

Supporting Information.

The selective oxidation of methane to methanol using *in situ* generated H₂O₂ over palladium-based bimetallic catalysts.

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Table S.1. Theoretical and actual catalyst formulations, based on ICP-MS analysis of microwave-assisted aqua-regia digestion of catalytic samples.

Catalyst	Actual Au Loading / wt. %	Actual Pd Loading / wt. %	Actual X Loading (X=Pt, Cu, Ni, Mn) / wt. %
2.5wt. %Au-2.5wt. %Pd/TiO ₂	2.503	2.460	-
2.5wt. %Au-2.5wt. %Pd/ZSM-5	2.480	2.500	-
2.4wt. %Au-2.4wt. %Pd- 0.2wt. %Pt/TS-1	2.410	2.380	0.197
0.66wt. %Au/TS-1	0.655	-	-
0.55wt. %Au-0.11wt. %Pd/TS-1	0.541	0.106	-
0.44wt. %Au-0.22wt. %Pd/TS-1	0.429	0.215	-
0.33wt. %Au-0.33wt. %Pd/TS-1	0.330	0.325	-
0.11 wt. % Au-0.55wt. %Pd/TS-1	0.118	0.546	-
0.66wt. %Pd/TS-1	-	0.648	-
0.33wt. %Cu-0.33wt. %Pd/TS-1	-	0.312	0.327
0.33wt. %Ni-0.33wt. %Pd/TS-1	-	0.315	0.319
0.33wt. %Mn-0.33wt. %Pd/TS-1	-	0.325	0.31

Table S.2. Stability of the 0.33%Au-0.33%Pd/TS-1 catalyst in the oxidation of methane via *in situ* H₂O₂ synthesis.

Reaction number	Metal Leached / %	
	Au	Pd
1	0	1.9
2	0	0.2
3	0	0

Note: The actual loading of the AuPd/TS-1 catalyst was determined as 0.33%Au-0.325%Pd/TS-1 via microwave-assisted aqua regia digestion of the as-prepared material (Table S.1). Metal leaching was determined by ICP-MS analysis of post-reaction solutions.

