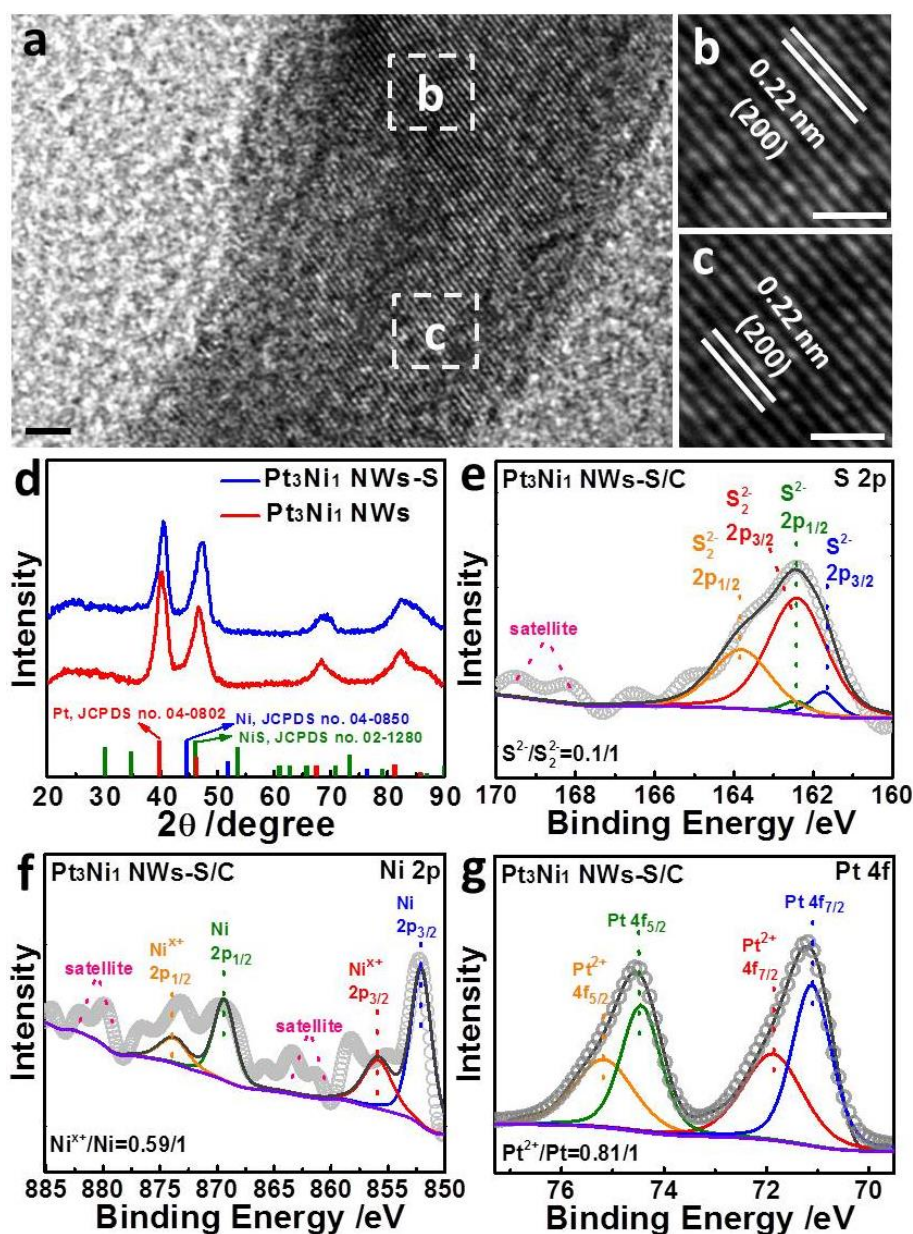
**Supplementary Figure 4.** Additional HAADF-STEM images and TEM images of (a, b)  $\text{Pt}_3\text{Ni}_1$  NWs-S, (c, d)  $\text{Pt}_3\text{Ni}_2$  NWs-S, (e, f)  $\text{Pt}_3\text{Ni}_3$  NWs-S and (g, h)  $\text{Pt}_3\text{Ni}_4$  NWs-S. The scale bars in a-h are 100 nm.



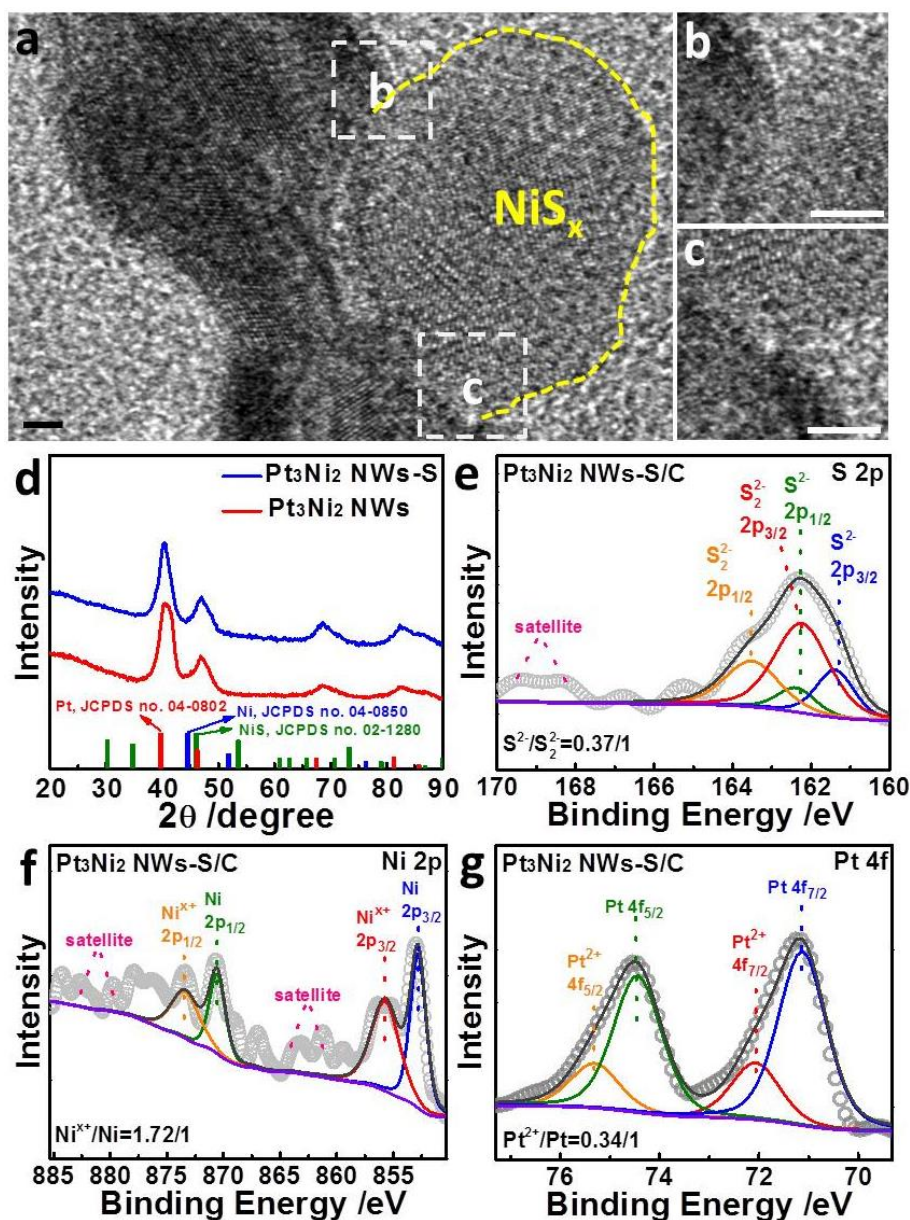
**Supplementary Figure 5.** SEM-EDS patterns of (a) Pt<sub>3</sub>Ni<sub>1</sub> NWs-S, (b) Pt<sub>3</sub>Ni<sub>2</sub> NWs-S, (c) Pt<sub>3</sub>Ni<sub>3</sub> NWs-S and (d) Pt<sub>3</sub>Ni<sub>4</sub> NWs-S.



