

## Electronic Supplementary Information

### **PdZn nanoparticle electrocatalysts synthesized by solution combustion for methanol oxidation reaction in alkaline medium**

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Table S1. Structural, electrochemical and compositional analysis on Pd and PdZn samples.

| Sample        | Crystallite size (nm) at (111) from XRD | ECSAs (cm <sup>2</sup> ) from CVs | Current density (mA mg <sup>-1</sup> ) from CVs on MOR at peak potential | Pd:Zn (atomic ratio in % from SEM) | Total content of catalyst (Wt. %) |
|---------------|---|-----------------------------------|--|------------------------------------|-----------------------------------|
| Pd/C          | 20.7                                    | 15.246                            | 511.14 (0.33)  | 100:0                              | 33.33                             |
| PdZn/C (1.75) | 13.6                                    | 9.476                             | 961.21 (-0.21)   | 39: 61                             | 33.92                             |
| PdZn/C (0.5)  | 16.9                                    | 12.462                            | 690 (0.11)   | 37: 63                             | 36.98                             |

Table S2. Summary of XPS data on Pd/C and PdZn/C.

| Sample        | Pd 3d  |        | $\Delta eV$ in 3d5/2 |
|---------------|--------|--------|----------------------|
|               | 5/2    | 3/2    |                      |
| Pd/C          | 335.34 | 340.81 | -                    |
| PdZn/C (1.75) | 335.1  | 340.46 | 0.24                 |
| PdZn/C (0.5)  | 335.22 | 340.52 | 0.12                 |