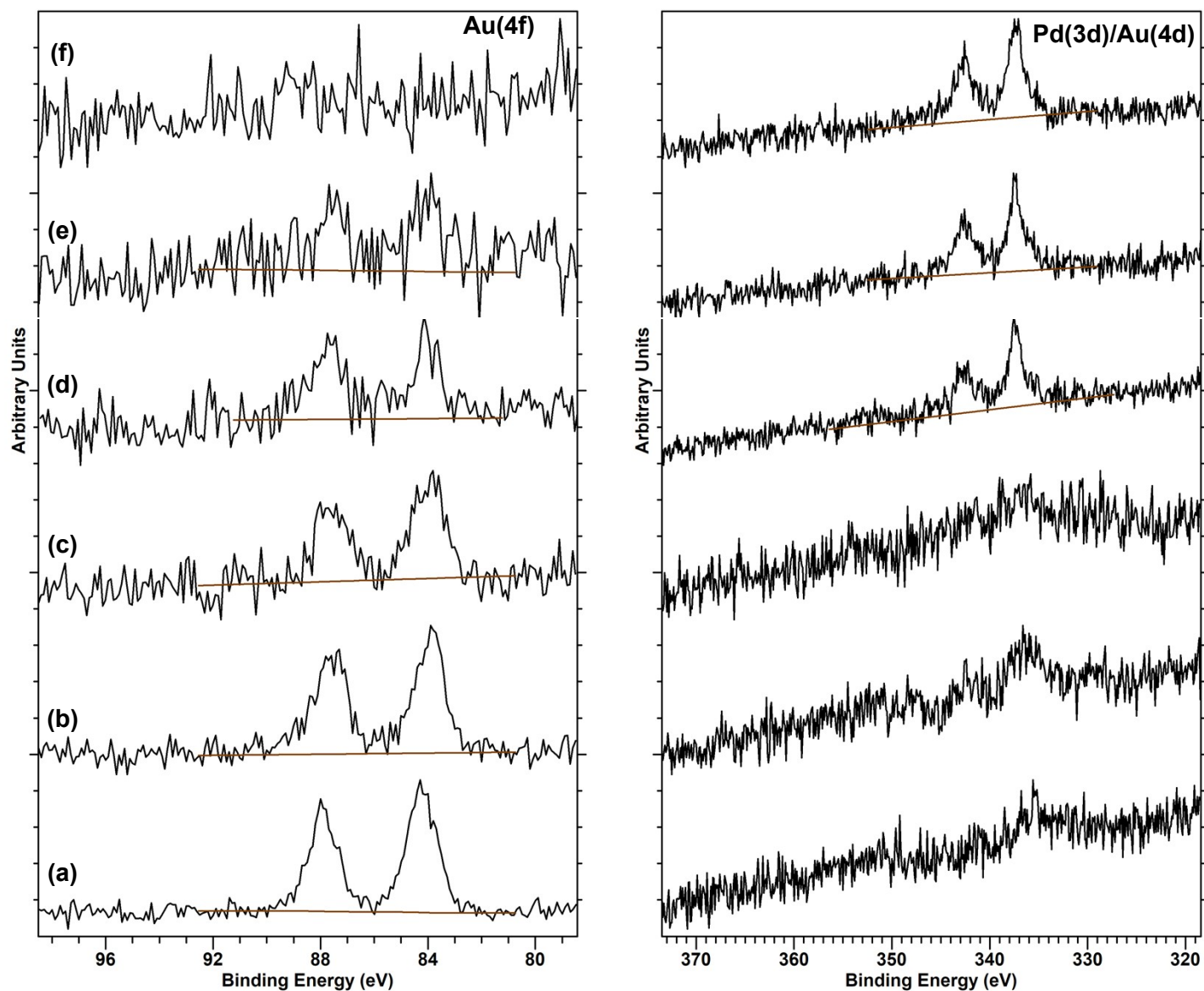


Figure S1. XPS spectra of Au (4f) and Pd (3d)/Au (4d) regions of the 0.66%PdAu/TS-1 catalysts as a function of Pd: Au ratio. **(a)** 0.66wt.%Au/TS-1, **(b)** 0.55wt.%Au-0.11wt.%Pd/TS-1, **(c)** 0.44wt.%Au-0.22wt.%Pd/TS-1, **(d)** 0.33wt.%Au-0.33wt.%Pd/TS-1, **(e)** 0.11wt.%Au-0.55wt.%Pd/TS-1 and **(f)** 0.66 wt.%Pd/TS-1. **Note:** Catalysts exposed to an oxidative heat treatment (static air, 400 °C, 3h, 10 °Cmin⁻¹).

