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# AuPd/NiO as effective catalyst for the base -free oxidation of HMF at mild reaction conditions

Danilo Bonincontro[a], Alice Lolli[a], Alberto Villa[b], Laura Prati[b], Nikolaos Dimitratos[a], Gabriel M. Veith[c], Lidia E. Chinchilla[d], Gianluigi A. Botton[d] Fabrizio Cavani[a], Stefania Albonetti[a]

[a]Dipartimento di Chimica Industriale "Toso Montanari", Università degli Studi di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy.

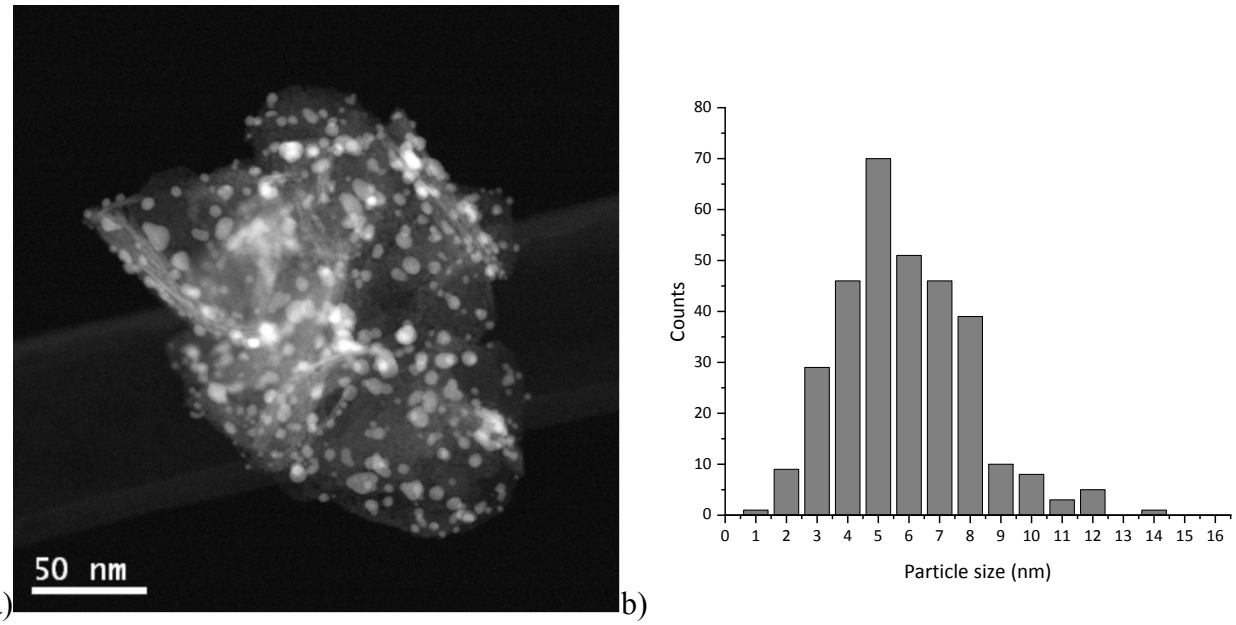
[b] Dipartimento di Chimica, Università degli Studi di Milan, Milan Italy.

[c] Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

[d] Canadian Centre of Electron Microscopy and Department of Materials Science and Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4M1, Canada.

