

## Supporting Online Material for

### Synthetic Control of FePtM Nanorods (M = Cu, Ni) to Enhance Oxygen Reduction Reaction

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#### Experimental Section

**Chemicals and Materials.** Sodium oleate, oleylamine (OAm, >70%), oleic acid (OA), 1-octadecene (ODE), Pt(acac)<sub>2</sub> (acac = acetylacetonate), Cu(acac)<sub>2</sub>, Ni(acac)<sub>2</sub>, iron pentacarbonyl (Fe(CO)<sub>5</sub>), hexane, isopropanol, ethanol, acetic acid (99%) and Nafion (5%) were all purchased from Sigma Aldrich. C-Pt (20% mass loading with a diameter of 2.5-3.5 nm) catalyst was obtained from Fuel Cell Store.

**Instrumentation.** TEM images were obtained from a Philips CM 20 operating at 200 kV. High-resolution TEM (HRTEM) images were obtained from a JEOL 2010 with an accelerating voltage of 200 kV. TEM and HRTEM samples were prepared by depositing a single drop of diluted nanorod (NR) dispersion in hexane on amorphous carbon coated copper grids. The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements were carried on a JY2000 Ultrace ICP Atomic Emission Spectrometer equipped with a JY AS 421 autosampler and 2400g/mm holographic grating. Electrochemical measurements were performed on a Fuel Cell Electrocatalyst RDE bundle from PINE Instrument Company with a model AFCBP1 with a three-electrode system consisting of a glassy carbon (GC) working electrode (5-mm in diameter), an Ag/AgCl reference electrode (10% KNO<sub>3</sub>), and a platinum wire counter electrode.

**Synthesis of FePtCu and FePtNi Nanorods (NRs).** A mixture solution of sodium oleate (0.3g) and ODE (12 mL) in a four-necked flask was heated to 200 °C under nitrogen flow and magnetic stirring to make sodium oleate dissolved thoroughly. Then the solution was cooled down to room temperature and a mixture of Pt(acac)<sub>2</sub> (98 mg) and OAm (8 mL) was added into the solution and heated to 120 °C. Under the blanket of nitrogen, Fe(CO)<sub>5</sub> (0.03 mL) was added into the solution that was then further heated to 160 °C. At this temperature, a mixture of Cu(acac)<sub>2</sub> (32 mg) and OAm (3 mL) was added into the solution followed by heating to 240 °C and keeping at this temperature for 1 h. After cooled down to room temperature, the FePtCu NRs were collected and washed by addition of isopropanol (20 mL) and subsequent centrifugation at 8500 rpm for 8 min. The

product was redispersed into hexane and precipitated out by addition of ethanol and centrifugation to remove all residual impurities. Final product was FePtCu NRs and was dispersed in hexane for further use. Under the identical condition, by changing  $\text{Cu}(\text{acac})_2$  to  $\text{Ni}(\text{acac})_2$ , FePtNi NRs were prepared. Different composition was obtained by varying the amount of  $\text{Cu}(\text{acac})_2$  or  $\text{Ni}(\text{acac})_2$  at a fixed ratio between  $\text{Fe}(\text{CO})_5$  and  $\text{Pt}(\text{acac})_2$ , as summarized in **Table S1**.

**FePtCu NWs.** The synthetic procedure of FePtCu NWs was similar to that of NRs except 0.07 ml of  $\text{Fe}(\text{CO})_5$  was added at 120 °C.

**FePt NRs.** Similar to the synthesis of FePtCu NRs, FePt NRs were obtained by direct injection of  $\text{Fe}(\text{CO})_5$  and by heating the mixture to 240 °C for 60 min at the heating rate of about 4-5 °C/min without the presence of  $\text{Cu}(\text{acac})_2$ .

**Catalyst Preparation.** The as-synthesized NRs and Ketjen-300 J carbon at the weight ratio of 4:6 were mixed in 20 mL mixture of hexane and acetone ( $V/V=1/1$ ) and sonicated for 1 h to deposit NRs on carbon. The product was separated from the solvent by centrifugation and was suspended in 30 ml acetic acid at 70 °C for overnight to remove the surfactant.<sup>1</sup> The resultant solid product was separated from the acid by centrifugation and washed with ethanol and deionized water. The product was then redispersed in a mixture of deionized water, isopropanol and Nafion ( $V/V/V = 4/1/0.05$ ). 20  $\mu\text{L}$  catalyst ink was deposited on the working electrode (glassy carbon rotating disk electrode, GC-RDE) that was polished prior to catalyst deposition by 0.1  $\mu\text{m}$  and 0.05  $\mu\text{m}$  alumina powder and rinsed by sonication in ethanol and in deionized water. The catalyst was dried at ambient condition.