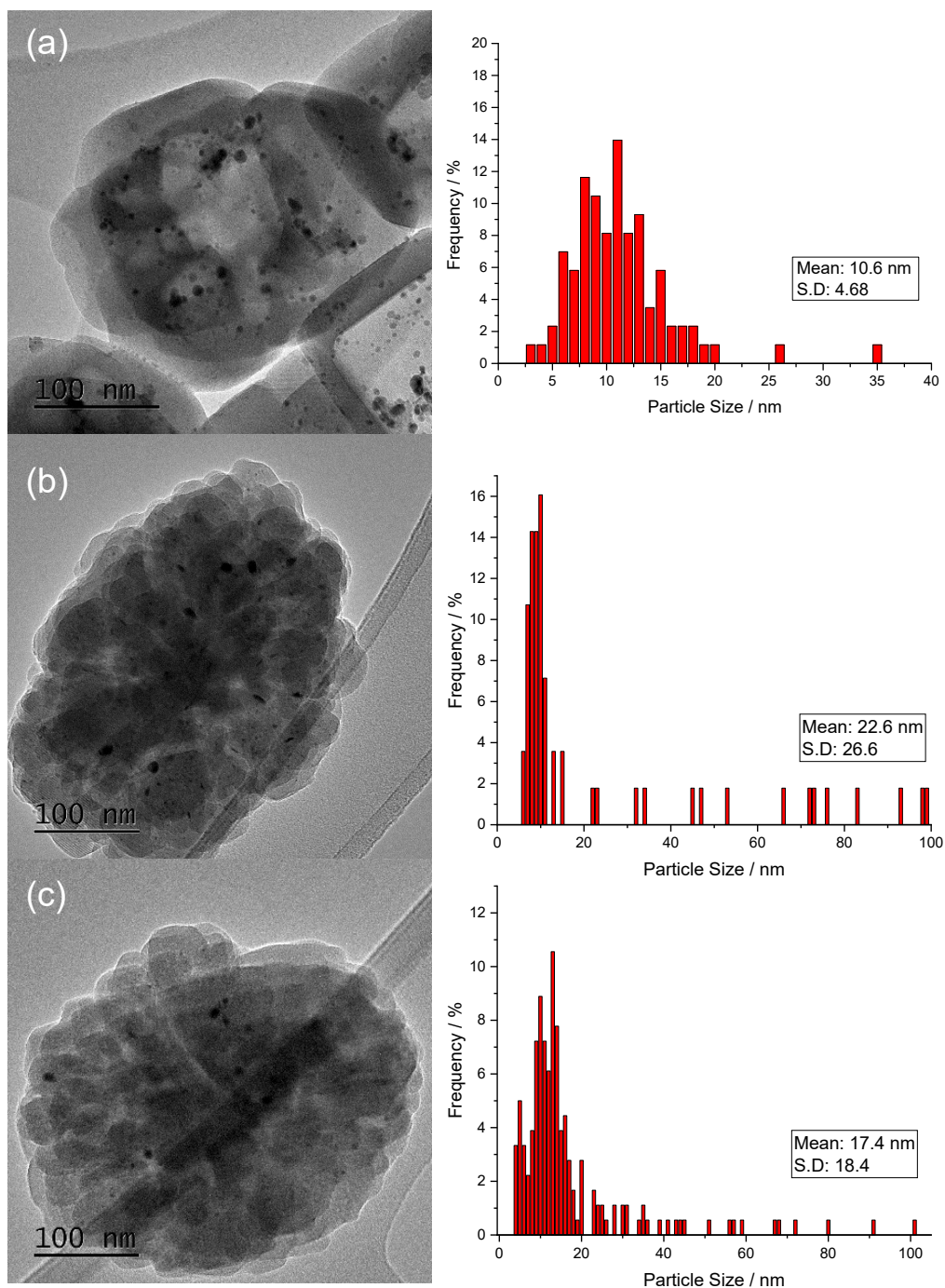


Figure S.2.A. Transmission electron microscopy of 0.66wt.%AuPd/TS-1 catalysts as a function of Au: Pd ratio. **(a)** 0.66wt.%Au/TS-1, **(b)** 0.55wt.%Au-0.11wt.%Pd/TS-1 and **(c)** 0.44wt.%Au-0.22wt.%Pd/TS-1. **Note:** Catalysts exposed to an oxidative heat treatment (static air, 400 °C, 3h, 10 °Cmin⁻¹).