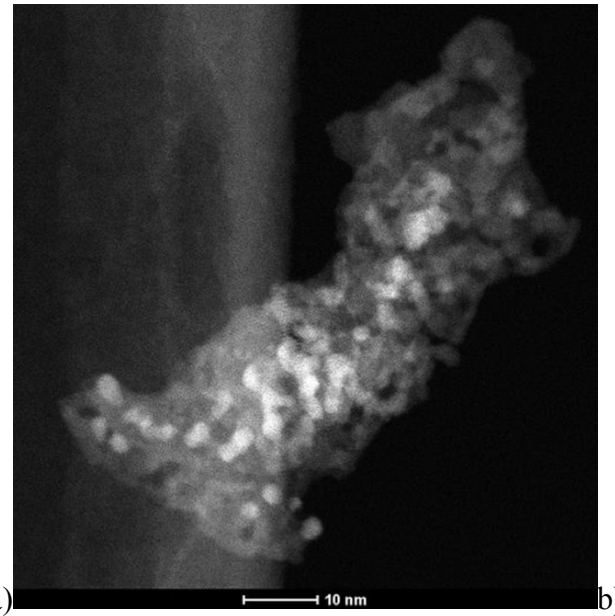
## Supporting Information

**Figure S1** a) STEM-HAADF image of fresh Au-nNiO, and b) particle size distribution.

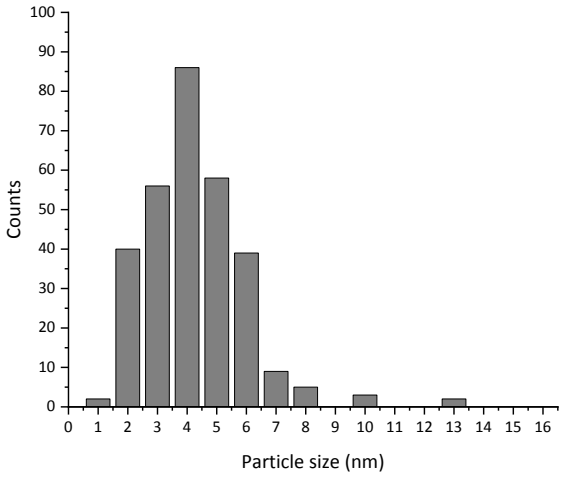



a) b)

**Figure S2** a) STEM-HAADF image of fresh Pd-nNiO and b) particle size distribution.

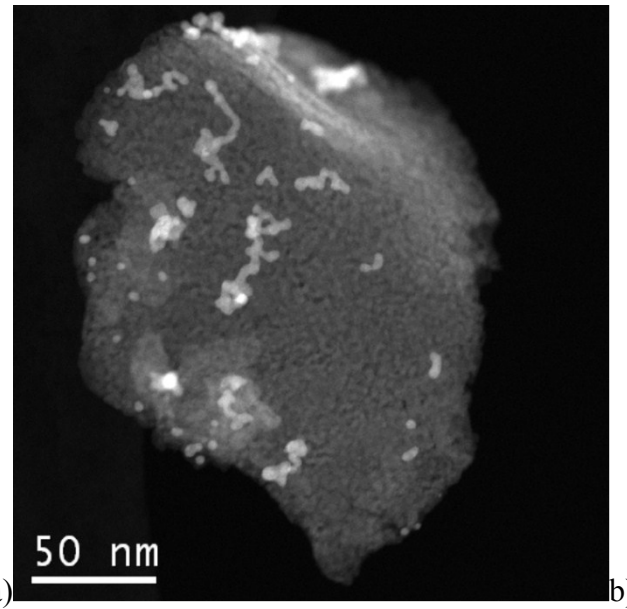



a)




b)

**Figure S3** a) STEM-HAADF image of fresh AuPd-nNiOand b) particle size distribution.

a) 

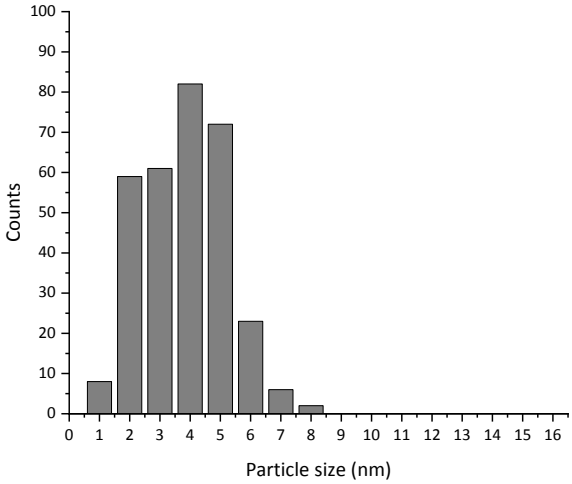
b) 