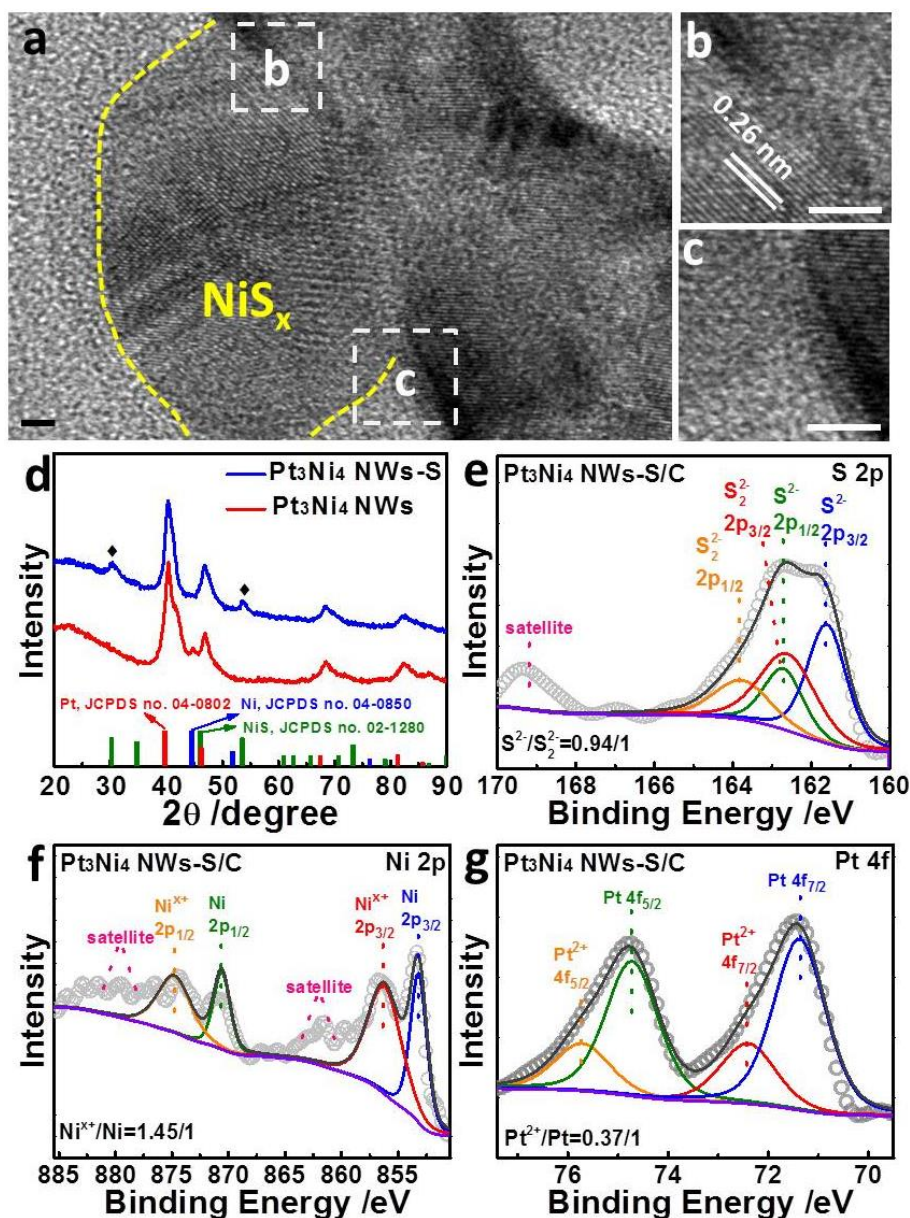
**Supplementary Figure 6.** Additional HRTEM images of (a, b, c, d) Pt<sub>3</sub>Ni<sub>3</sub> NWs-S. The scale bars in a-d are 2 nm.



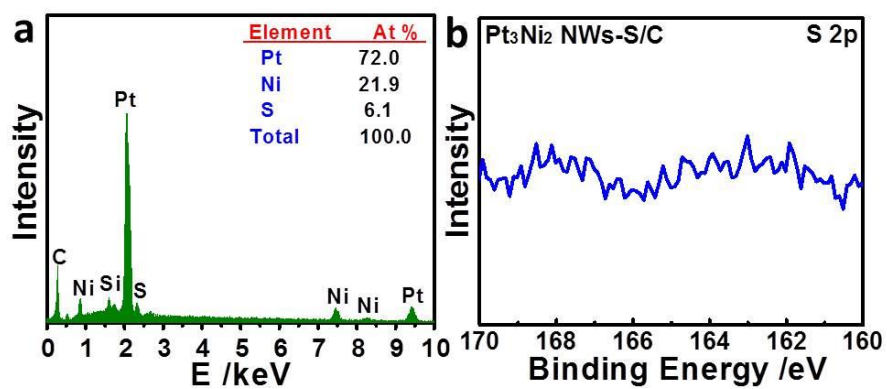
**Supplementary Figure 7.** (a) HRTEM image of Pt<sub>3</sub>Ni<sub>1</sub> NWs-S and (b, c) the magnified HRTEM images recorded from regions b and c marked in (a). (d) XRD patterns of Pt<sub>3</sub>Ni<sub>1</sub> NWs-S and Pt<sub>3</sub>Ni<sub>1</sub> NWs. XPS patterns of (e) S 2p, (f) Ni 2p and (g) Pt 4f of Pt<sub>3</sub>Ni<sub>1</sub> NWs-S. The scale bars in a-c are 2 nm.



