

## Supplementary Information

### Controlling Product Selectivity with Nanoparticle Composition in Tandem Chemo-Biocatalytic Styrene Oxidation.

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**Table S1.** Catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis and its subsequent degradation under high pressure batch conditions.

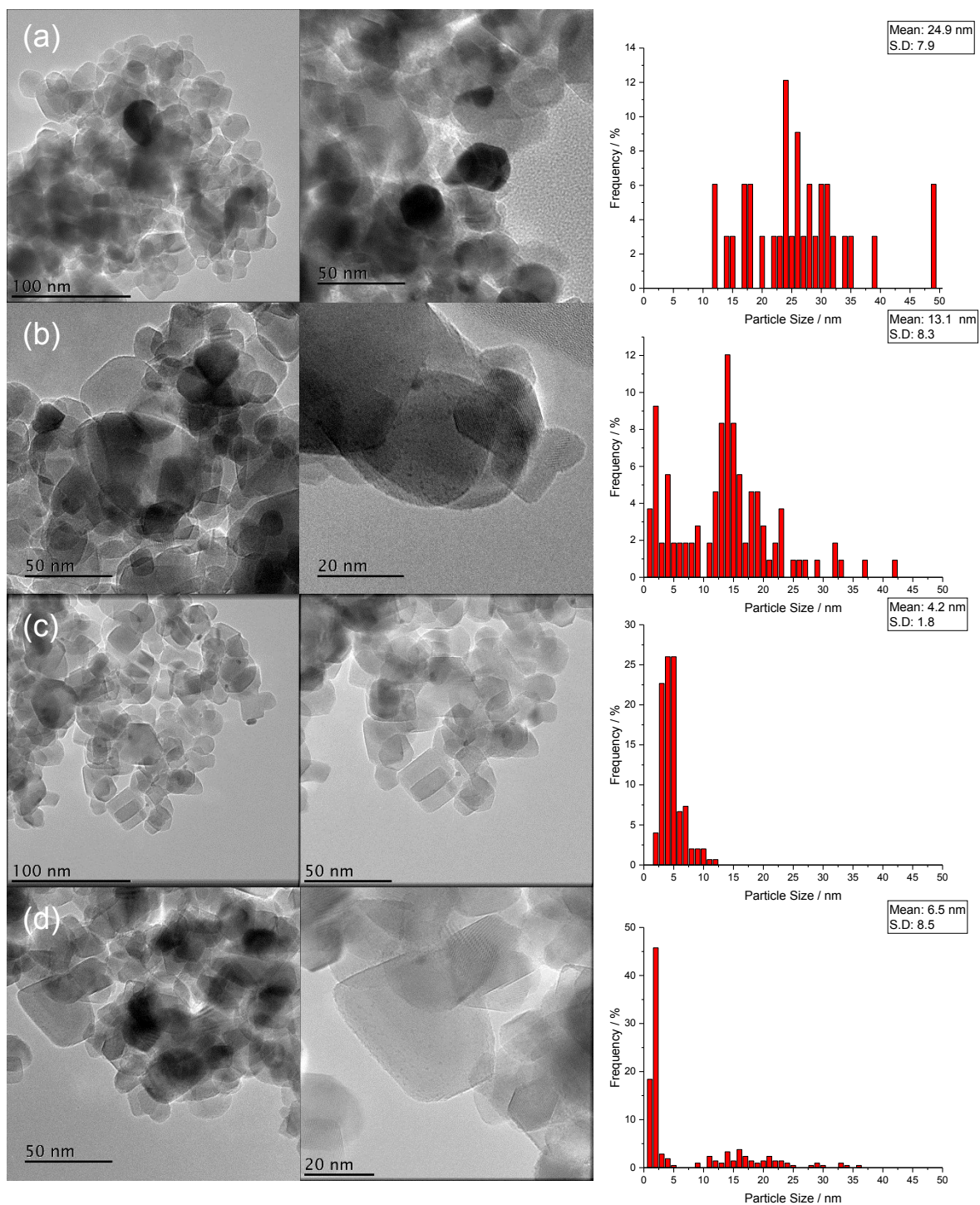
Catalyst	Productivity / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Degradation / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>
Au <sub>100</sub> /TiO <sub>2</sub>	1	9
Au <sub>75</sub> Pd <sub>25</sub> /TiO <sub>2</sub>	32	70
Au <sub>50</sub> Pd <sub>50</sub> /TiO <sub>2</sub>	93	227
Au <sub>25</sub> Pd <sub>75</sub> /TiO <sub>2</sub>	87	247
Pd <sub>100</sub> /TiO <sub>2</sub>	26	269
Lindlar's Catalyst	12	994