**Figure S4** Binding energy of Au4f and Pd3d, for Au-nNiO, Pd-nNiO, AuPd-nNiO samples.

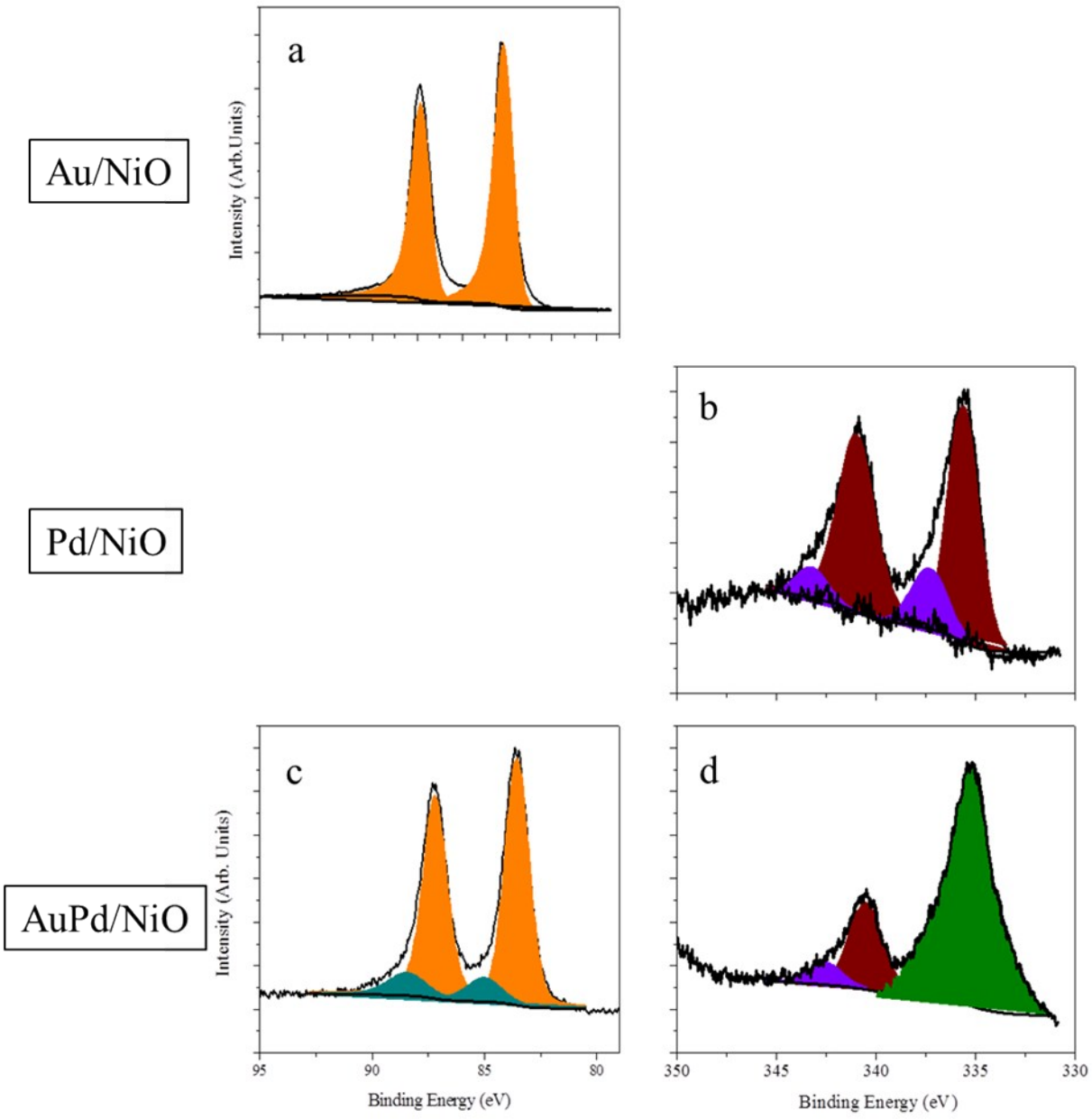