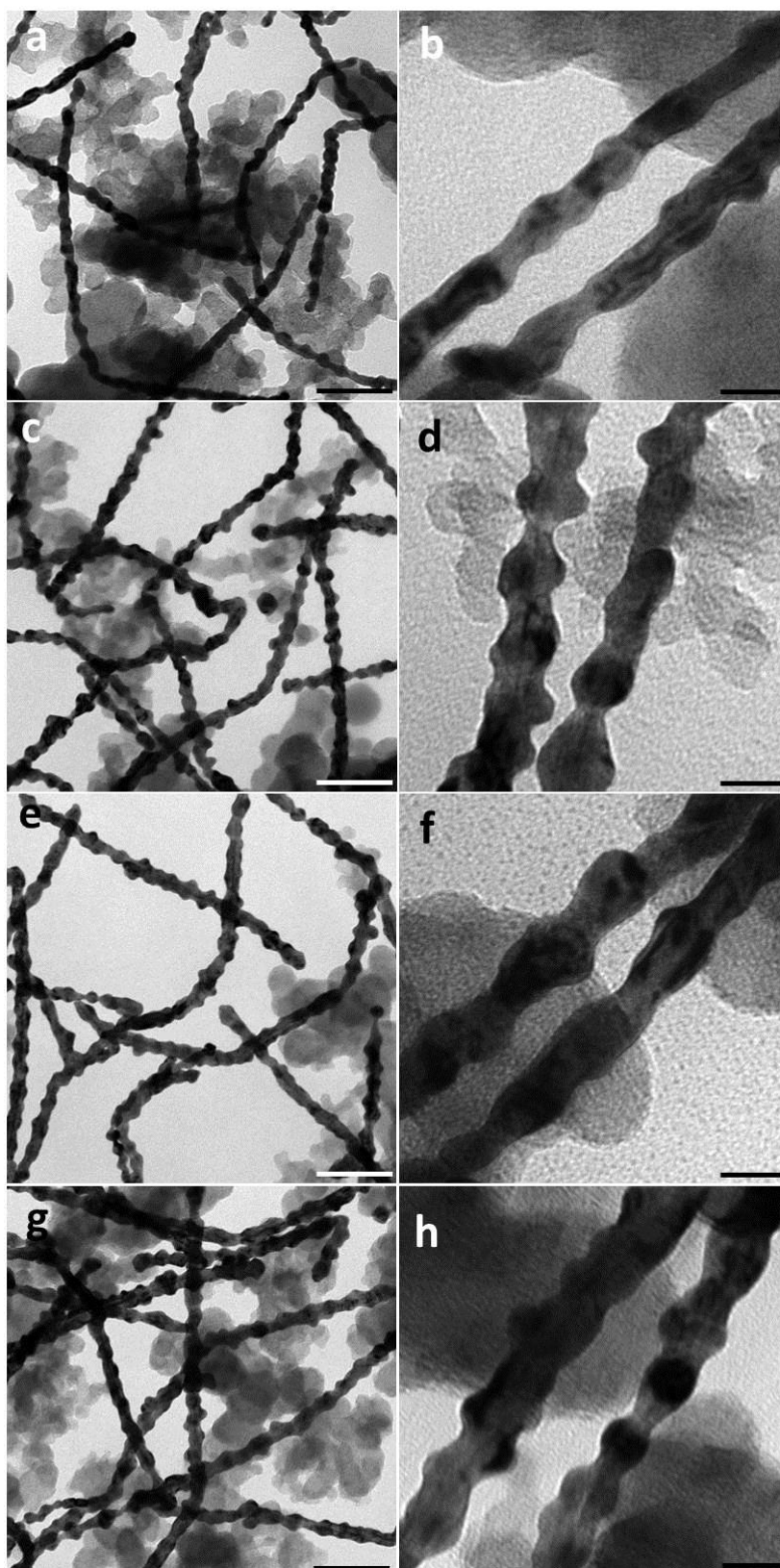
**Supplementary Figure 8.** (a) HRTEM image of  $\text{Pt}_3\text{Ni}_2$  NWs-S and (b, c) the magnified HRTEM images recorded from regions b and c marked in (a). (d) XRD patterns of  $\text{Pt}_3\text{Ni}_2$  NWs-S and  $\text{Pt}_3\text{Ni}_2$  NWs. XPS patterns of (e) S 2p, (f) Ni 2p and (g) Pt 4f of  $\text{Pt}_3\text{Ni}_2$  NWs-S. The scale bars in a-c are 2 nm.



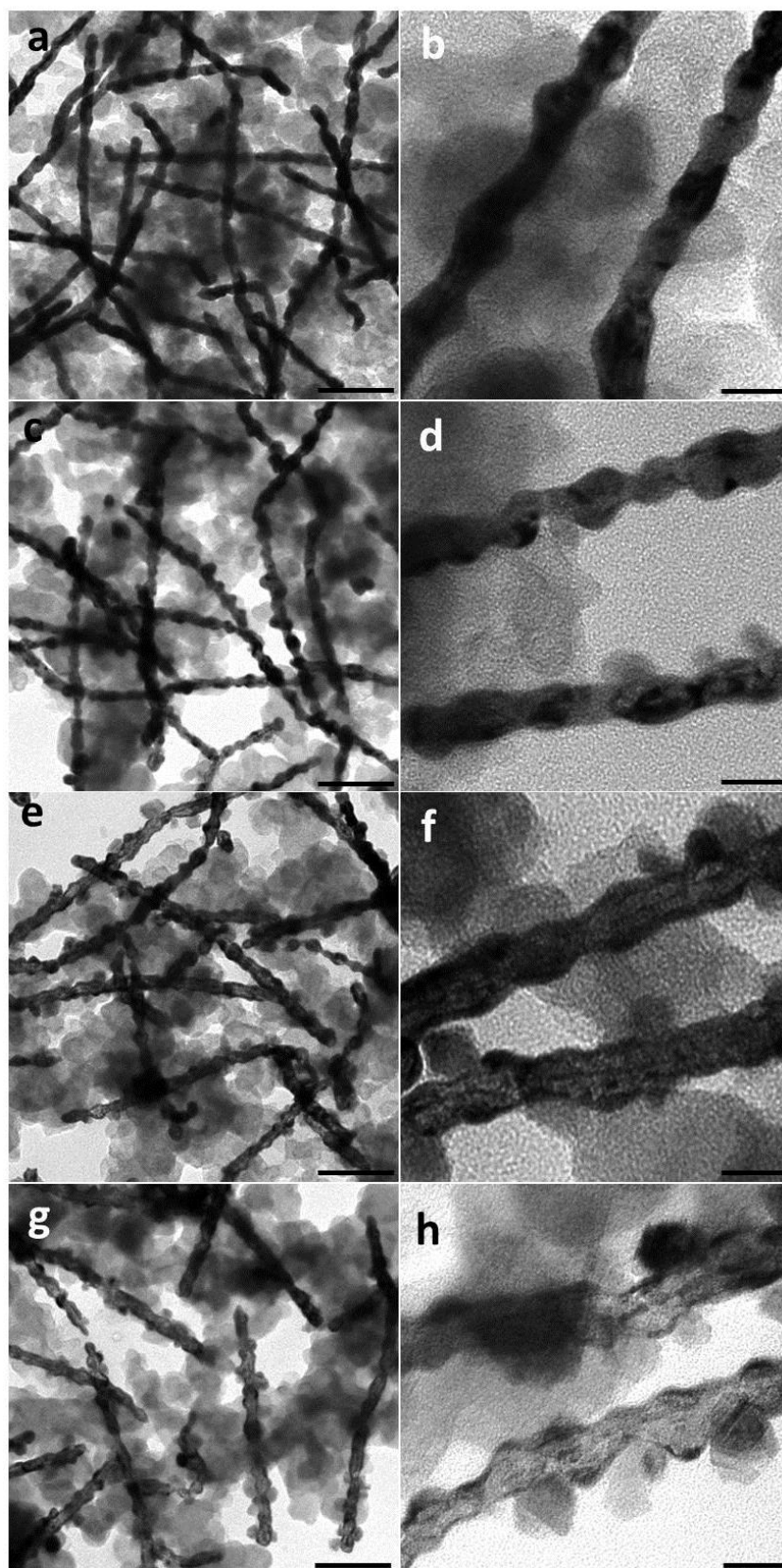
**Supplementary Figure 9.** (a) HRTEM image of Pt<sub>3</sub>Ni<sub>4</sub> NWs-S and (b, c) the magnified HRTEM images recorded from regions b and c marked in (a). (d) XRD patterns of Pt<sub>3</sub>Ni<sub>4</sub> NWs-S and Pt<sub>3</sub>Ni<sub>4</sub> NWs. XPS patterns of (e) S 2p, (f) Ni 2p and (g) Pt 4f of Pt<sub>3</sub>Ni<sub>4</sub> NWs-S. The scale bars in a-c are 2 nm.