**Electrochemical Measurements.** Cyclic voltammograms (CVs) were obtained by scanning between -0.2 V-1.0 V vs Ag/AgCl at a scan rate of 50 mV/s in  $\text{N}_2$ -saturated 0.1M  $\text{HClO}_4$ . ORR polarization curves were obtained by scanning the potentials from 1.0 to -0.2 V vs Ag/AgCl at a scan rate of 10 mV/s in  $\text{O}_2$ -saturated 0.1 M  $\text{HClO}_4$  with the GC-RDE rotating at 1600 rpm.

## References

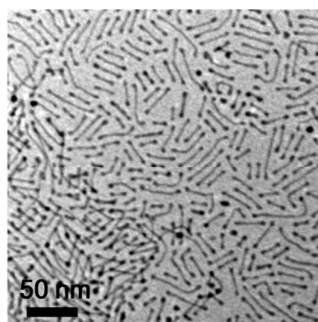
- (1) Mazumder, V.; Sun, S. *J. Am. Chem. Soc.* **2009**, *131*, 4588-4589.

**Table S1:** Composition control of FePtCu and FePtNi NRs by varying the precursor ratio.

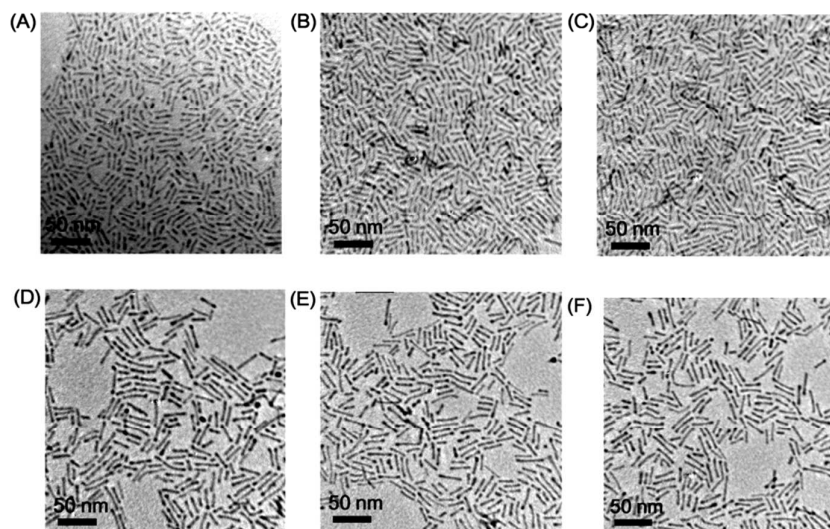
Precursor ratio Fe:Pt:Cu	4:4:1	2:2:1	4:4:3
Composition from ICP-AES	Fe <sub>42</sub> Pt <sub>44</sub> Cu <sub>14</sub>	Fe <sub>38</sub> Pt <sub>42</sub> Cu <sub>20</sub>	Fe <sub>29</sub> Pt <sub>41</sub> Cu <sub>30</sub>
Precursor ratio Fe:Pt:Ni	4:4:1	2:2:1	4:4:3
Composition from ICP-AES	Fe <sub>43</sub> Pt <sub>45</sub> Ni <sub>12</sub>	Fe <sub>35</sub> Pt <sub>44</sub> Ni <sub>21</sub>	Fe <sub>31</sub> Pt <sub>37</sub> Ni <sub>32</sub>