**Figure S5** O1s and Ni2p peaks for Pd and AuPd-nNiO.

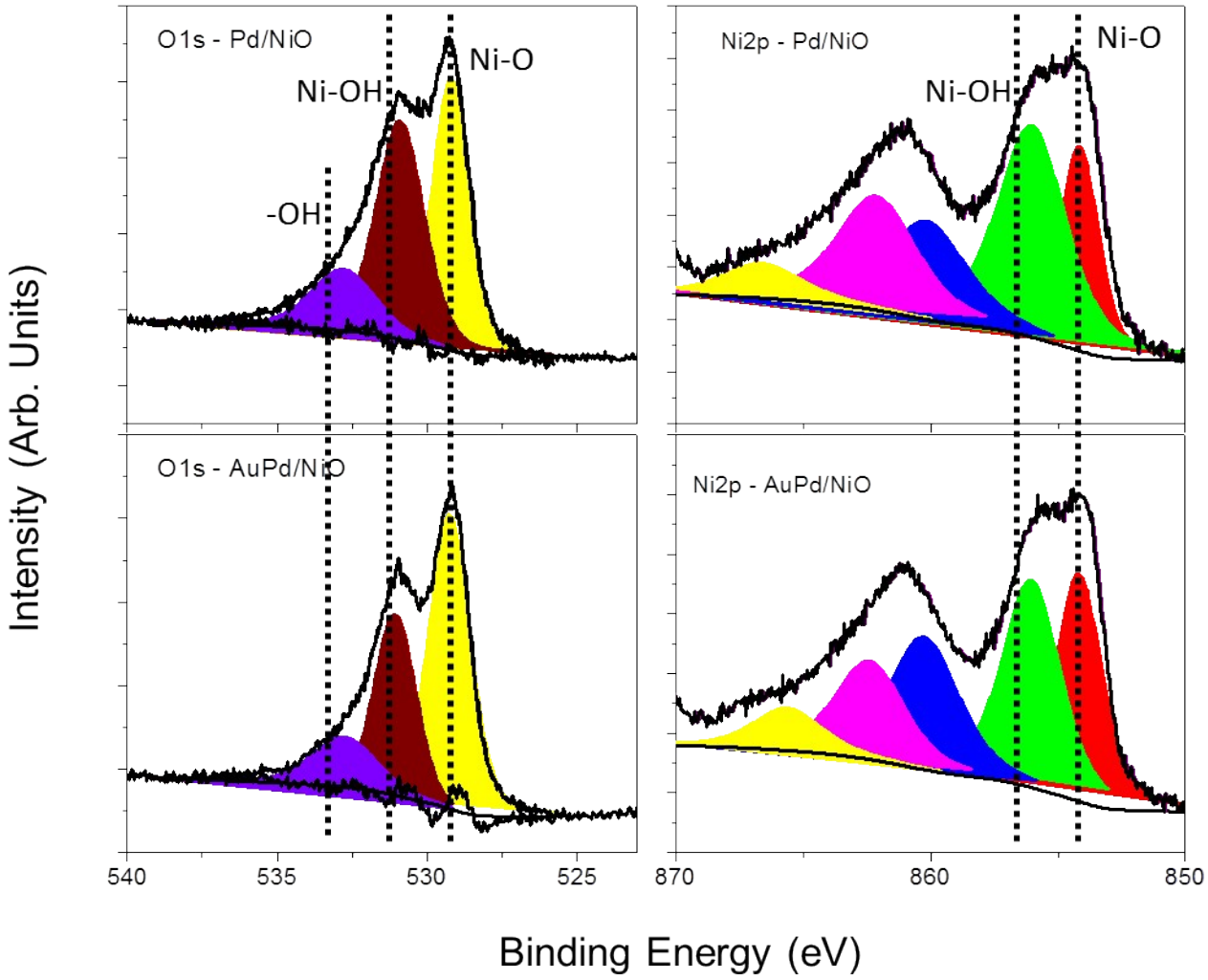


**Figure S6** Temperature and