

Supplementary Materials: Ultra-small Pd Nanoparticles on Ceria as an Advanced Catalyst for CO Oxidation

Au/CeO₂ reference material

The Au NPs on the ceria support modified by TEPA (Au/CeO₂) were used as the reference material in this study. The same approach was used to synthesize this material, but we used sodium tetrachloroaurate (III) dihydrate Alfa Aesar 99.99% as a precursor without substitution of chlorine by amine-groups to create larger nanoparticles with a better Z-contrast due to the higher atomic number of gold. All used amounts of reagents are shown in Table S1 (both for Pd/CeO₂ and for Au/CeO₂).

Table S1. Amounts of used reagents.

Sample Name	Salt precursor	m(Pd prec.), mg / n(Pd prec.), mmol	m(Au prec.), mg / n(Au prec.), mmol	m(CeO ₂), mg
Pd/CeO ₂	[Pd(NH ₃) ₄]Cl ₂	12.4 / 0.0505	—	129
Au/CeO ₂	Na[AuCl ₄]·2H ₂ O	—	12.6 / 0.0317	150

HRTEM of Au/CeO₂

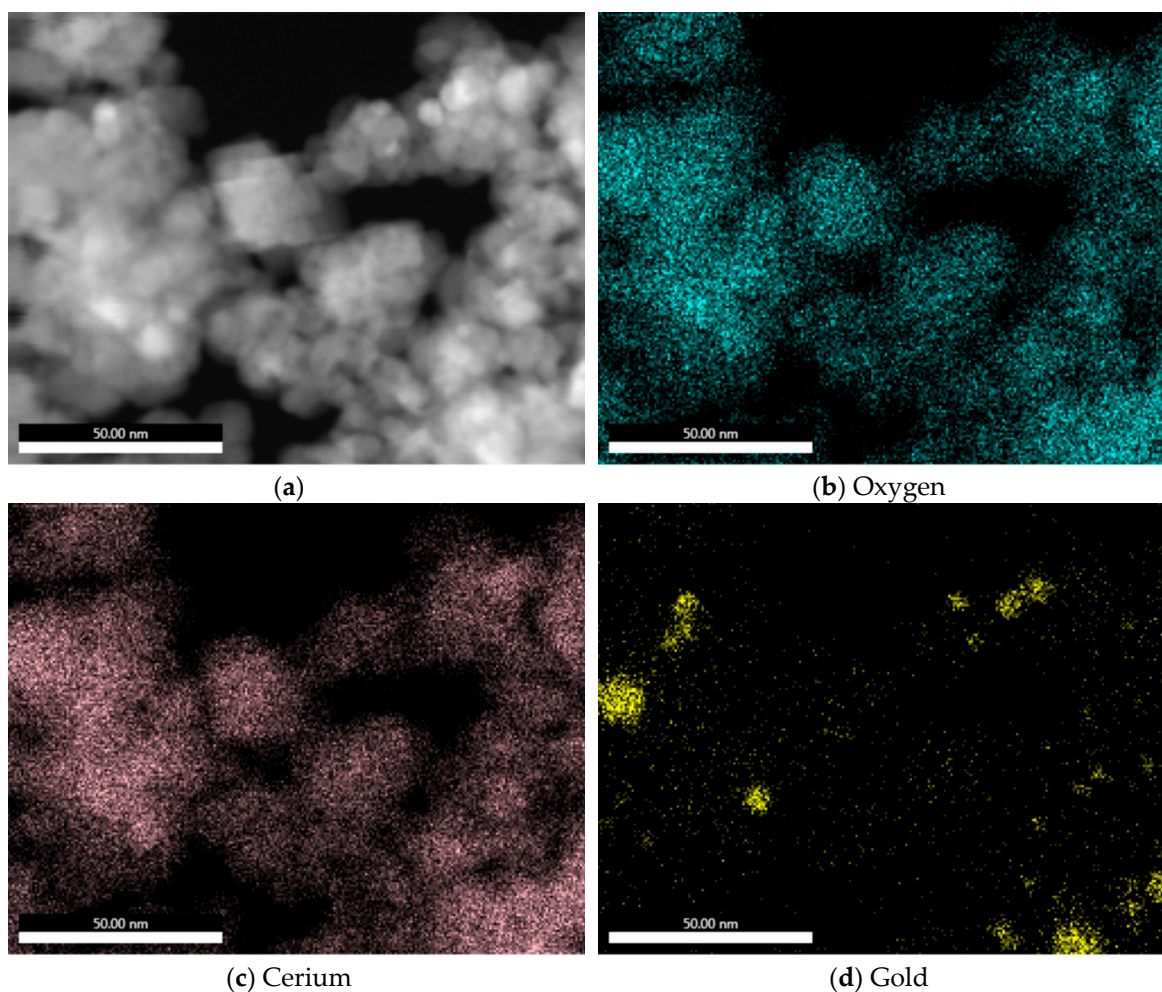


Figure S1. (a) SEM/EDS micro-image of Au/CeO₂; element distribution maps of (b) oxygen (blue); (c) cerium (beige); (d) gold (yellow). SEM micro-images show some large agglomerates of gold for Au/CeO₂. The concentration of Au estimated by SEM was 2 wt%.

XRPD Patterns

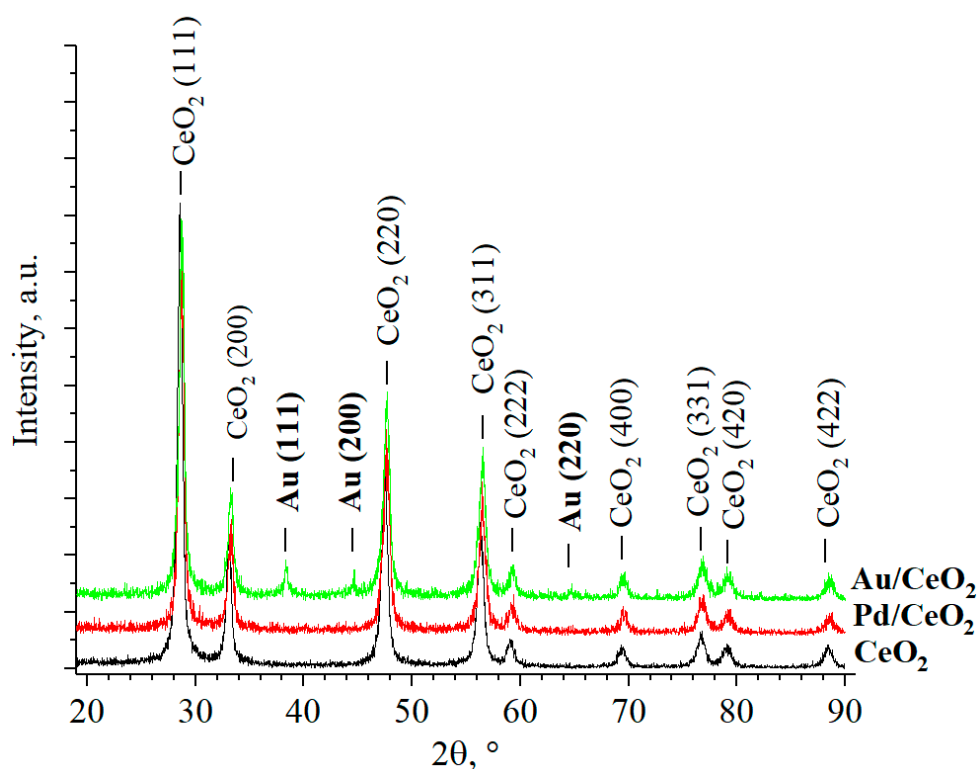


Figure S2. X-ray diffraction patterns of CeO₂ (black), Pd/CeO₂ (red) and Au/CeO₂ (green). $\lambda(\text{CuK}\alpha) = 0.15406 \text{ nm}$. Peaks related to diffraction on Pd are not visible; the Au phase is clearly observed for Au/CeO₂ with bigger NPs (average size 13 nm according to Debye–Scherrer analysis).