**Table S2:** Composition change of FePtCu and FePtNi NRs before and after acetic acid wash.

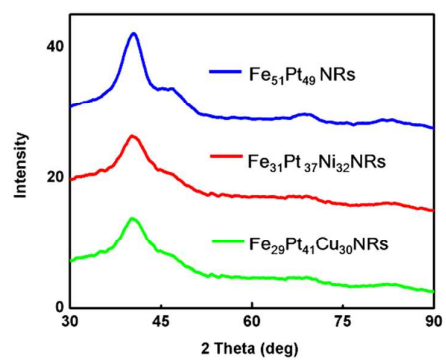
Before acetic acid wash	Fe <sub>42</sub> Pt <sub>44</sub> Cu <sub>14</sub>	Fe <sub>38</sub> Pt <sub>42</sub> Cu <sub>20</sub>	Fe <sub>29</sub> Pt <sub>41</sub> Cu <sub>30</sub>
After acetic acid wash	Fe <sub>25</sub> Pt <sub>58</sub> Cu <sub>17</sub>	Fe <sub>21</sub> Pt <sub>54</sub> Cu <sub>25</sub>	Fe <sub>12</sub> Pt <sub>54</sub> Cu <sub>34</sub>
Before acetic acid wash	Fe <sub>43</sub> Pt <sub>45</sub> Ni <sub>12</sub>	Fe <sub>35</sub> Pt <sub>44</sub> Ni <sub>21</sub>	Fe <sub>31</sub> Pt <sub>37</sub> Ni <sub>32</sub>
After acetic acid wash	Fe <sub>24</sub> Pt <sub>69</sub> Ni <sub>7</sub>	Fe <sub>20</sub> Pt <sub>67</sub> Ni <sub>13</sub>	Fe <sub>20</sub> Pt <sub>64</sub> Ni <sub>16</sub>



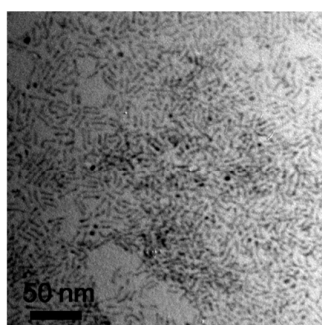
**Figure S1.** TEM image of the Fe<sub>51</sub>Pt<sub>49</sub> NRs.



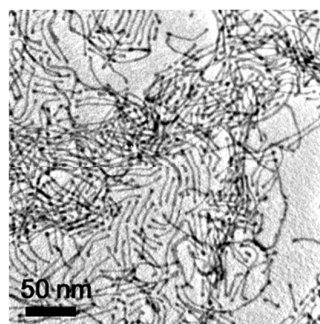
**Figure S2.** TEM images of (A) Fe<sub>42</sub>Pt<sub>44</sub>Cu<sub>14</sub>, (B) Fe<sub>38</sub>Pt<sub>42</sub>Cu<sub>20</sub>, (C) Fe<sub>29</sub>Pt<sub>41</sub>Cu<sub>30</sub>, (D) Fe<sub>43</sub>Pt<sub>45</sub>Ni<sub>12</sub>, (E) Fe<sub>35</sub>Pt<sub>44</sub>Ni<sub>21</sub>, and (F) Fe<sub>31</sub>Pt<sub>37</sub>Ni<sub>32</sub> NRs.



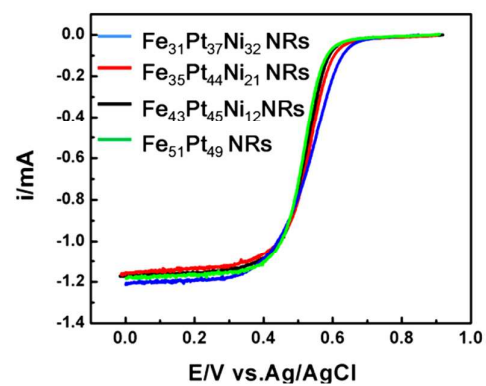
**Figure S3.** XRD patterns of  $\text{Fe}_{51}\text{Pt}_{49}$ ,  $\text{Fe}_{31}\text{Pt}_{37}\text{Ni}_{32}$ ,  $\text{Fe}_{29}\text{Pt}_{41}\text{Cu}_{30}$  NRs.



**Figure S4.** TEM image of the sample separated from the 160 °C solution in the syntehsis of FePtCu NRs before  $\text{Cu}(\text{acac})_2$  was added.



**Figure S5.** TEM image of the  $\text{Fe}_{38}\text{Pt}_{40}\text{Cu}_{22}$  NWs.



**Figure S6.** Polarization curves of the FePtNi and FePt NRs with different initial compositions in  $\text{O}_2$ -saturated 0.1 M  $\text{HClO}_4$  at 295 K.