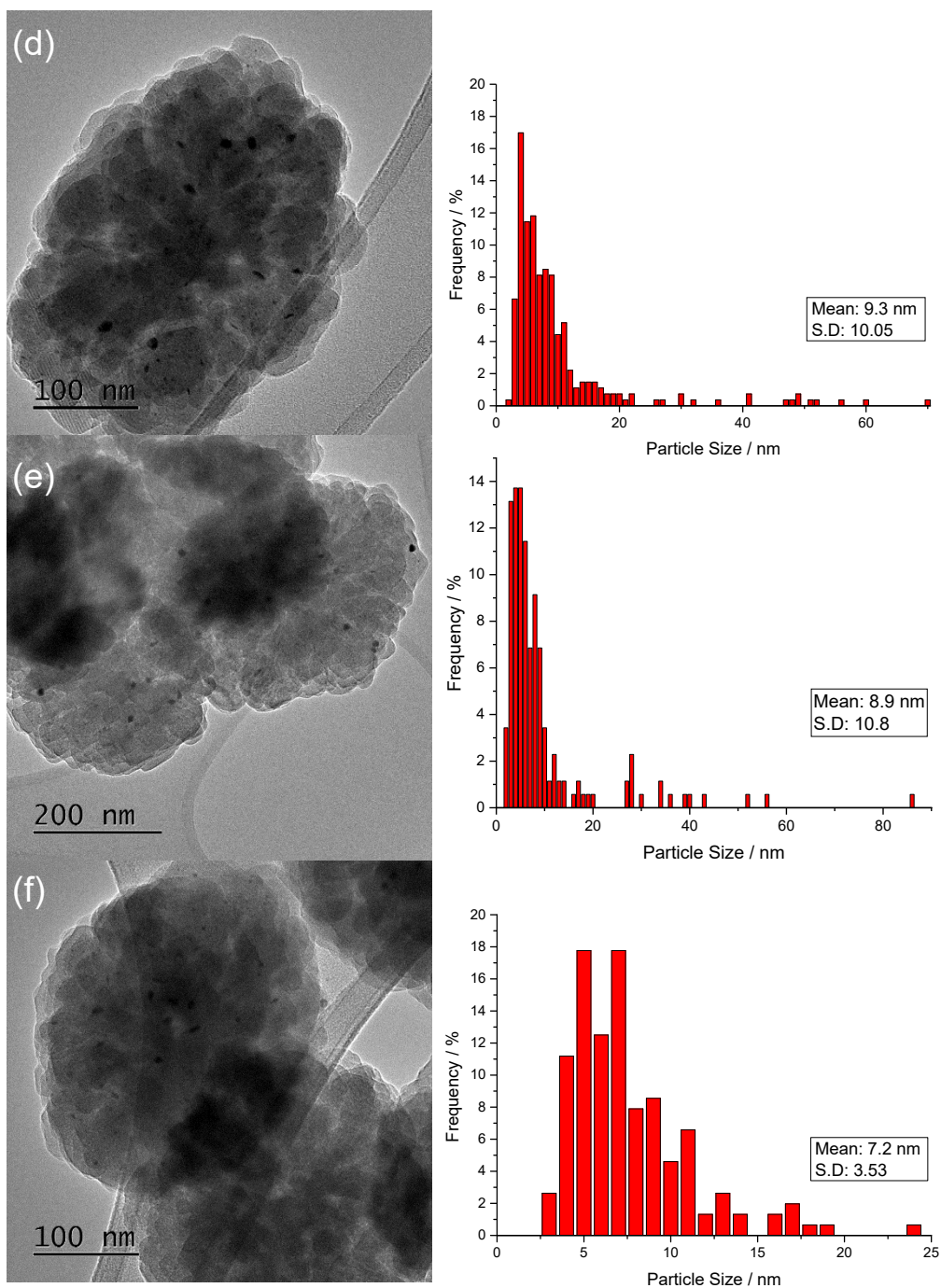


Figure S.2.B Transmission electron microscopy of 0.66wt.%AuPd/TS-1 catalysts as a function of Au: Pd ratio. **(d)** 0.33wt.%Au-0.33wt.%Pd/TS-1, **(e)** 0.11wt.%Au-0.55wt.%Pd/TS-1 and **(f)** 0.66wt.%Pd/TS-1. **Note:** Catalysts exposed to an oxidative heat treatment (static air, 400 °C, 3h, 10 °Cmin⁻¹).