#### **Direct synthesis of H<sub>2</sub>O<sub>2</sub> using high-pressure batch autoclave.**

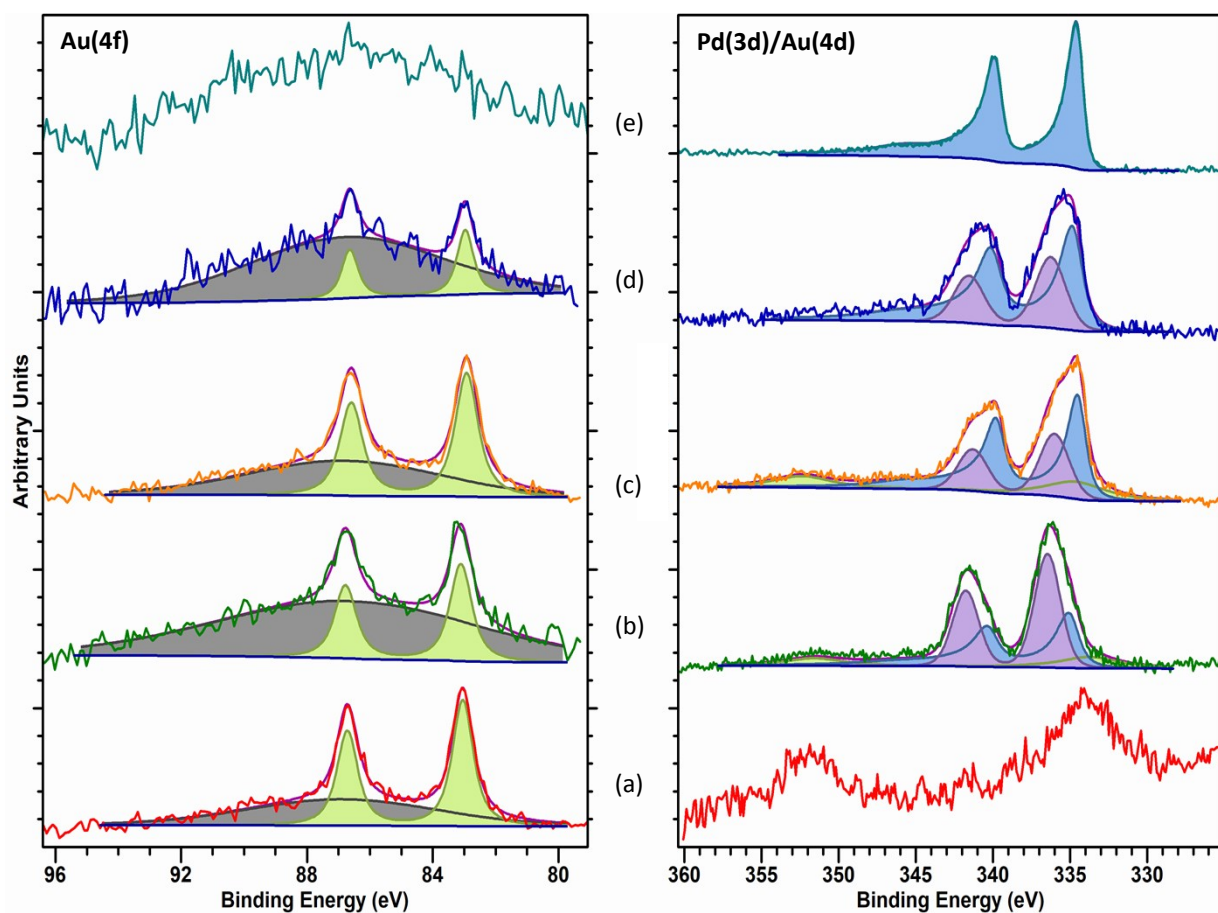
H<sub>2</sub>O<sub>2</sub> synthesis was evaluated using a Parr Instruments stainless steel autoclave with a nominal volume of 100 mL and a maximum working pressure of 14 MPa using procedures outlined in Santos et al.<sup>18</sup>. To test each catalyst for H<sub>2</sub>O<sub>2</sub> synthesis, the autoclave was charged with catalyst (0.01 g) and solvent (5.6 g MeOH (HPLC grade) and 2.9 g H<sub>2</sub>O (HPLC grade)). The charged autoclave was then purged three times with 5% H<sub>2</sub> / CO<sub>2</sub> (7 bar) before filling with 5% H<sub>2</sub> / CO<sub>2</sub> (29 bar), followed by the addition of 25 % O<sub>2</sub> / CO<sub>2</sub> (11 bar). The reaction mixture was cooled to a temperature of 2 °C prior to stirring (1200 rpm) for 0.5 h. H<sub>2</sub>O<sub>2</sub> productivity was determined by titrating aliquots of the final solution after reaction with acidified Ce(SO<sub>4</sub>)<sub>2</sub> (0.01 M) in the presence of ferroin indicator.