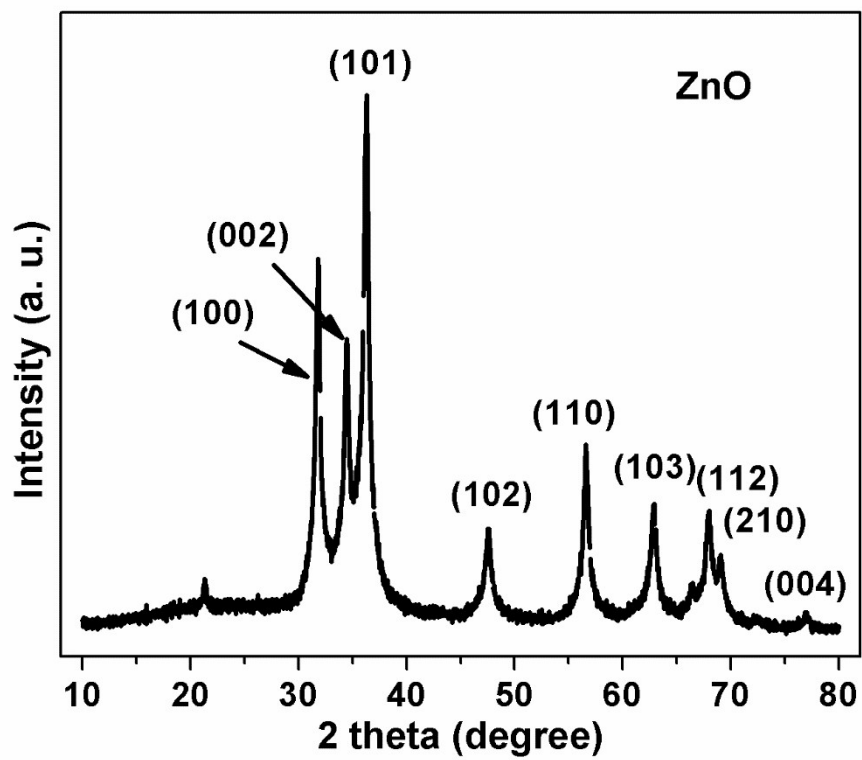
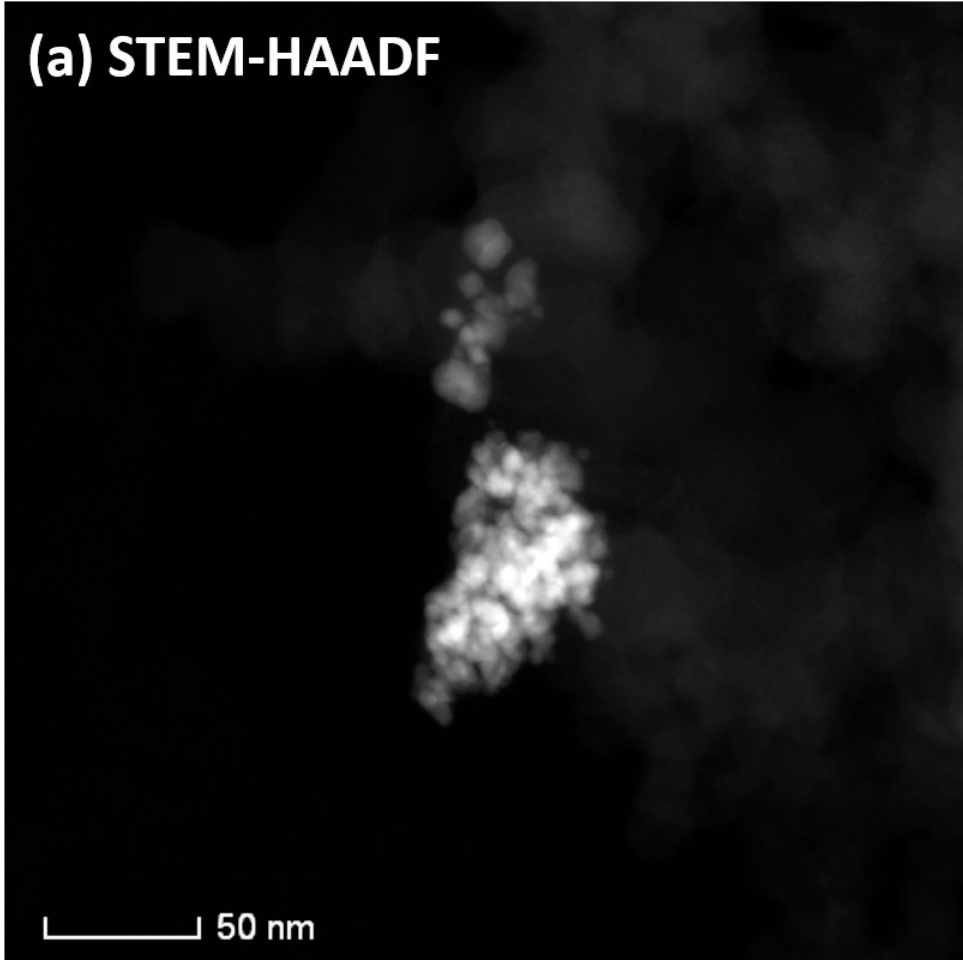
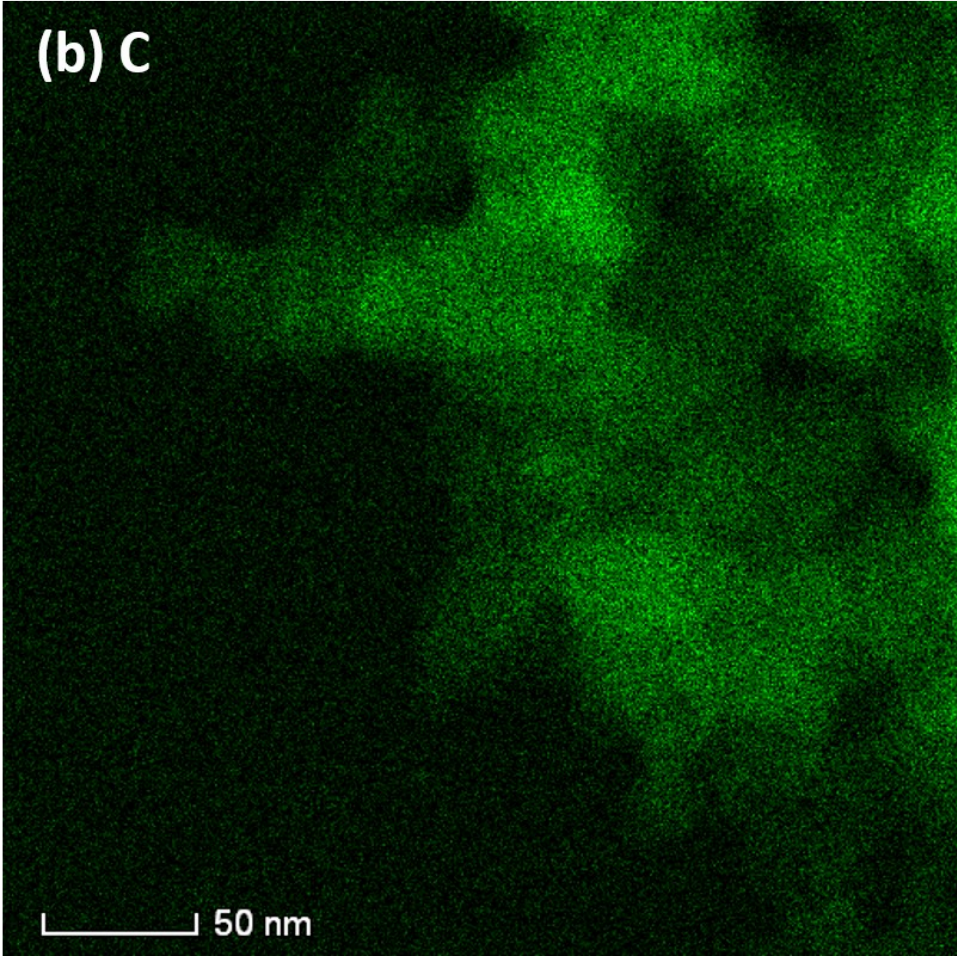


Fig. S1 XRD patterns on ZnO sample.