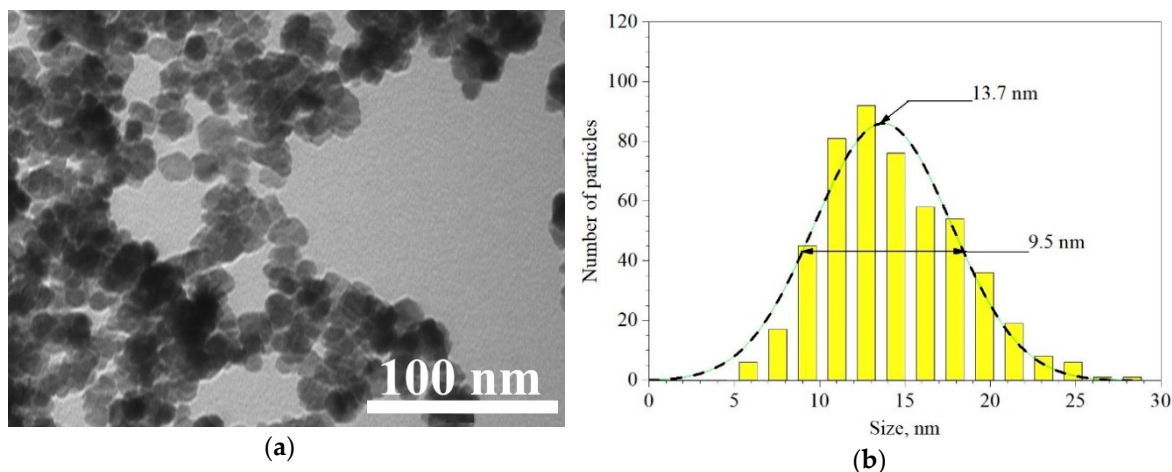
TEM of CeO₂

Figure S3. (a) TEM micro-image of the CeO₂; (b) particle size distribution (total number of measured particles was 500).

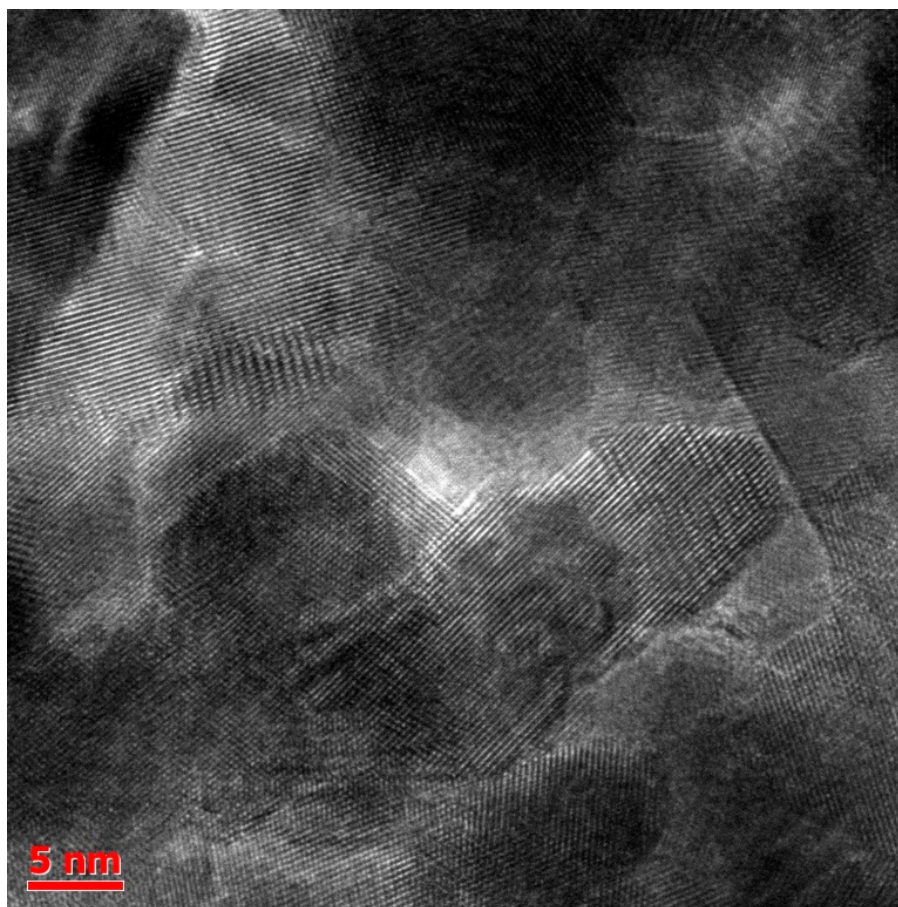
HRTEM of Pd/CeO₂

Figure S4. HRTEM micro-image of Pd/CeO₂ used for FT (see Figure 2b).