#### **Degradation of H<sub>2</sub>O<sub>2</sub> using high-pressure batch autoclave.**

Catalytic activity towards H<sub>2</sub>O<sub>2</sub> degradation was determined in a manner similar to that used to evaluate catalytic performance towards H<sub>2</sub>O<sub>2</sub> synthesis. The autoclave was charged with 0.01 g catalysts and 4 wt. % H<sub>2</sub>O<sub>2</sub> solution composed of MeOH (5.6 g), H<sub>2</sub>O<sub>2</sub> (50 wt. % 0.69 g) HPLC standard H<sub>2</sub>O (2.21 g). Before every reaction, 2 aliquots of 0.05 g were removed and titrated with acidified Ce(SO<sub>4</sub>)<sub>2</sub> solution using ferroin as an indicator to confirm the H<sub>2</sub>O<sub>2</sub> concentration. The autoclave was pressurized with 5 % H<sub>2</sub> / CO<sub>2</sub> (29 bar) and reaction temperature subsequently reduced to 2 °C. Once at the desired temperature the reactor was stirred (1200 rpm) for 0.5 h. After the reaction was complete the catalyst was removed from the reaction solvents via filtration and as previously two aliquots of post reaction solution (0.05 g) were titrated against the acidified Ce(SO<sub>4</sub>)<sub>2</sub> solution using ferroin as an indicator. The degradation activity is reported as mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>.