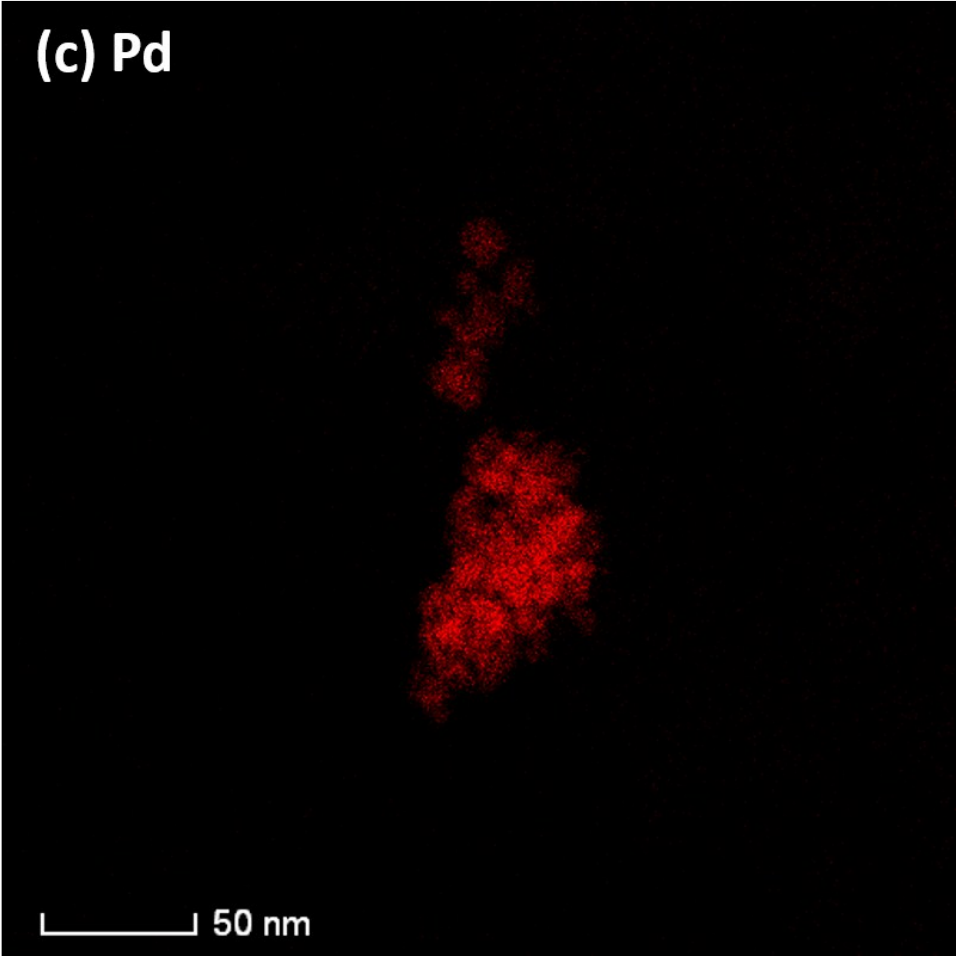
**(a) STEM-HAADF**



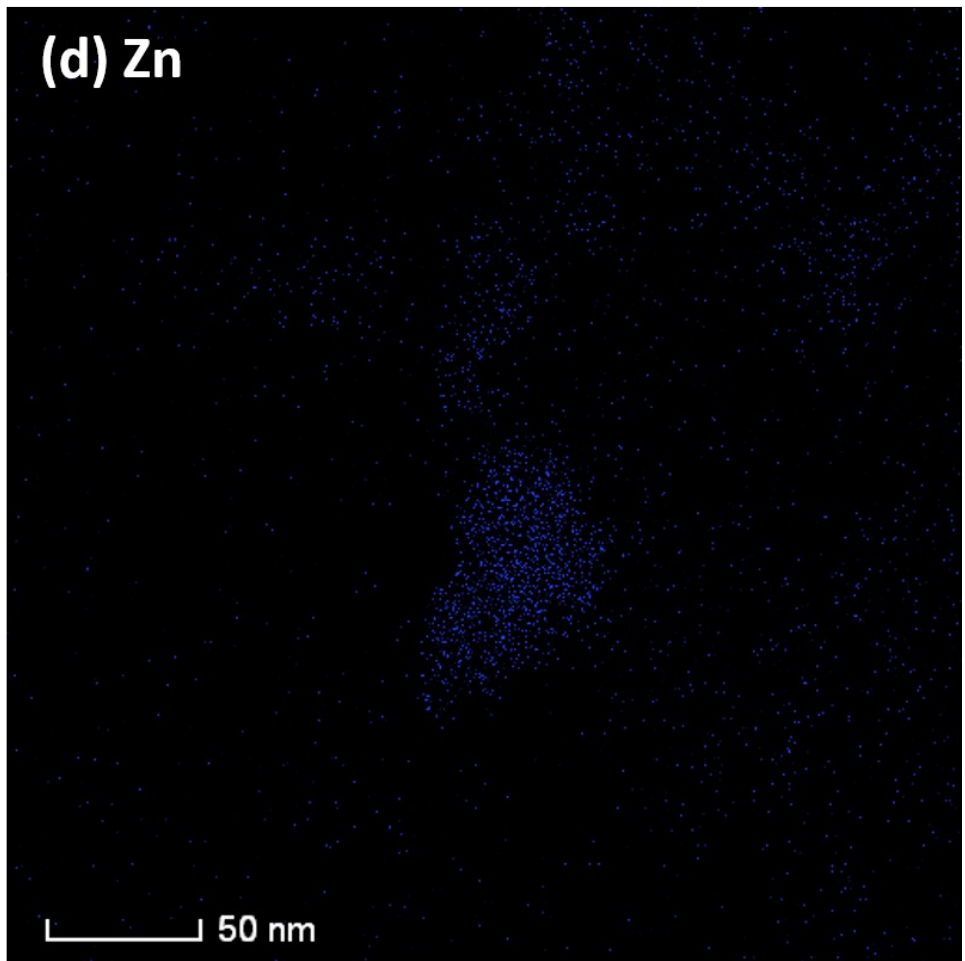
