

### Supplementary information

#### **Synthesis of Small Ni-core-Au-shell Catalytic Nanoparticles on TiO<sub>2</sub> by Galvanic Replacement Reaction**

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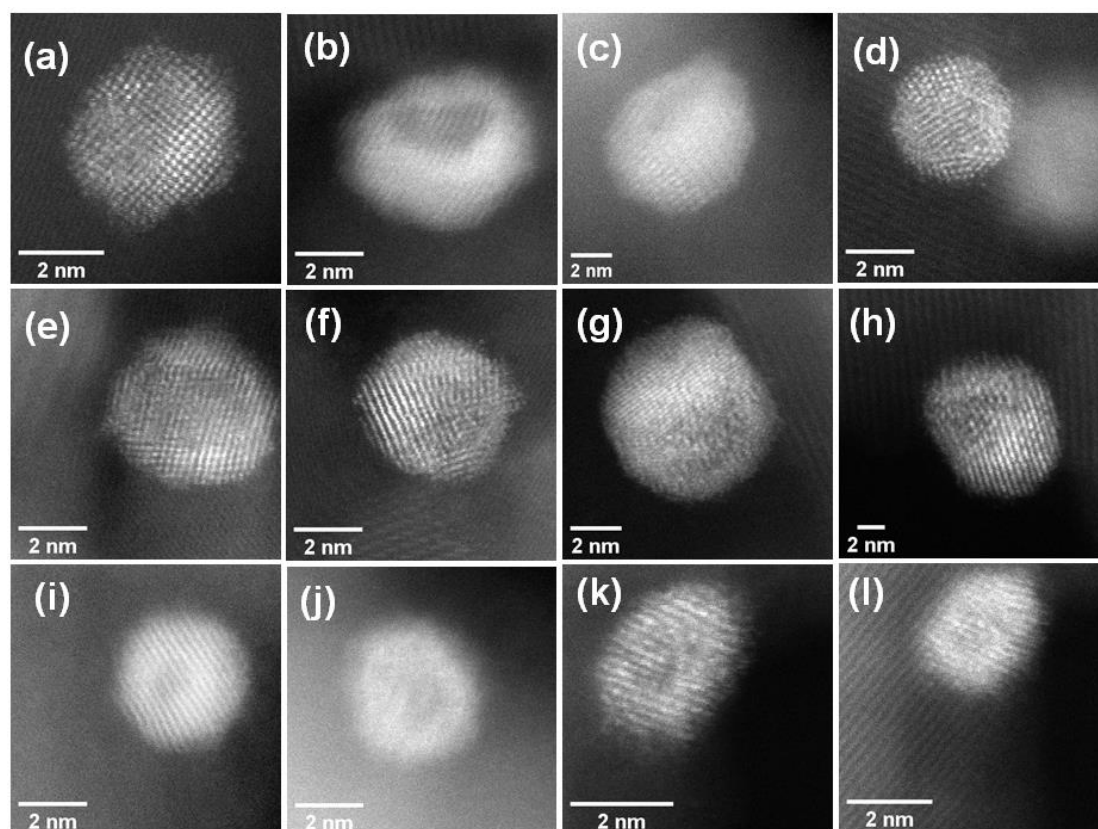
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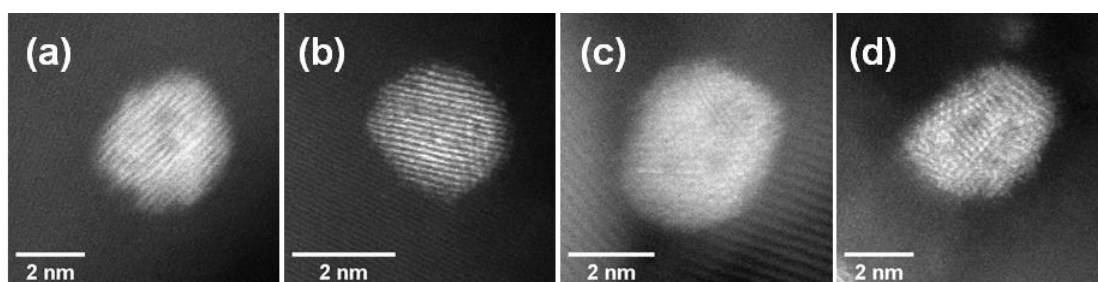
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**Figure SI-1** HAADF-STEM images, showing centered and off-centered core-shell nanoparticles, from Au(10)Ni/TiO<sub>2</sub> before (a-c) and after reduction (d-h); and Au(30)Ni/TiO<sub>2</sub> samples before (i) and after (j-l) reduction.