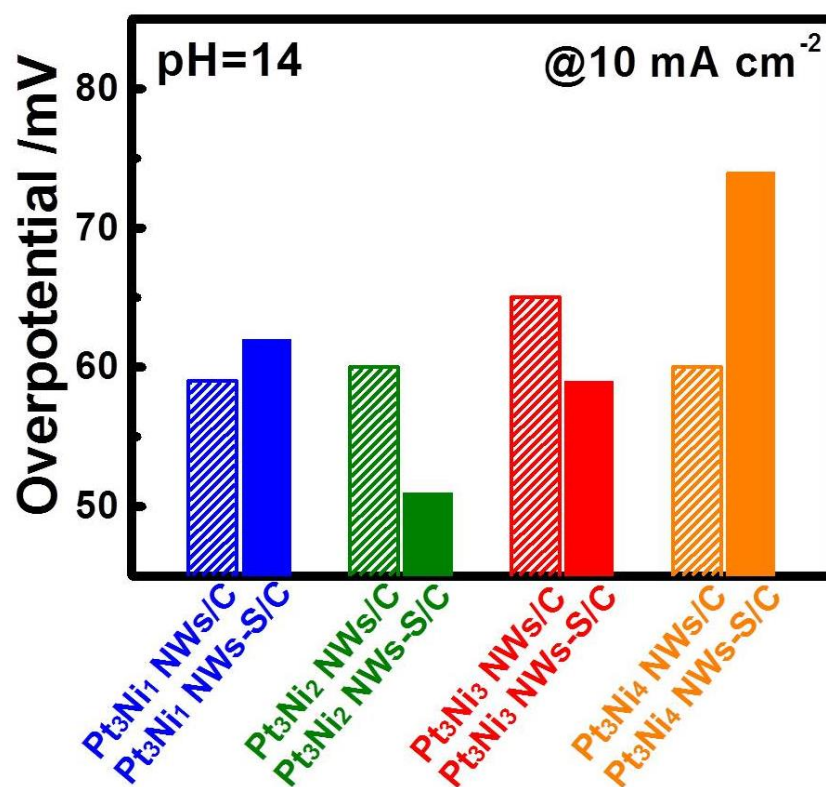
**Supplementary Figure 10.** (a) SEM-EDS and (b) S 2p XPS spectrum of Pt<sub>3</sub>Ni<sub>1</sub> NWs-S after their washed with CS<sub>2</sub> and ethanol to remove the adsorbed sulfur on NW surface.



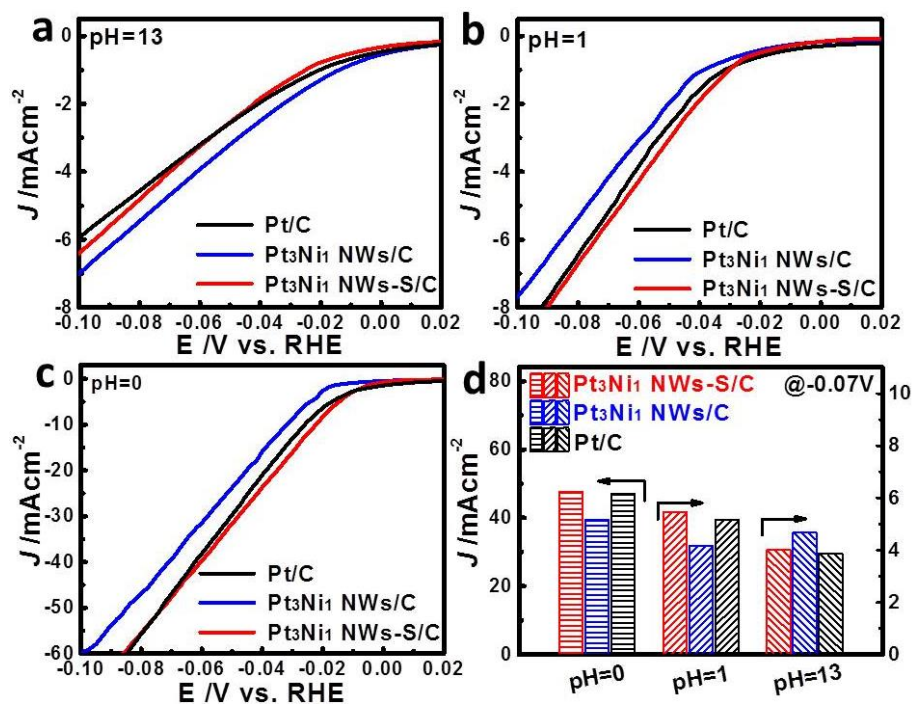
**Supplementary Figure 11.** TEM images of (a)  $\text{Pt}_3\text{Ni}_1$  NWs/C, (b)  $\text{Pt}_3\text{Ni}_2$  NWs/C, (c)  $\text{Pt}_3\text{Ni}_3$  NWs/C and (d)  $\text{Pt}_3\text{Ni}_4$  NWs/C. The scale bars in a, c, e and g are 100 nm. The scale bars in b, d, f and h are 20 nm.



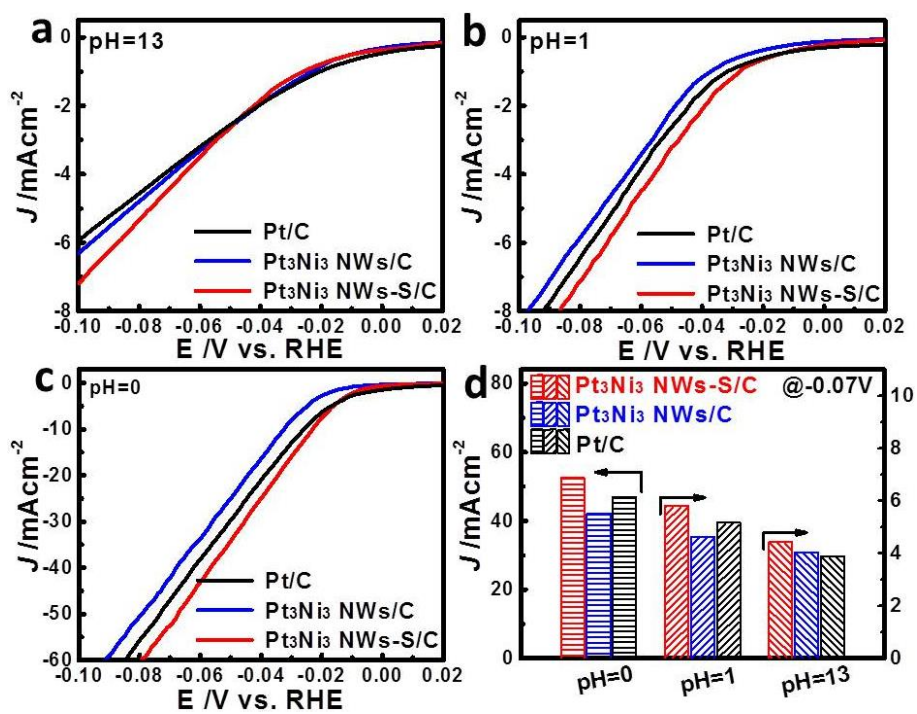
**Supplementary Figure 12.** TEM images of (a, b)  $\text{Pt}_3\text{Ni}_1$  NWs-S/C , (c, d)  $\text{Pt}_3\text{Ni}_2$  NWs-S/C, (e, f)  $\text{Pt}_3\text{Ni}_3$  NWs-S/C and (g, h)  $\text{Pt}_3\text{Ni}_4$  NWs-S/C. The scale bars in a, c, e and g are 100 nm. The scale bars in b, d, f and h are 20 nm.