**(b) C**



**(c) Pd**



**(d) Zn**



50 nm

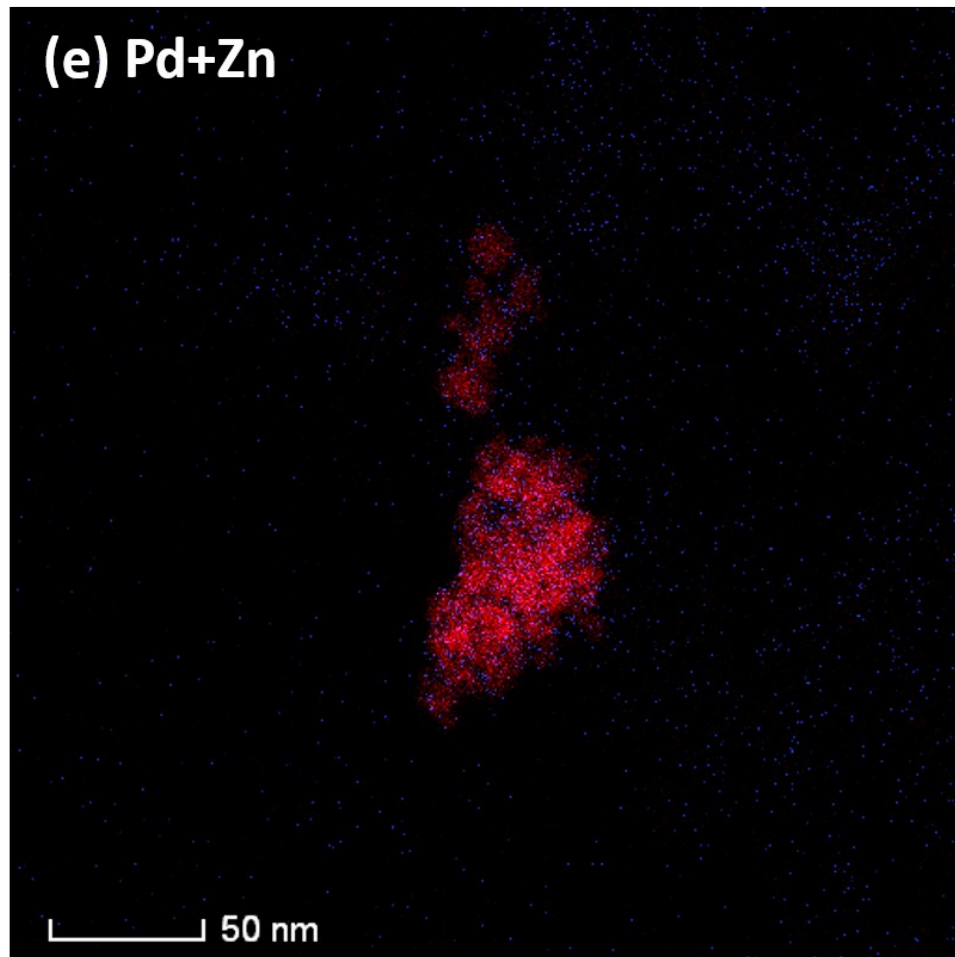
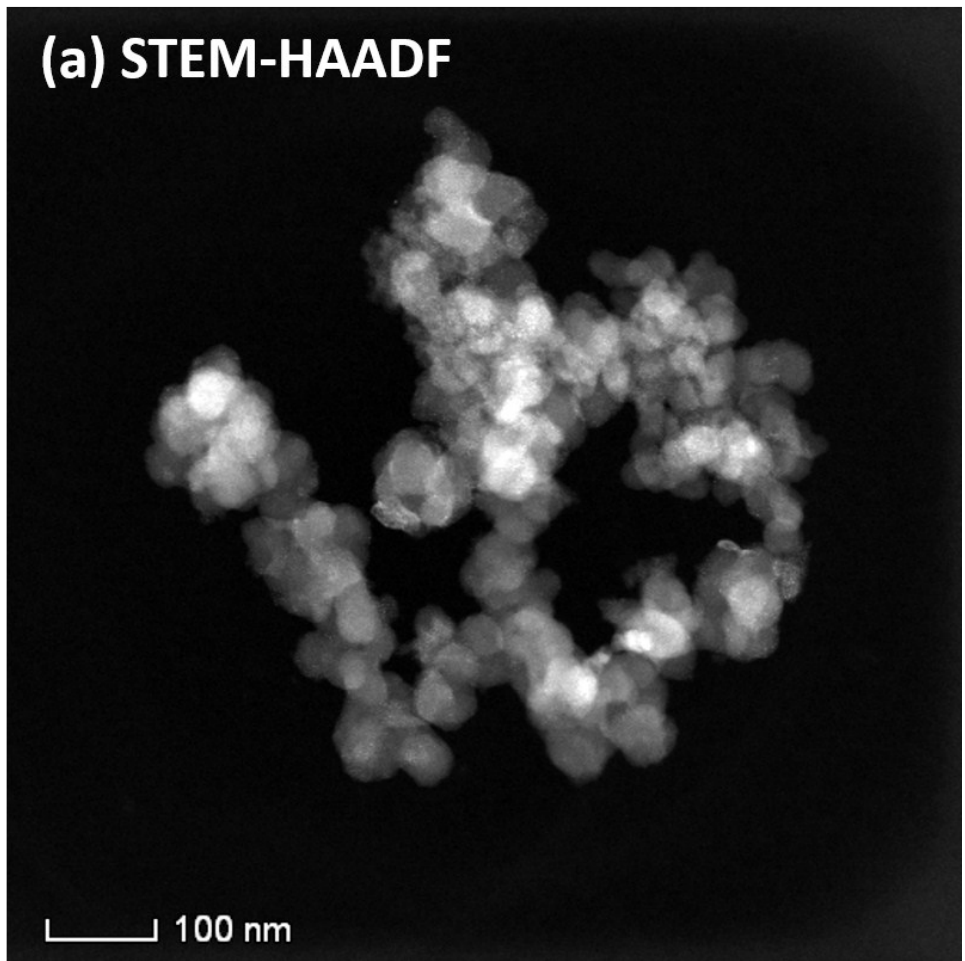