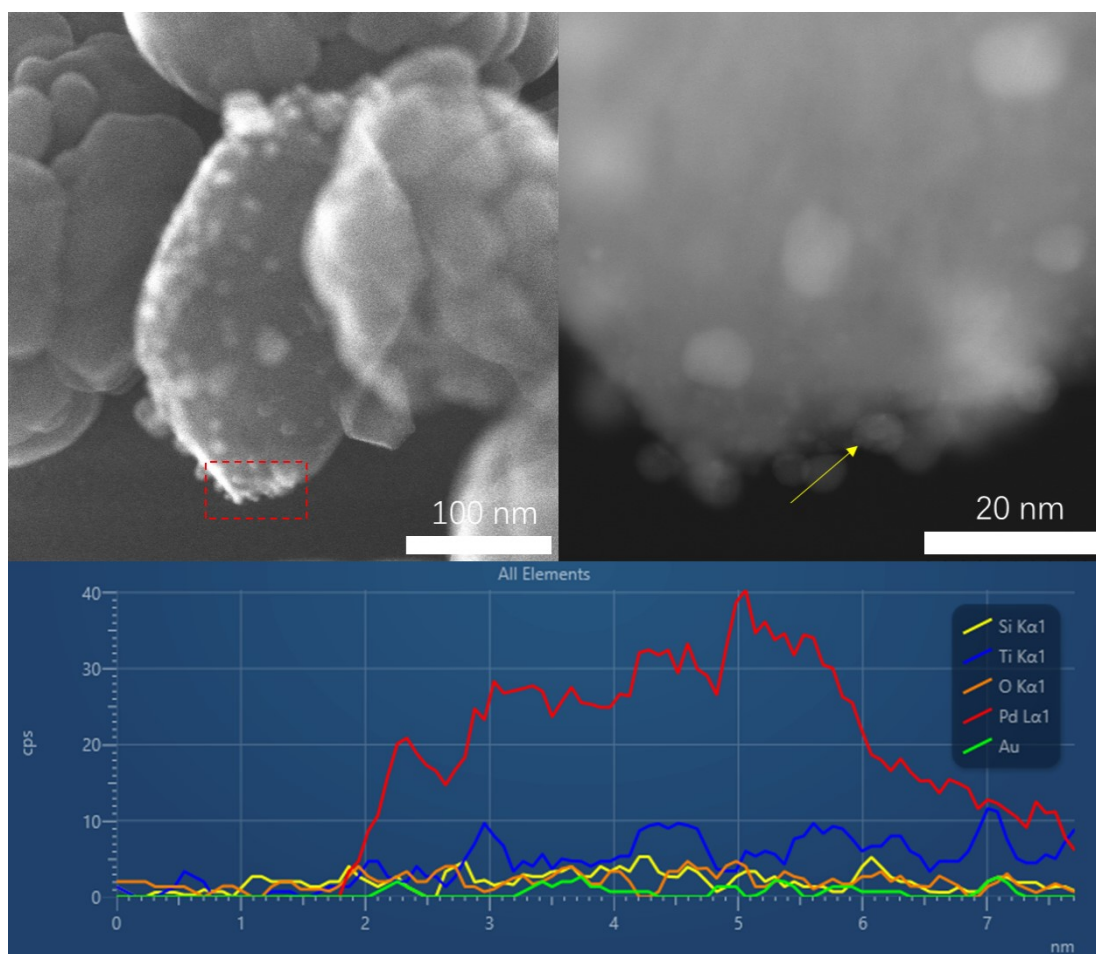


Figure S.3. HAADF-STEM image of the 0.33wt.%Au-0.33wt.%Pd/TS-1 catalyst and corresponding XEDS line scans of the smaller particles showing the presence of Pd (red trace) and highlighting the absence of Au (green trace).