**Figure SI-2** HAADF-STEM images, showing multi-cored nanoparticles, from Au(10)Ni/TiO<sub>2</sub> (a) as prepared; (b, c) reduced Au(10)Ni/TiO<sub>2</sub>; and (d) reduced Au(30)Ni/TiO<sub>2</sub> samples.

**SI-3:** Among all the particles that we examined by electron microscopy, we also observed very few particles in AuNi/TiO<sub>2</sub> samples, showing no difference of contrast suggesting the formation of apparently pure Au nanoparticles (see **Figure SI-3**). However, one could not exclude the presence of a small percentage of nickel dissolved or segregated inside them [8].

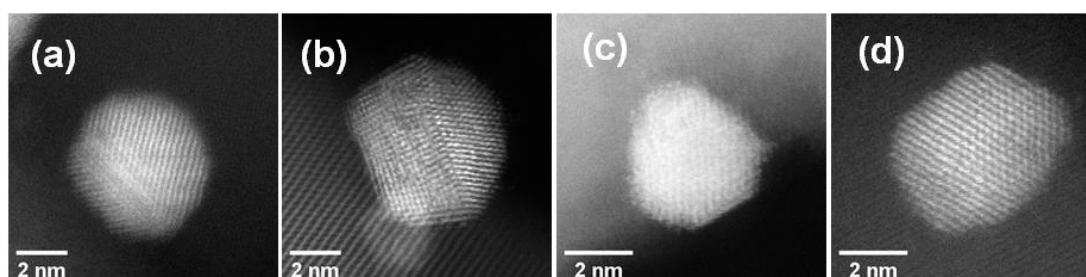
However, to investigate whether gold particles could form as the result of mere Au adsorption on TiO<sub>2</sub>, we performed the following experiment: A gold solution (6.17  $\mu\text{mol}$  of Au, i.e., the equivalent Au loading of around 1 wt% Au, see Table 1) was added to TiO<sub>2</sub> first treated in the same conditions as for DPU but in the absence of Ni precursor. The suspension of TiO<sub>2</sub> in the gold solution had a pH  $\sim 3$ , i.e., a pH lower than  $\text{PZC}_{\text{TiO}_2}$ , so the pH condition allowed  $\text{AuCl}_4^-$  to interact with the positively charged TiO<sub>2</sub> surface. After washing with water and drying at RT under vacuum, the gold loadings were 0.9 wt%. The sample was colored after drying, indicating that at least part of gold was already reduced, probably because of TiO<sub>2</sub> (photoactive), and TEM showed the presence of both small (around 2-3 nm) and larger NPs (around 5-7 nm).

However, the following facts observed in the Au-Ni samples:

(i) the large majority of the particles observed by TEM are bimetallic (and the Au shells formed on the Ni NPs are often much thicker than expected as already mentioned on p. 14 and discussed on p. 18),

(ii) one cannot exclude the presence of small percentage on nickel in the seemingly pure Au nanoparticles

(iii) Table 1 shows that the Ni loading in AuNi/TiO<sub>2</sub> decreased when the Au loading increased and that the resulting Au/Ni atomic ratios corresponded to those expected according to Equation 2, are an indication that the mechanism of GRR is predominant compared to Au adsorption.



**Figure SI-3** HAADF-STEM images of nanoparticles, from Au(10)Ni/TiO<sub>2</sub> (a,b) and Au(30)Ni/TiO<sub>2</sub> (c,d) samples before and after reduction. They showed no core-shell or multi-centered contrasts and are likely Au-only particles.