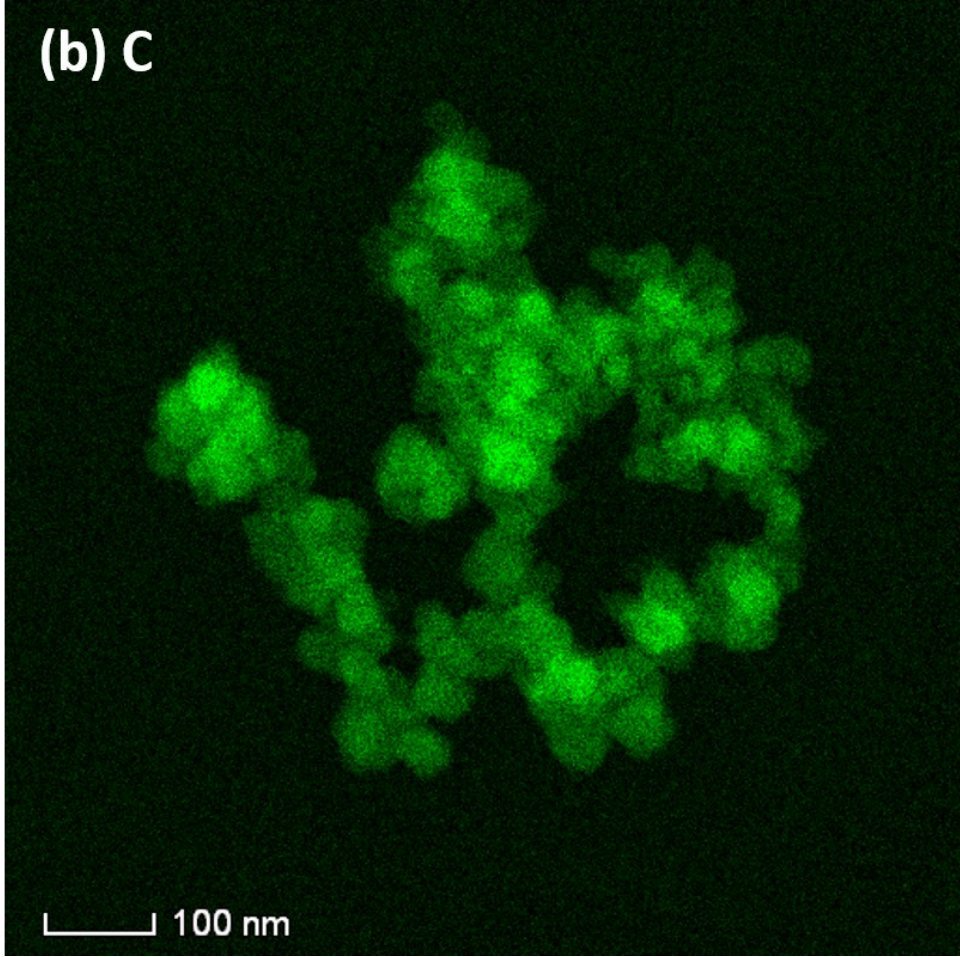
Fig. S2 (a) STEM-HAADF image and EDS elemental maps of (b) C, (c) Pd, (d) Zn and (e) Pd+Zn on PdZn/C (1.75).