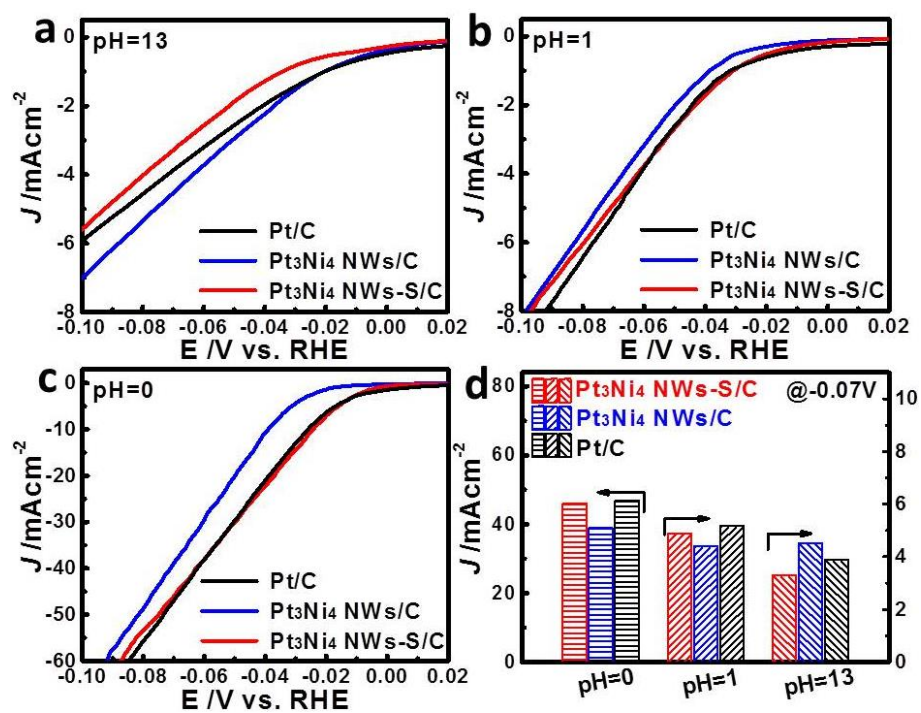
**Supplementary Figure 13.** The overpotential of different Pt-Ni NWs/C and corresponding Pt-Ni NWs-S/C at the current density of 10 mA cm<sup>-2</sup>.



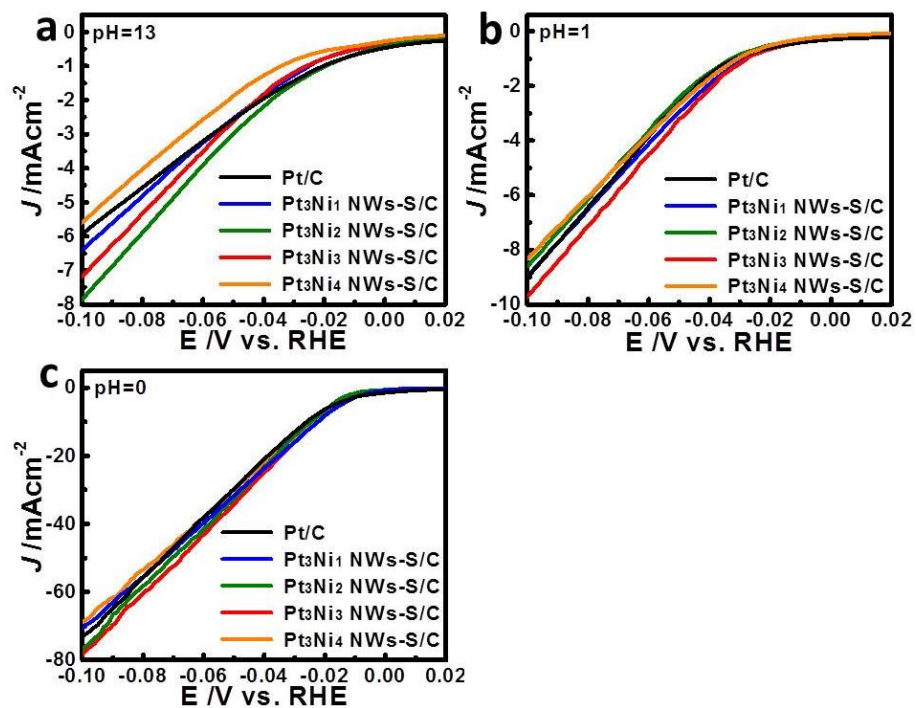
**Supplementary Figure 14.** HER polarization curves of Pt<sub>3</sub>Ni<sub>1</sub> NWs/C, Pt<sub>3</sub>Ni<sub>1</sub> NWs-S/C and Pt/C at pH of (a) 13, (b) 1 and (c) 0. (d) Histograms of current densities at -0.07 V *versus* RHE from (a)-(c).



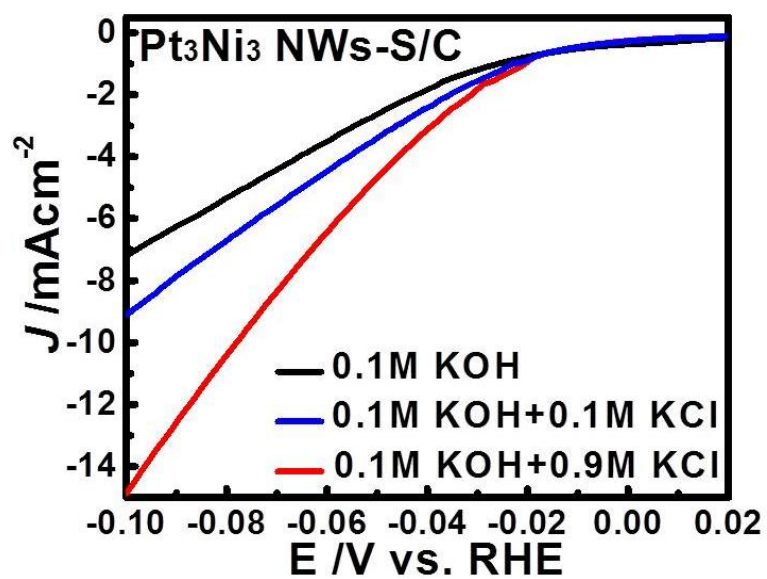
**Supplementary Figure 15.** HER polarization curve of Pt<sub>3</sub>Ni<sub>3</sub> NWs/C, Pt<sub>3</sub>Ni<sub>3</sub> NWs-S/C and Pt/C at pH of (a) 13, (b) 1 and (c) 0. (d) Histograms of current densities at -0.07 V *versus* RHE from (a)-(c).