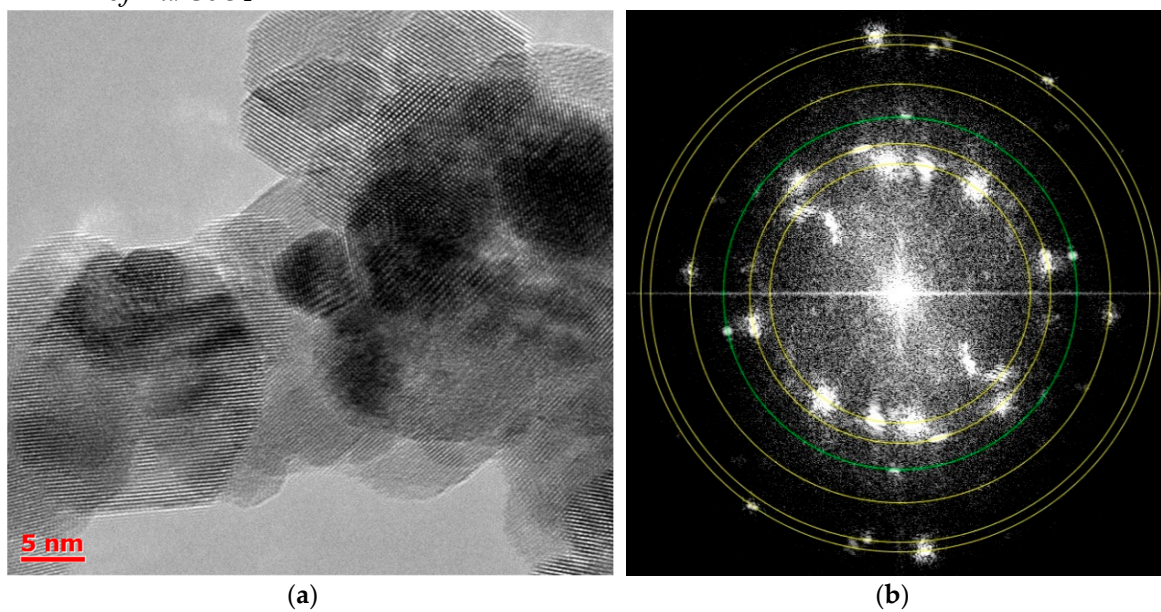
HRTEM of Au/CeO₂

Figure S5. (a) HRTEM micro-image of the Au/CeO₂ reference sample; (b) FT image with circles marking the spacing between atomic planes of CeO₂ (yellow) and Au (green).

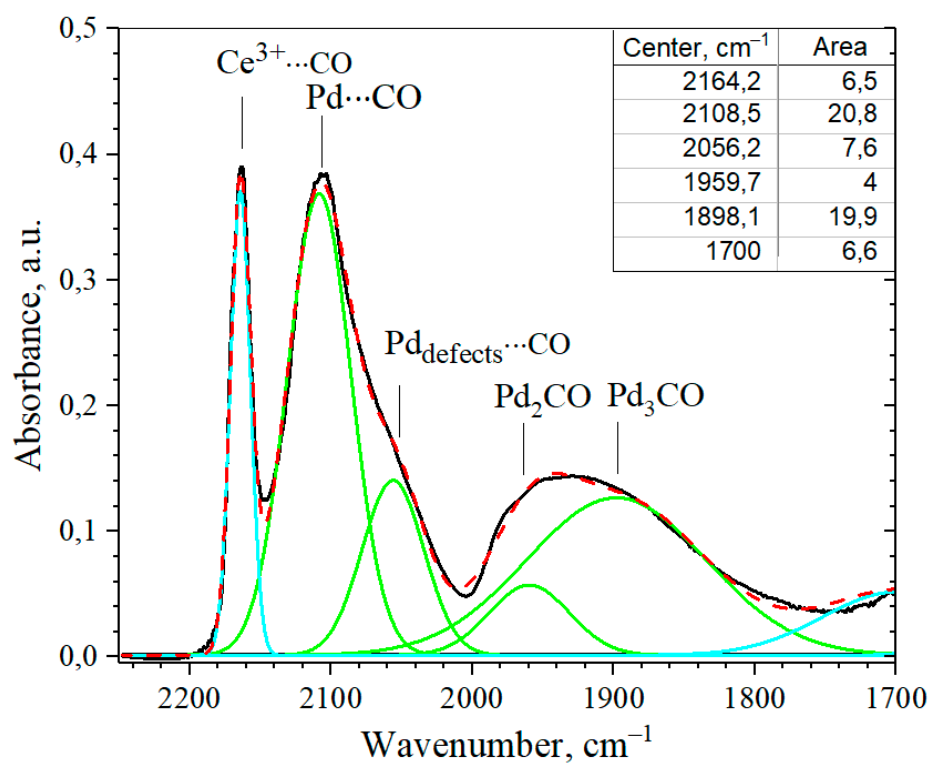
Deconvolution of Pd/CeO₂ FTIR Spectrum

Figure S6. Deconvolution of Pd/CeO₂ FTIR spectrum at P_{CO} = 7.5 mbar (max. coverage).