**(a) STEM-HAADF**



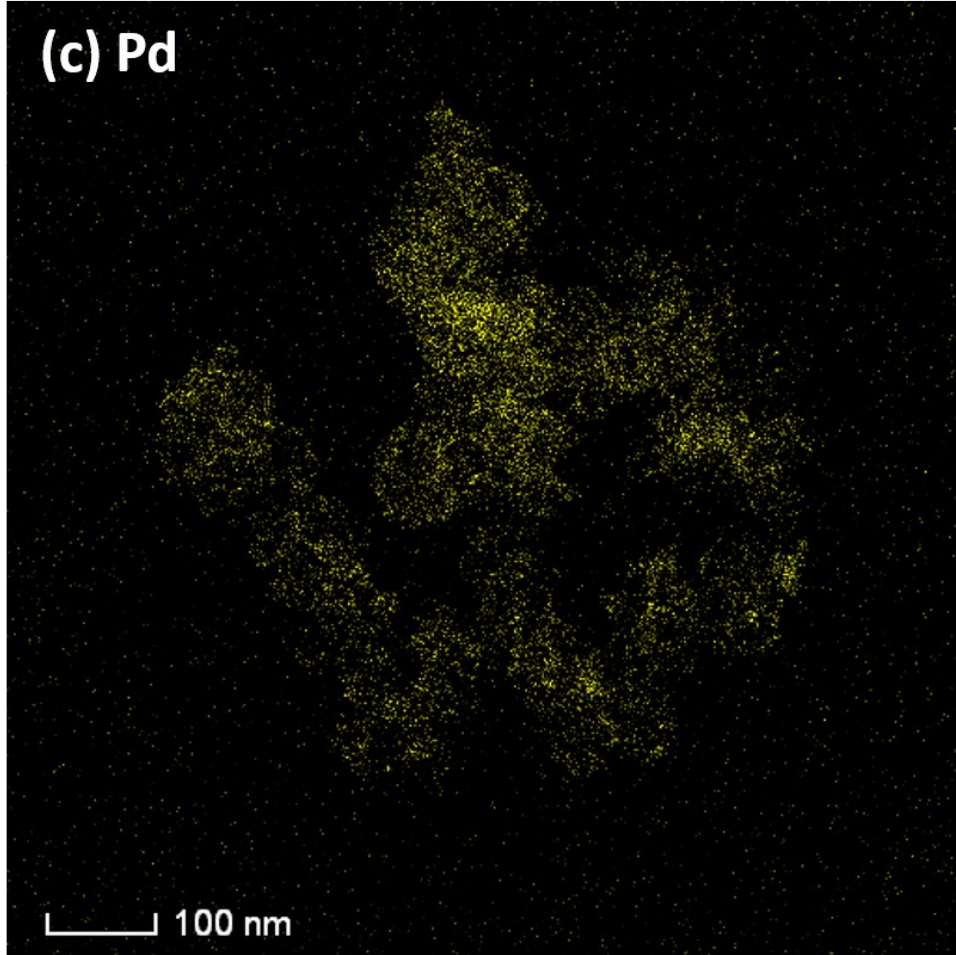


**(b) C**

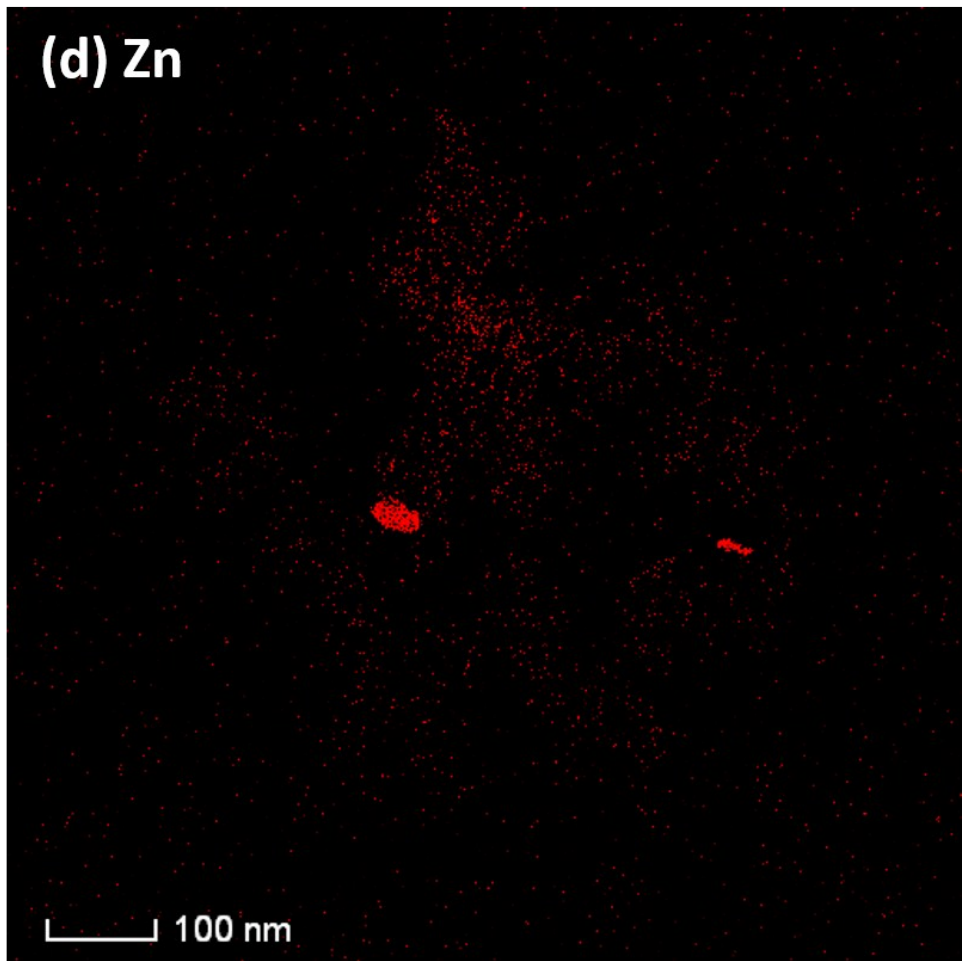


100 nm

**(c) Pd**



**(d) Zn**



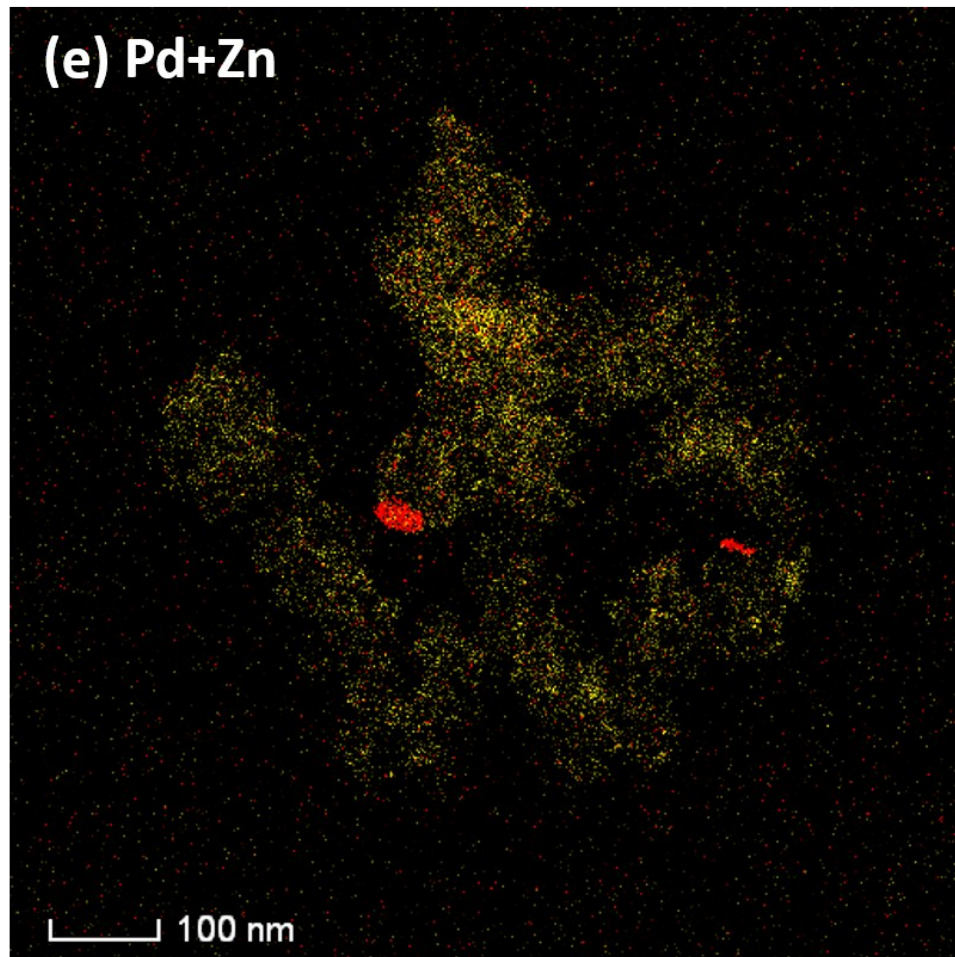


Fig. S3 (a) STEM-HAADF image and EDS elemental maps of (b) C, (c) Pd, (d) Zn and (e) Pd+Zn on PdZn/C (0.5).