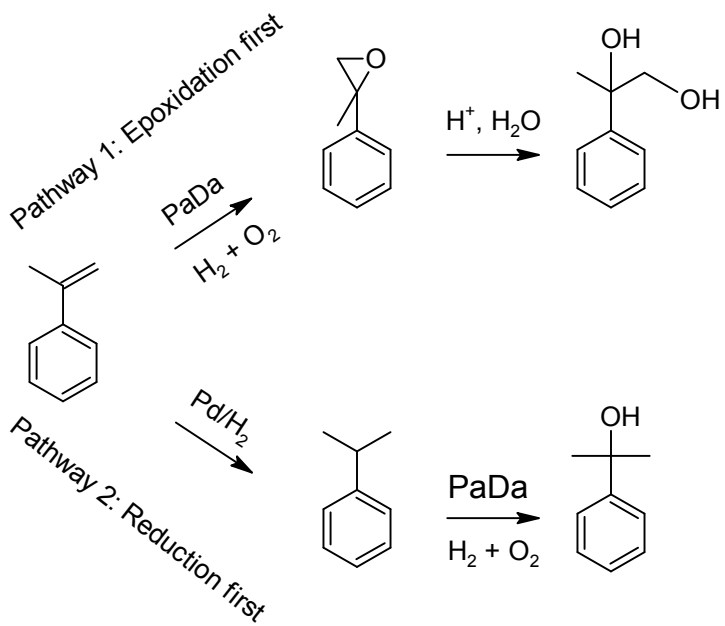
**Figure S1:** Transmission electron microscopy of (a) Au<sub>100</sub>/TiO<sub>2</sub>, (b) Au<sub>75</sub>Pd<sub>25</sub>/TiO<sub>2</sub>, (c) Au<sub>50</sub>Pd<sub>50</sub>/TiO<sub>2</sub> and (d) Au<sub>25</sub>Pd<sub>75</sub>/TiO<sub>2</sub> catalysts prepared by modified impregnation H<sub>2</sub>/Ar, 400° C, 4 h, ramp rate = 10 °C min<sup>-1</sup>).



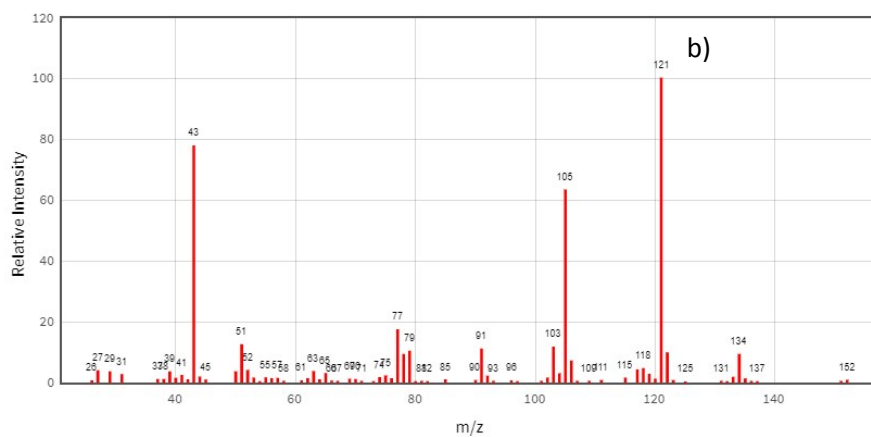
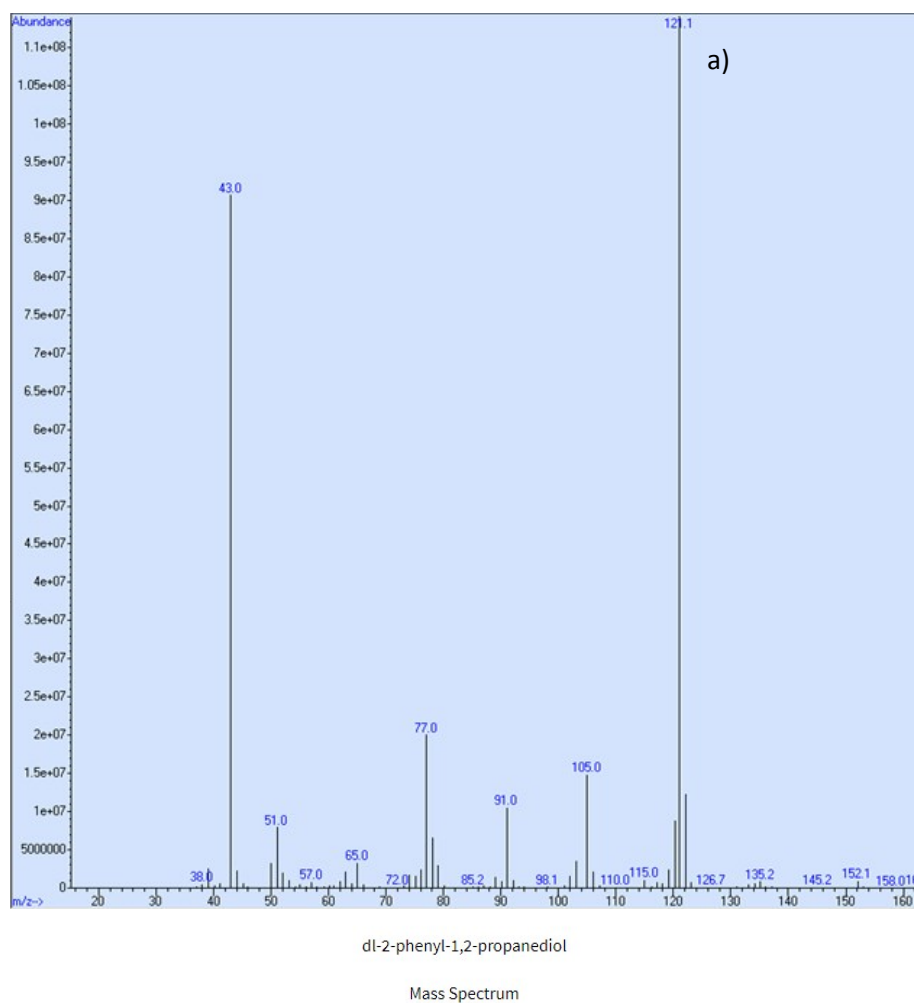
**Figure S.2.** Surface atomic compositions of as-prepared 1%AuPd/TiO<sub>2</sub> catalysts as determined by XPS using Au (4f) and Pd (3d) regions. (a) Au<sub>100</sub>/TiO<sub>2</sub>, (b) Au<sub>75</sub>Pd<sub>25</sub>/TiO<sub>2</sub>, (c) Au<sub>50</sub>Pd<sub>50</sub>/TiO<sub>2</sub> (d) Au<sub>25</sub>Pd<sub>75</sub>/TiO<sub>2</sub>, (e) Pd<sub>100</sub>/TiO<sub>2</sub>. **Key:** Au<sup>0</sup> (Green), Pd<sup>0</sup> (Blue), Pd<sup>2+</sup> (Purple), Loss of structure (Grey).