Catalytic Tests

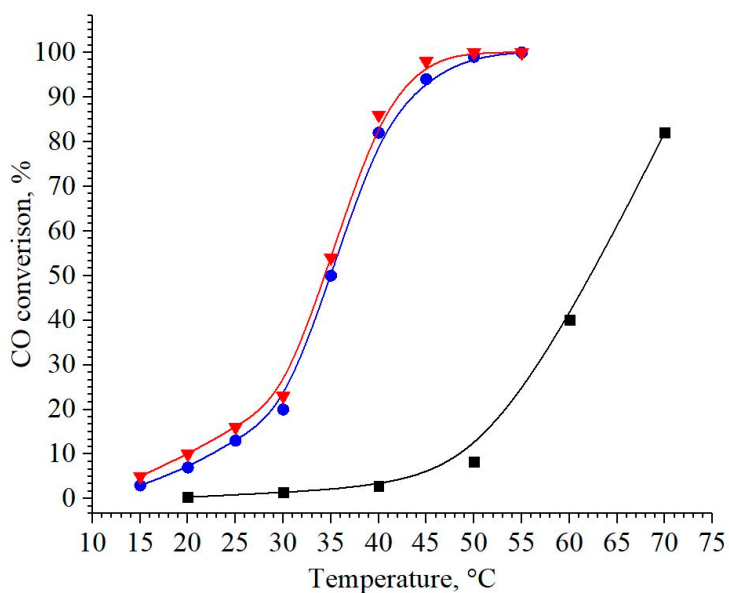


Figure S7. CO conversion vs oxidation reaction temperature for Pd/CeO₂ (blue and red lines for first and third cycles) and Au/CeO₂ reference sample (black line) in a mixture of 16.9% O₂, 62.4% N₂ and 20.7% CO at a flow rate of 120,000 h⁻¹.

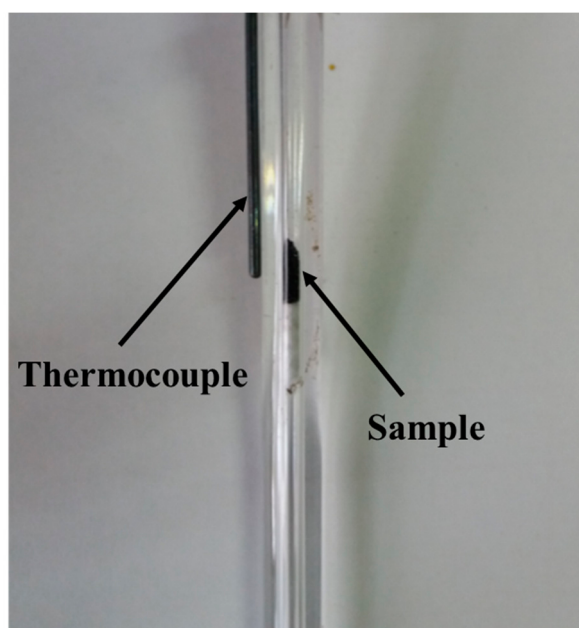


Figure S8. Microreactor for tests of catalytic activity with a catalyst.

Electrochemical Measurements (CV)

Cyclic voltammetry (CV) measurements were carried out in a 0.1-M HClO_4 solution in an argon atmosphere on a stationary working electrode with the help of the PARSTAT 4000 potentiostat/galvanostat. A platinum electrode was used as a counter electrode with a silver/silver chloride (Ag/AgCl , $\text{KCl}(\text{sat.})$) electrode as a reference. Experiments were performed in the potential range of 1.545 to -0.355 V vs Ag/AgCl , $\text{KCl}(\text{sat.})$ with a potential sweep rate of 500 mV/s. A total of 10 cycles for each experiment were carried out and averaged later.

Sample preparation for each measurement was conducted in the following order [1,2]: 0.0025 g of the sample was mixed with 450 μl of isopropanol and 50 μl of 0.5% aqueous Nafion solution. The obtained substance was sonicated for 30 min, then stirred for at least 1 h with a magnetic stirrer. After that, four drops of the sample suspension were placed on the surface of the glassy carbon working electrode ($S = 0.19625 \text{ cm}^2$) sequentially, after drying of each previous drop. A detailed description of the masses is given in Table S2.