reaction time optimization for Au-nNiO catalyst.

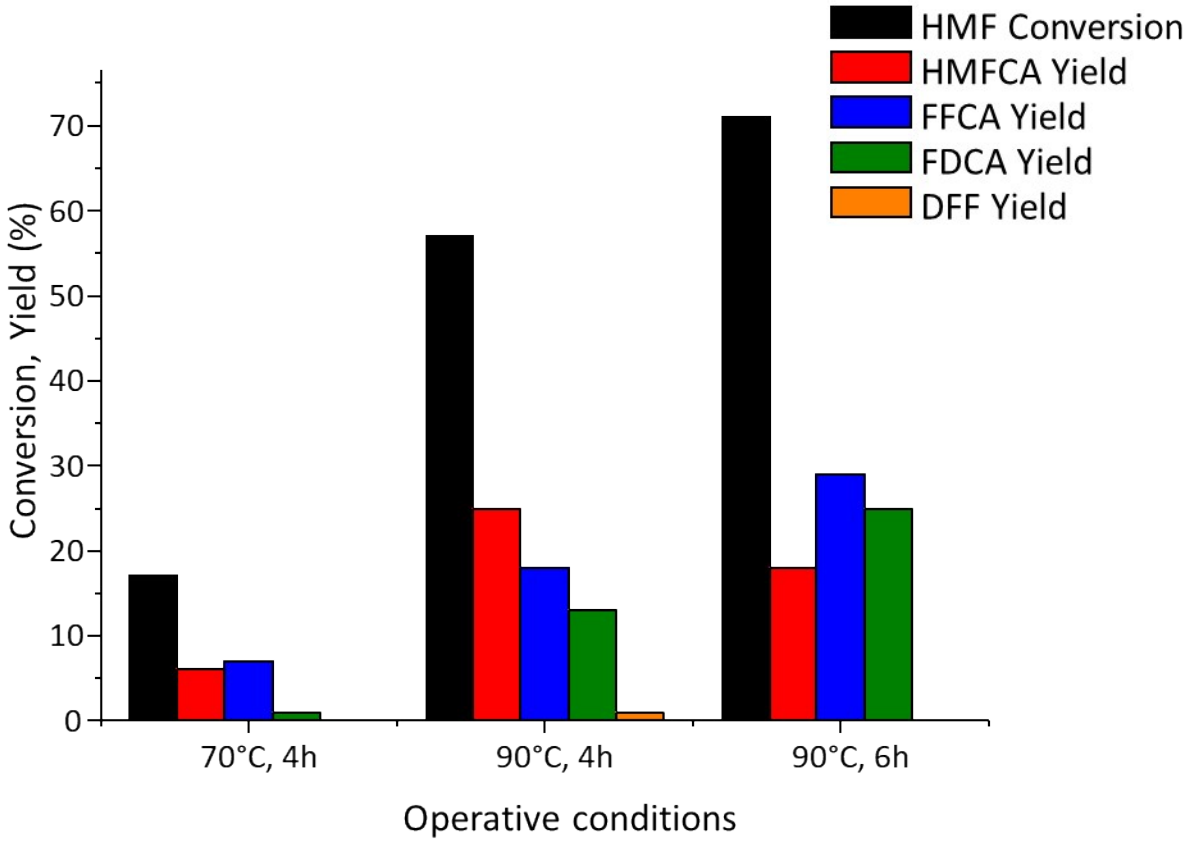
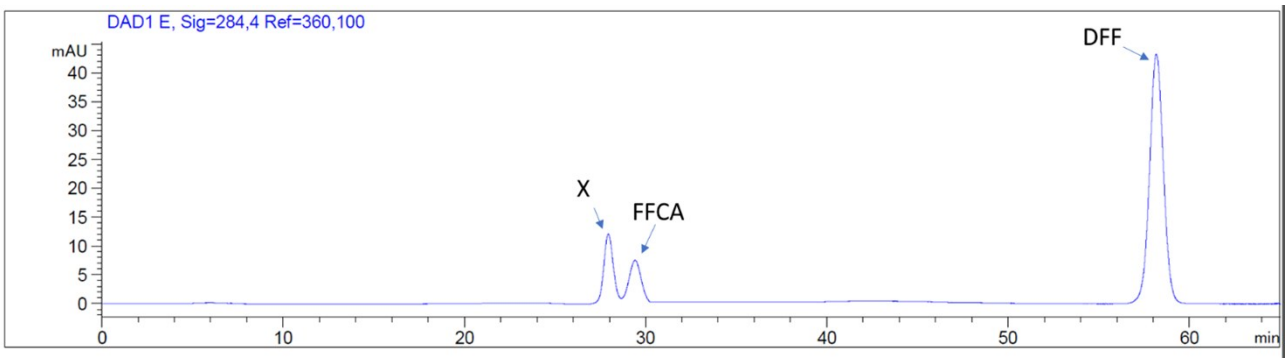