**Table S.2.** Surface atomic composition of 1%AuPd/TiO<sub>2</sub> catalysts as determined via XPS, using Pd (3d) and Au (4f) regions.

Catalyst	Pd <sup>2+</sup> / Pd <sup>0</sup>	(Pd <sup>2+</sup> + Pd <sup>0</sup> ) / Au <sup>0</sup>	Pd <sup>0</sup> /Au <sup>0</sup>
1%Au/TiO <sub>2</sub>	-	-	-
0.75%Au-0.25%Pd/TiO <sub>2</sub>	1.39	7.0	3.05
0.5%Au-0.5%Pd/TiO <sub>2</sub>	0.55	4.78	2.92
0.25%Au-0.75%Pd/TiO <sub>2</sub>	0.53	19.5	17.43
1%Pd/TiO <sub>2</sub>	All Pd <sup>0</sup>	-	-



**Scheme S1:** Divergent Reaction Pathways Obtained when Employing  $\alpha$ -Methylstyrene as Substrate



**Figure S3:** Comparison of experimentally obtained (a) and NIST database<sup>1</sup> reference(b) GC-MS spectra for the major product formed during  $\alpha$ -methylstyrene tandem conversion.

## References

1. NIST/NIH/EPA Mass Spectral Library, Standard Reference Database 1, NIST 11. Standard Reference Data Program, National Institute of Standards and Technology: Gaithersburg, MD, USA, 2011