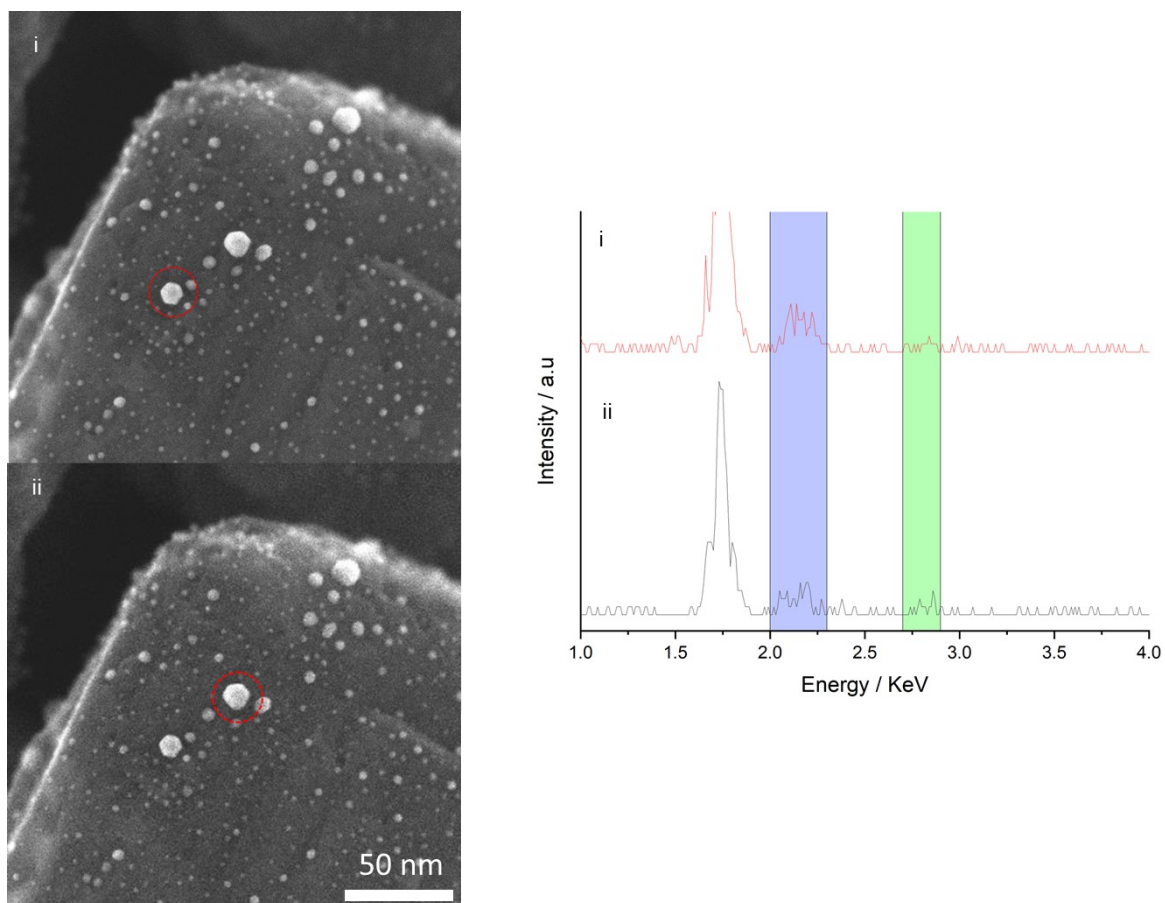


Figure S.4. Secondary electron (SE in STEM) imaging corresponding XEDS analysis (Au ($M\alpha$) and Pd ($L\alpha$) centred at 2.12 and 2.84 KeV respectively) of the indicated nanoparticle, present on the 0.33wt.%Au-0.33wt.%Pd/TS-1 catalyst, demonstrating the presence of large AuPd nanoalloys.