**Figure S7** Comparison of a typical solution after reaction (left, carbon balance >98%) and a reaction carried out under high pH conditions (right, carbon balance <60%).

**Figure S8** HPLC analysis of solution at the end of reaction: catalyst Au-nNiO, reactant DFF (entry 2 table 2), operative conditions: 90°C, $O_2$ pressure 10bar.




HPLC-MS undefined compound "X"

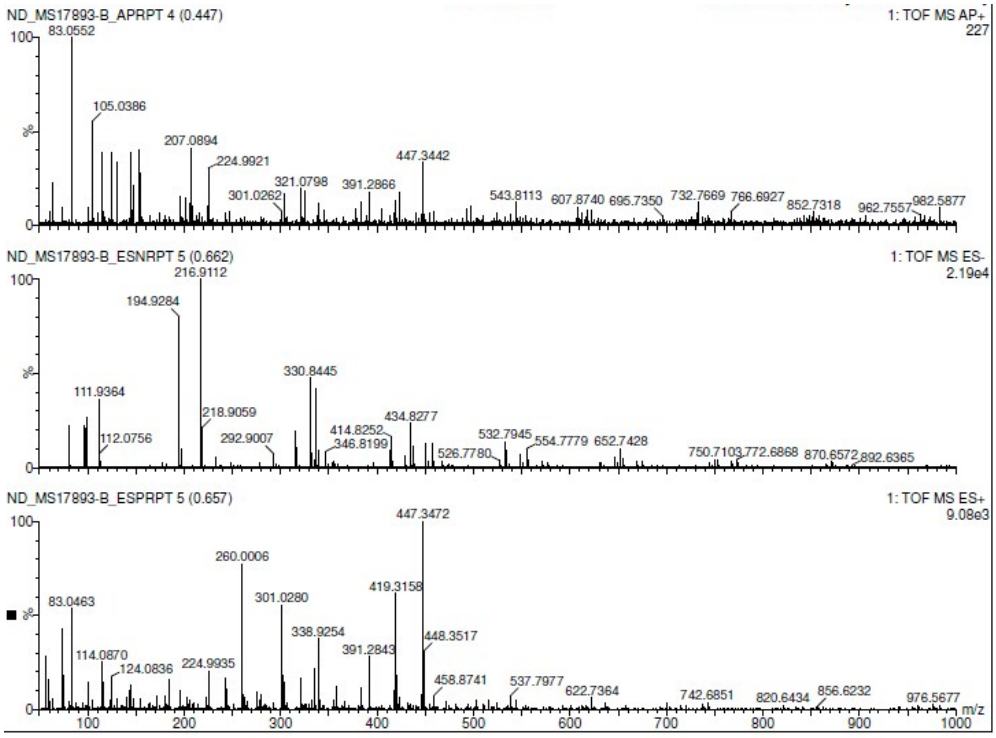
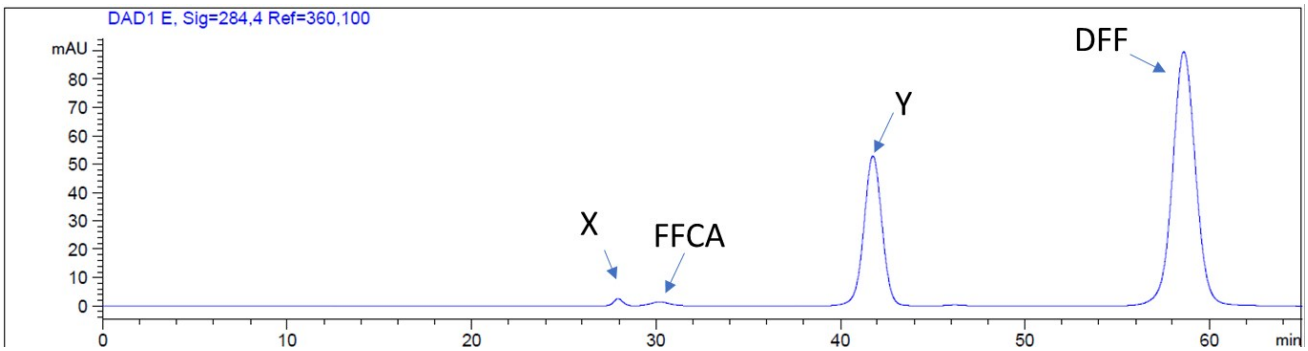


**Figure S9** HPLC analysis of solution at the end of reaction: catalyst nNiO, reactant DFF (entry 4 table 2) , operative conditions: 90°C, $O_2$ pressure 10bar.




HPLC-MS undefined compound "Y"