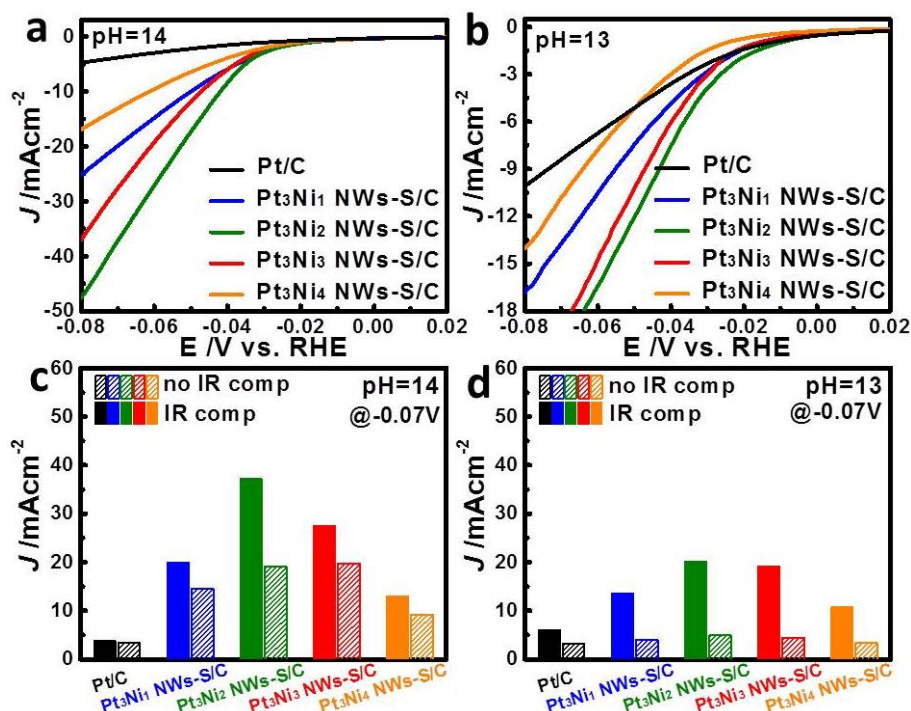
**Supplementary Figure 16.** HER polarization curve of Pt<sub>3</sub>Ni<sub>4</sub> NWs/C, Pt<sub>3</sub>Ni<sub>4</sub> NWs-S/C and Pt/C at pH of (a) 13, (b) 1 and (c) 0. (d) Histograms of current densities at -0.07 V versus RHE from (a)-(c).



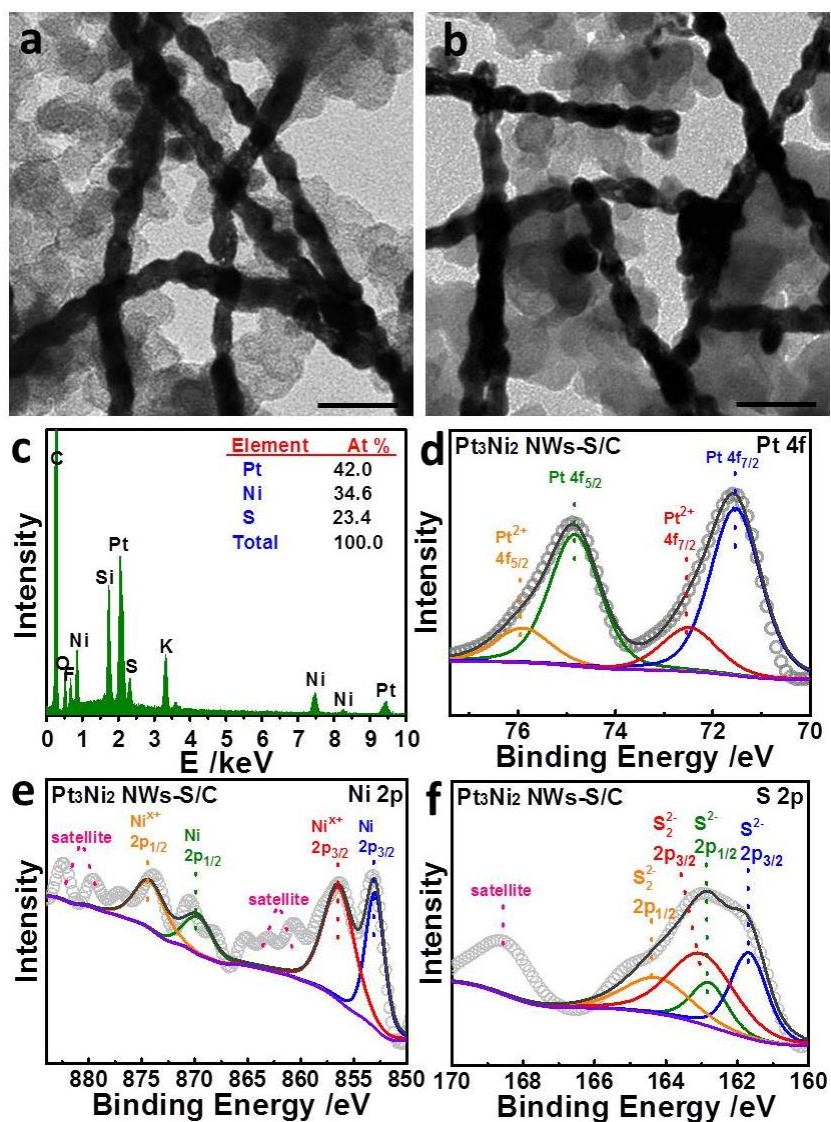
**Supplementary Figure 17.** HER polarization curves of Pt-Ni NWs-S /C with different compositions and Pt/C at pH of (a) 13, (b) 1 and (c) 0.



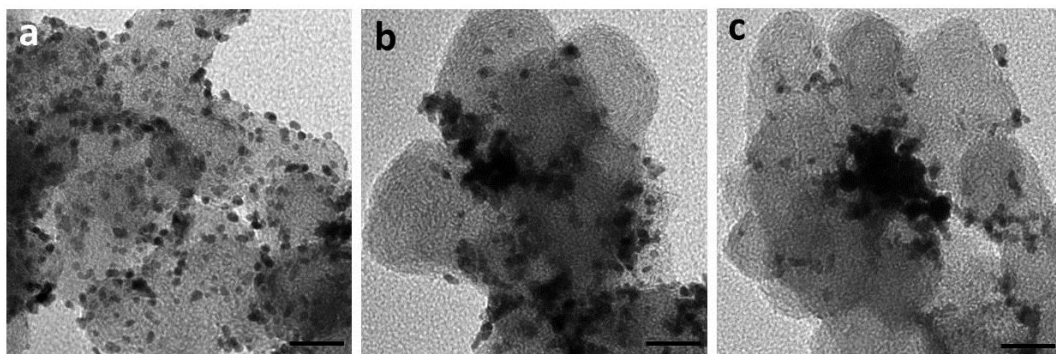
**Supplementary Figure 18.** HER activities of Pt<sub>3</sub>Ni<sub>3</sub> NWs-S/C in pH of 13 with different concentrations of K<sup>+</sup>.