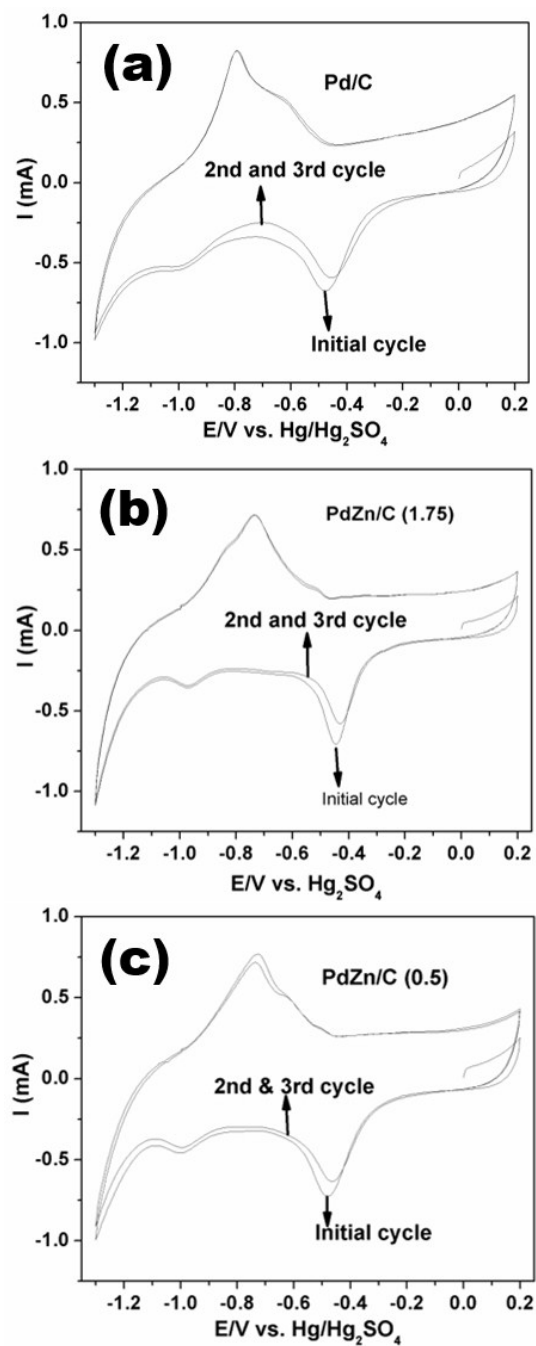


Fig. S4 CVs of (a) Pd/C, (b) PdZn/C (1.75) and (c) PdZn/C (0.5) in an electrolyte of 1 M KOH at a  $50 \text{ mVs}^{-1}$  under a  $N_2$  environment ( CV for each sample is composed of 3 cycles).