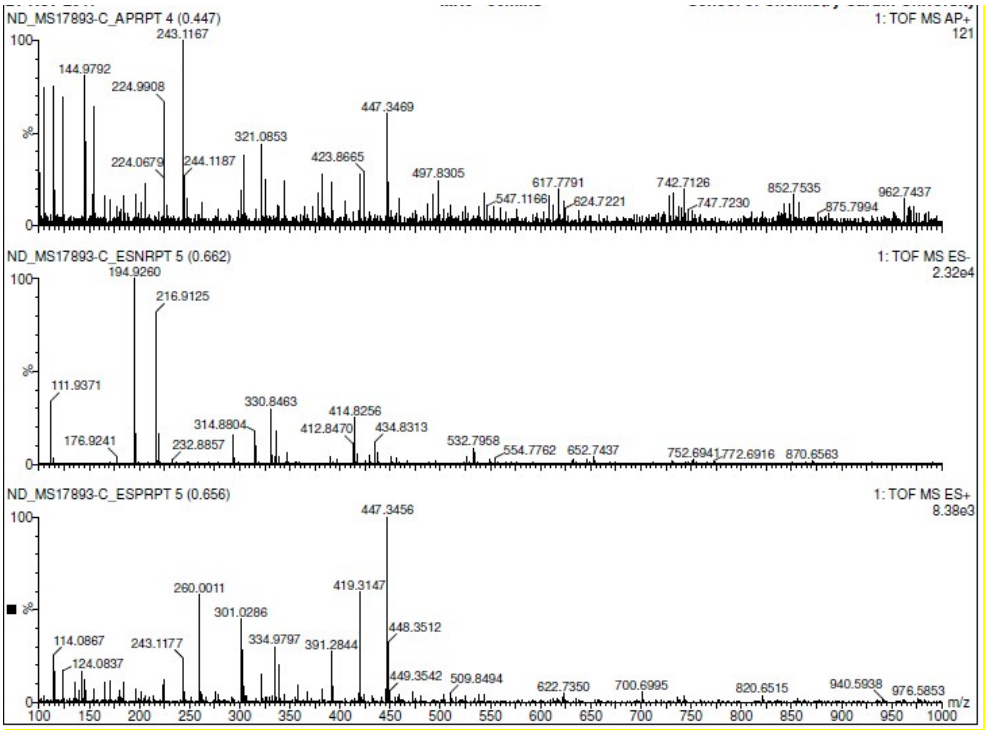
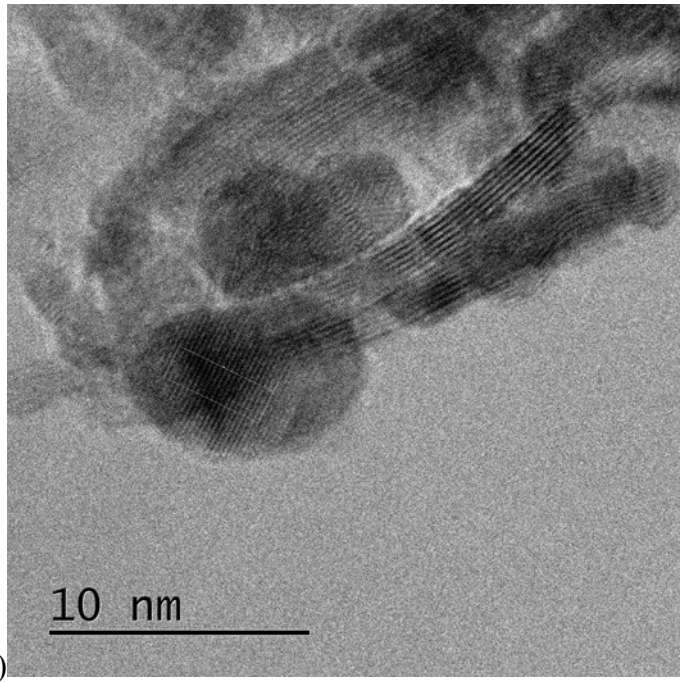
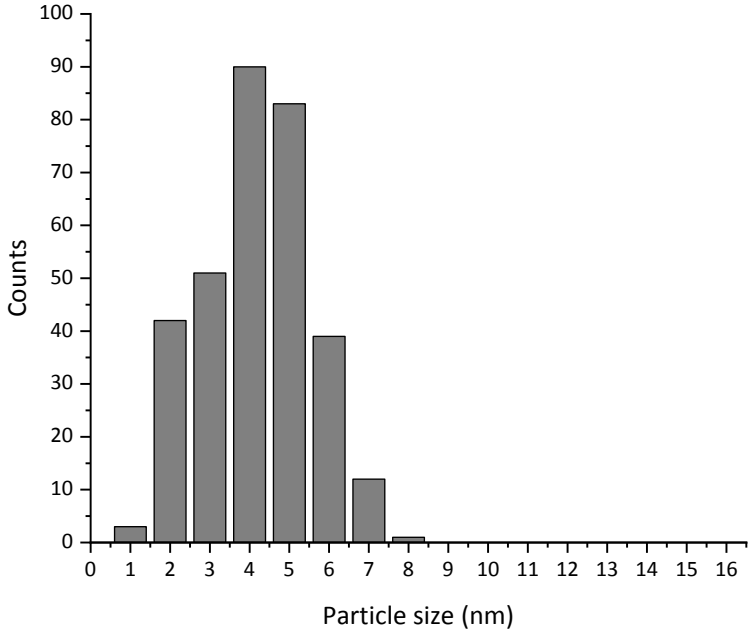


**Figure S10** a) TEM image and b) particle size distribution of used AuPd-nNiO.



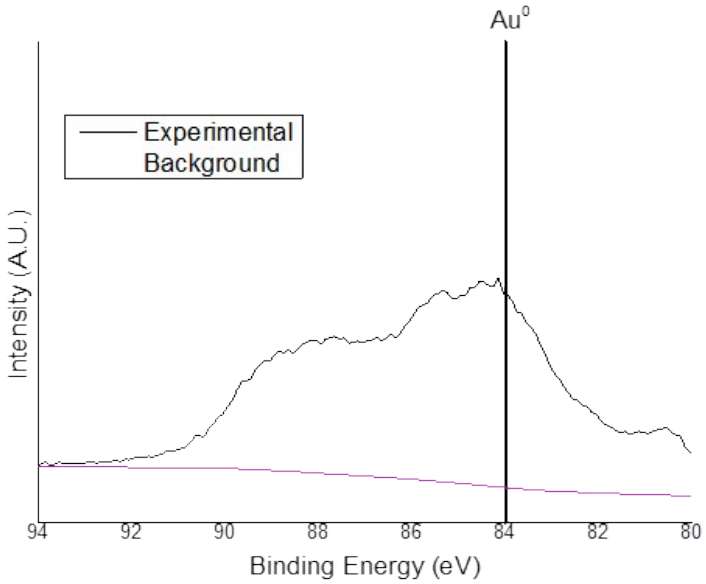

a)




b)