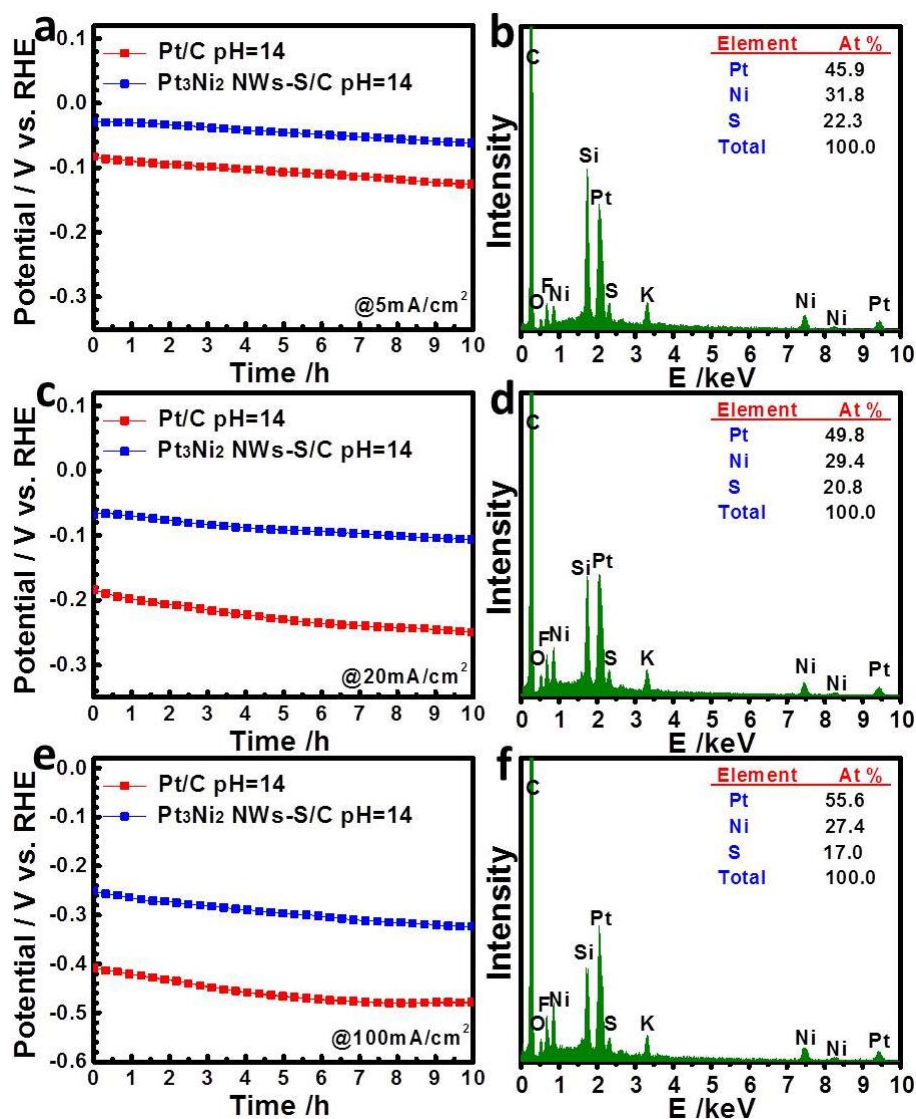
**Supplementary Figure 19.** HER polarization curves of Pt<sub>3</sub>Ni<sub>1</sub> NWs-S/C, Pt<sub>3</sub>Ni<sub>2</sub> NWs-S/C, Pt<sub>3</sub>Ni<sub>3</sub> NWs-S/C, Pt<sub>3</sub>Ni<sub>4</sub> NWs-S/C and Pt/C at pH of (a) 14 and (b) 13. Histograms of current densities at -0.07 V *versus* RHE with IR compensation or no IR compensation at pH of (c) 14 and (d) 13.



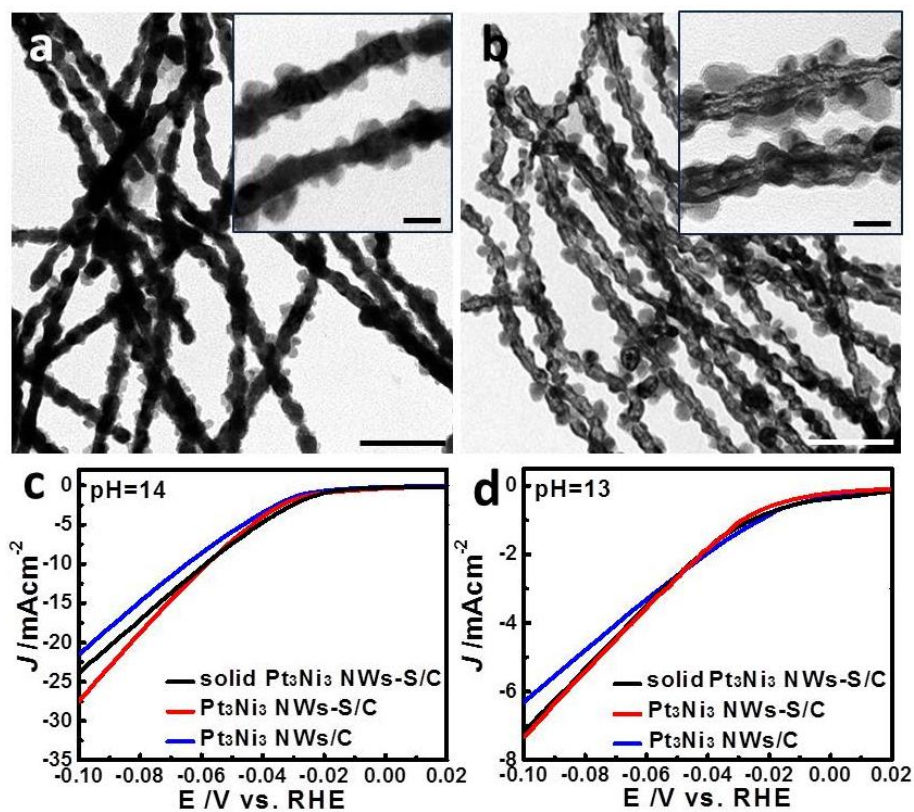
**Supplementary Figure 20.** TEM images of Pt<sub>3</sub>Ni<sub>2</sub> NWs-S/C after 5 h chronopotentiometry test in (a) 0.1 M KOH and (b) 1 M KOH. (c) SEM-EDS and (d-f) XPS patterns of Pt<sub>3</sub>Ni<sub>2</sub> NWs-S/C after 5 h chronopotentiometry test in 1 M KOH. (d) Pt 4f, (e) Ni 2p and (f) S 2p. The scale bars in a and b are 50 nm.