Table S2. Sample preparation for the electrochemical tests

	Pd/CeO_2	CeO_2	CeO_2/TEPA
Mass of the sample, g	0.0026	0.0025	0.0026
Mass of the final suspension, g	0.4073	0.3879	0.4027
	0.0045	0.0053	0.0053
Mass of the drops, g	0.0053	0.0051	0.0055
	0.0052	0.0051	0.0050
	0.0053	0.0053	0.0054

Figure S9 shows the voltammetric behaviors of the obtained catalyst (Pd/CeO_2) and modified support (CeO_2/TEPA) in a 0.1-M Ar-saturated HClO_4 solution.

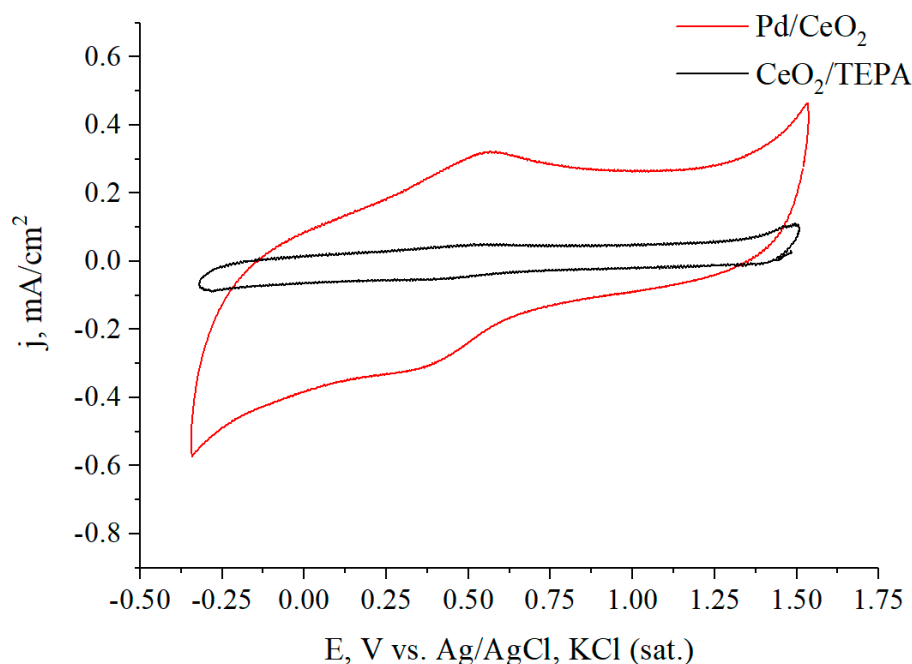
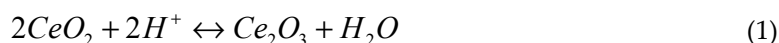


Figure S9. The resulting CV curves (averaged over 10 cycles) of Pd/CeO₂ (red) and CeO₂/TEPA (black).

For Pd/CeO₂, an oxidation peak around 0.6 V and a reduction one around 0.4 V were observed. At first, we tended to attribute them both to the formation and destruction of surface metal oxides. However, if normalized, both CV curves demonstrated oxidation and reduction peaks at almost the same potential values, which led us to consider them associated with the changes of CeO₂ surface, possibly through the following reversible process:



The larger amplitude of these peaks for Pd-promoted sample was explained by a better release of lattice oxygen via a ceria-noble metal interface. Due to the small size of Pd nanoparticles, we did not observe characteristic peaks of hydrogen desorption (adsorption) in the region of low potentials, as usually reported for larger particles [3].

It should be noted that the absence of a peak at 0.845 V indicated a low concentration of Ce³⁺ in the system [4]. The relative amount of Ce⁴⁺/Ce³⁺ redox couple, which was the result of the intrinsic defective chemistry of ceria (Ce³⁺ and O vacancy concentrations) [5], was a function of particle size, wherein the fraction of Ce³⁺ ions in the particles increases with decreasing particle size [6]. The absence of Ce⁴⁺/Ce³⁺ reversible transformation can be explained by a particular covering of the ceria surface by polymer molecules at room temperature.

Also, it could be easily observed that, in the case of Pd/CeO₂, the double-layer charging region of CV curves widened drastically in comparison with pure support (Figure S9). We speculate that such behavior occurred because of two possible reasons. Firstly, many small nanoparticles placed on the ceria significantly increased its cumulative surface area, which led to a greater double-layer area. Secondly, the CV curve change may have been observed after the modification of the support's nature due to the carbon formation on the ceria surface.

References

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