**Figure S11** XPS of used AuPd-nNiO a) Au4f and b) Pd3d.

a)




b)

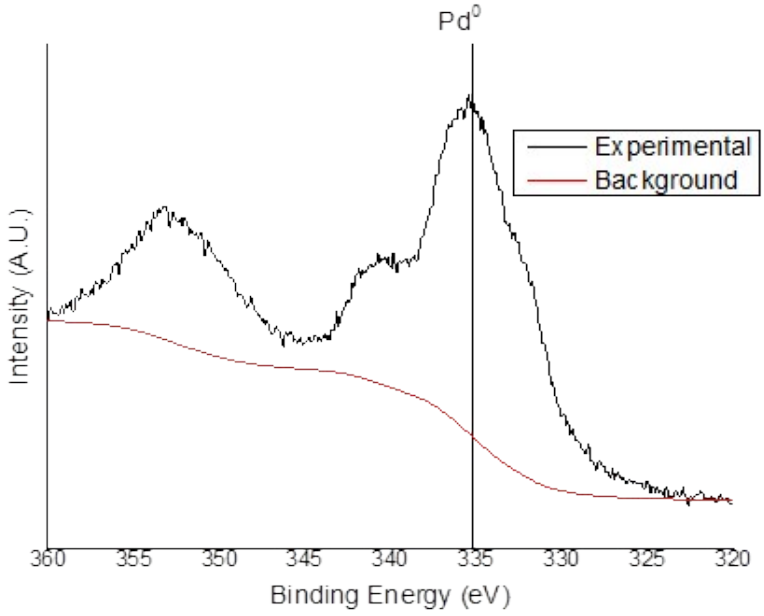


**Table S1** Comparison of different catalytic systems for base-free HMF oxidation.

| Catalyst | metal/HMF ratio | Temperature | Oxidant (pressure) | Time | FDCA yield | Reference |
|---|---|---|---|---|---|---|
| AuPd/CNT | 1/100 | 100 | O2 (5) | 12 | 94 | [1] |
| Pt/CNT | 1/100 | 100 | O2 (5) | 14 | 98 | [2] |
| Ru/C | 1/10 | 120 | O2 (2) | 10 | 88 | [3] |
| Au/HT | 1/40 | 95 | O2 (flow) | 7 | >99 | [4] |
| AuPd/LDH | 1/50 | 100 | O2 (5) | 6 | 84.5 | [5] |
| Ru/CTFs | 1/40 | 140 | Air (2) | 1 | 41.4 | [6] |
| $Ru/MnCo_2O_4$ | 1/33.6 | 100 | Air (24) | 10 | 99.1 | [7] |
| $Ce_{0.5}Fe_{0.15}Zr_{0.35}O_2$ | - | 160 | O2 (20) | 24 | 44.7 | [8] |
| AuPd-nNiO | 1/100 | 90 | O2 (10) | 14 | 100 | This work |

**Table S2** Catalytic behavior of Pd-nNiO and Au-nNiO under different operative conditions (HMF:metal molar ratio = 100:1, $O_2$ pressure 10 bar).

| Catalyst | Time (h) | HMF:NaOH molar ratio | HMF conversion (%) | DFF yield (%) | HMFCA yield (%) | FFCA yield (%) | FDCA yield (%) |
|---|---|---|---|---|---|---|---|
| Pd-nNiO | 15 | - | 8 | 1 | 2 | 4 | 1 |
| Pd-nNiO | 6 | - | 6 | 9 | 3 | 4 | 1 |
| Pd-nNiO | 6 | 1:2 | 77 | 0 | 13 | 4 | 1 |
| Au-nNiO | 0.5 | - | 15 | 2 | 5 | 0 | 7 |
| Au-nNiO | 0.5 | 1:2 | 72 | 0 | 36 | 6 | 1 |

**Table S3** Effect of DFF:FFCA molar ratio on Au-nNiO catalytic performances.

| Reactant | Time | DFF:FFCA molar ratio | DFF conversion | FDCA yield |
|---|---|---|---|---|
| DFF+FFCA | 2 | 2.9 | 21 | 2 |
| DFF+FFCA | 2 | 0.45 | 30 | 1 |

**Table S4** XRF analyses on AuPd-nNiO samples.

| Sample | Nominal Au/Pd molar rario | Measured Au/Pd molar ratio | Nominal metal loading (wt%) | Measured metal loading (wt%) |
|---|---|---|---|---|
| AuPd-nNiO fresh | 1.5 | 1.49 | 1.0 | 1.02 |
| AuPd-nNiO used | 1.5 | 1.45 | 1.0 | 1.03 |

References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