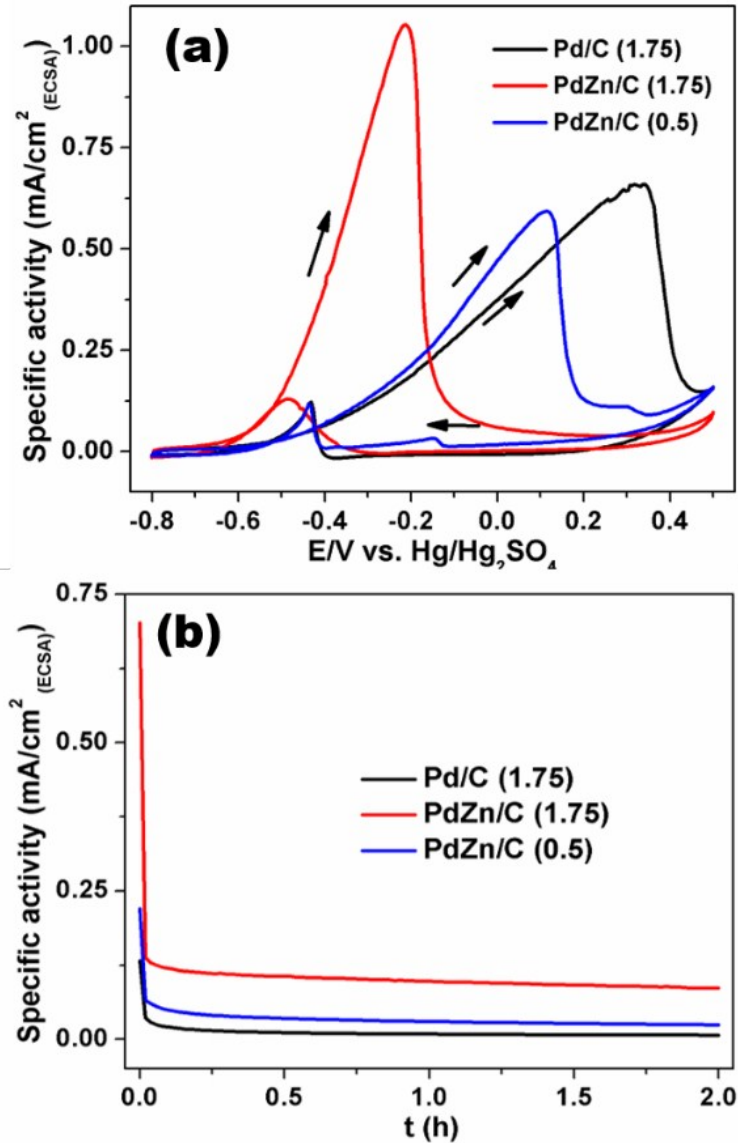


Figure S5 (a) CVs of MOR on Pd/C, PdZn/C (1.75) and PdZn/C (0.5) in an electrolyte of 1 M KOH containing 2 M CH<sub>3</sub>OH, and (b) Chronoamperometric curves on Pd/C, PdZn/C (1.75) and PdZn/C (0.5) at 0.325 V with 250 rpm for 2 h.

**Comment:** The ECSAs of Pd/C, PdZn/C (1.75), and PdZn/C (0.5) are 15.246, 9.476 and 12.462 cm<sup>2</sup>, respectively. For the normalization with ECSAs for CVs of MOR, the order of MOR is PdZn/C (1.75) > Pd/C > PdZn/C (0.5). This order affects the trend of the current density normalized by Pd-amount in samples. Pd/C is slightly higher in current density than PdZn/C (0.5) whereas PdZn/C (1.75) is slightly higher in current density than Pd/C when Pd-amount in samples is a factor for the normalization. This variation is dependent on ECSA and Pd-amount.

If we see Pd-amount in PdZn/C that is two times lower than Pd-single metal, the current density is highly suppressed by Pd-amount. We think the calculation of current density should be normalized by the mass of active metal because it is easy to calculate how the current and efficiency of the catalyst is produced by the mass of active metal. In order to design for the improvement of the catalytic performance, first we need to calculate the mass of active metal in the catalyst for the catalytic performance.

In case of chronoamperometric curve, there is no changes in two orders normalized by ECSAs and Pd-amount for the calculation of the current density. Only active metal, Pd is highly affected by carbonaceous species produced in the time of MOR if MOR persists for a longer time. Within a very short time, single active metal show poor performance for a long time due to accumulation of intermediate species on the catalyst's surface. On the other hand, PdZn/C can persist for a longer time than Pd/C. One of reasons is transition metal can release intermediates by MOR, thus generating more active sites for adsorption. Second, the interaction Pd atom and smaller Zn atom produce electronic effect that causes the changes in binding energy between catalyst and substrate. This is how they last for a longer time than single active element.