**Supplementary Figure 21.** TEM images of Pt/C catalyst (a) and after 5 h chronopotentiometry test in (b) 0.1M KOH and (c) 1M KOH. The scale bars in a-c are 20 nm.



**Supplementary Figure 22.** Chronopotentiometry of Pt<sub>3</sub>Ni<sub>2</sub> NWs-S/C and Pt/C at current densities of (a) 5 mA/cm<sup>2</sup>, (c) 20 mA/cm<sup>2</sup> and (e) 100 mA/cm<sup>2</sup> at pH of 14. SEM-EDS patterns of Pt<sub>3</sub>Ni<sub>2</sub> NWs-S/C after 10 h chronopotentiometry test at pH of 14 at current densities of (b) 5 mA/cm<sup>2</sup>, (d) 20 mA/cm<sup>2</sup> and (f) 100 mA/cm<sup>2</sup>.



**Supplementary Figure 23.** TEM images of (a) solid  $\text{Pt}_3\text{Ni}_3$  NWs-S and (b)  $\text{Pt}_3\text{Ni}_3$  NWs-S. The inset images of (a) and (b) are corresponding high-magnification TEM images. HER activities of solid  $\text{Pt}_3\text{Ni}_3$  NWs-S/C,  $\text{Pt}_3\text{Ni}_3$  NWs-S/C and  $\text{Pt}_3\text{Ni}_3$  NWs/C in pH of (c) 14 and (d) 13. The scale bars in a, b and inset of a, b are 100 nm and 20 nm, respectively.

**Supplementary Table 1.** ICP results of Pt-Ni NWs and Pt-Ni NWs-S.

| ICP                                   | Pt /At% | Ni /At% |
|---------------------------------------|---------|---------|
| Pt <sub>3</sub> Ni <sub>1</sub> NWs   | 74.4    | 25.6    |
| Pt <sub>3</sub> Ni <sub>2</sub> NWs   | 59.1    | 40.9    |
| Pt <sub>3</sub> Ni <sub>3</sub> NWs   | 48.8    | 51.2    |
| Pt <sub>3</sub> Ni <sub>4</sub> NWs   | 41.6    | 58.4    |
| Pt <sub>3</sub> Ni <sub>1</sub> NWs-S | 77.6    | 22.4    |
| Pt <sub>3</sub> Ni <sub>2</sub> NWs-S | 60.9    | 39.1    |
| Pt <sub>3</sub> Ni <sub>3</sub> NWs-S | 50.9    | 49.1    |
| Pt <sub>3</sub> Ni <sub>4</sub> NWs-S | 42.7    | 57.3    |

**Supplementary Table 2.** Summary of HER properties of the high performance electrode materials reported in recent literatures. (The current densities in the table are normalized to the geometric area of electrode).

| Sample                                                            | Loading<br>(mg cm <sup>-2</sup> ) | Overpotential at 10 mA cm <sup>-2</sup><br>(mV) |        | Current Density at -0.07 V<br>(mA cm <sup>-2</sup> ) |        | Reference                                            |
|-------------------------------------------------------------------|-----------------------------------|-------------------------------------------------|--------|------------------------------------------------------|--------|------------------------------------------------------|
|                                                                   |                                   | 0.1M KOH                                        | 1M KOH | 0.1M KOH                                             | 1M KOH |                                                      |
| Ni(OH) <sub>2</sub> /Pt-islands/<br>Pt(111) surface               | —                                 | ~138                                            | —      | ~2.2                                                 | —      | <i>Science</i> <b>2011</b> , 334, 1256               |
| Ni(OH) <sub>2</sub> /Pt/C (TTK)                                   | 0.06                              | ~90                                             | —      | ~9                                                   | —      | <i>Science</i> <b>2011</b> , 334, 1256               |
| Pt NWs/SL - Ni(OH) <sub>2</sub>                                   | 0.016                             | ~48                                             | ~70    | 26.6                                                 | 10.9   | <i>Nat. Commun.</i> <b>2015</b> , 6, 6430            |
| Ni(OH) <sub>2</sub> modified Pt surface                           | —                                 | ~75                                             | —      | ~9.5                                                 | —      | <i>Angew Chem. Int. Ed.</i> <b>2012</b> , 124, 12663 |
| Ni(OH) <sub>2</sub> modified Ir surface                           | —                                 | ~64                                             | —      | ~15                                                  | —      | <i>Angew Chem. Int. Ed.</i> <b>2012</b> , 124, 12663 |
| Zn <sub>0.30</sub> Co <sub>0.70</sub> S <sub>4</sub> nanocrystals | 0.285                             | —                                               | 85     | —                                                    | ~7     | <i>J. Am. Chem. Soc.</i> <b>2016</b> , 138, 1359     |
| Ni <sub>0.33</sub> Co <sub>0.67</sub> S <sub>2</sub> NWs /Ti foil | 0.3                               | —                                               | 88     | —                                                    | ~7     | <i>Adv. Energy Mater.</i> <b>2015</b> , 5,1402031    |
| NiS nanoframes                                                    | 2                                 | —                                               | ~94    | —                                                    | ~7     | <i>Angew Chem. Int. Ed.</i> <b>2015</b> , 54, 5331   |
| Ni <sub>3</sub> S <sub>2</sub> /Ni foam                           | 1.6                               | —                                               | 223    | —                                                    | ~1.5   | <i>J. Am. Chem. Soc.</i> <b>2015</b> , 137,          |

|                                              |       |    |      |      |      |                                                                |
|----------------------------------------------|-------|----|------|------|------|----------------------------------------------------------------|
|                                              |       |    |      |      |      | 14023                                                          |
| Ni <sub>5</sub> P <sub>4</sub> /Ni<br>films  | —     | —  | ~150 | —    | ~0   | <i>Angew Chem.<br/>Int. Ed.</i><br><b>2015</b> , 127,<br>12538 |
| NiO/Ni<br>-CNT                               | 0.28  | —  | ~80  | —    | ~8.5 | <i>Nat. Commun.</i><br><b>2014</b> , 5, 4695                   |
| CeO <sub>2</sub> /Ni<br>-CNT                 | 0.14  | —  | ~91  | —    | ~7.5 | <i>Nano Lett.</i><br><b>2015</b> , 15, 7704                    |
| CoP films                                    | 2.71  | —  | ~94  | —    | ~5   | <i>Angew Chem.<br/>Int. Ed.</i><br><b>2012</b> , 54, 6251      |
| CoP/Carbon<br>Cloth                          | 0.92  | —  | ~250 | —    | ~0   | <i>J. Am. Chem.<br/>Soc.</i><br><b>2014</b> , 136, 7587        |
| MoP                                          | 0.86  | —  | ~140 | —    | ~0   | <i>Energy<br/>Environ. Sci.</i><br><b>2014</b> , 7, 2624       |
| Mo <sub>2</sub> C@NC                         | 0.28  | —  | ~60  | —    | ~12  | <i>Angew. Chem.<br/>Int. Ed.</i><br><b>2015</b> , 54, 10752    |
| MoC <sub>x</sub>                             | 0.8   | —  | ~151 | —    | ~0   | <i>Nat. Commun.</i><br><b>2015</b> , 6, 6512                   |
| Pt <sub>3</sub> Ni <sub>2</sub> -NWs<br>-S/C | 0.015 | 45 | 42   | 20.2 | 37.2 | <b>This Work</b>                                               |