

Supporting Information

for

PdO/PdO₂ nanocluster – functionalized ZnO:Pd films for lower operating temperature hydrogen gas sensing

DOI: [10.1039/c8nr03260b](https://doi.org/10.1039/c8nr03260b)

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Keywords: Pd-doped ZnO, hydrogen sensor, nanostructured films, PdO, functionalized, nanocluster

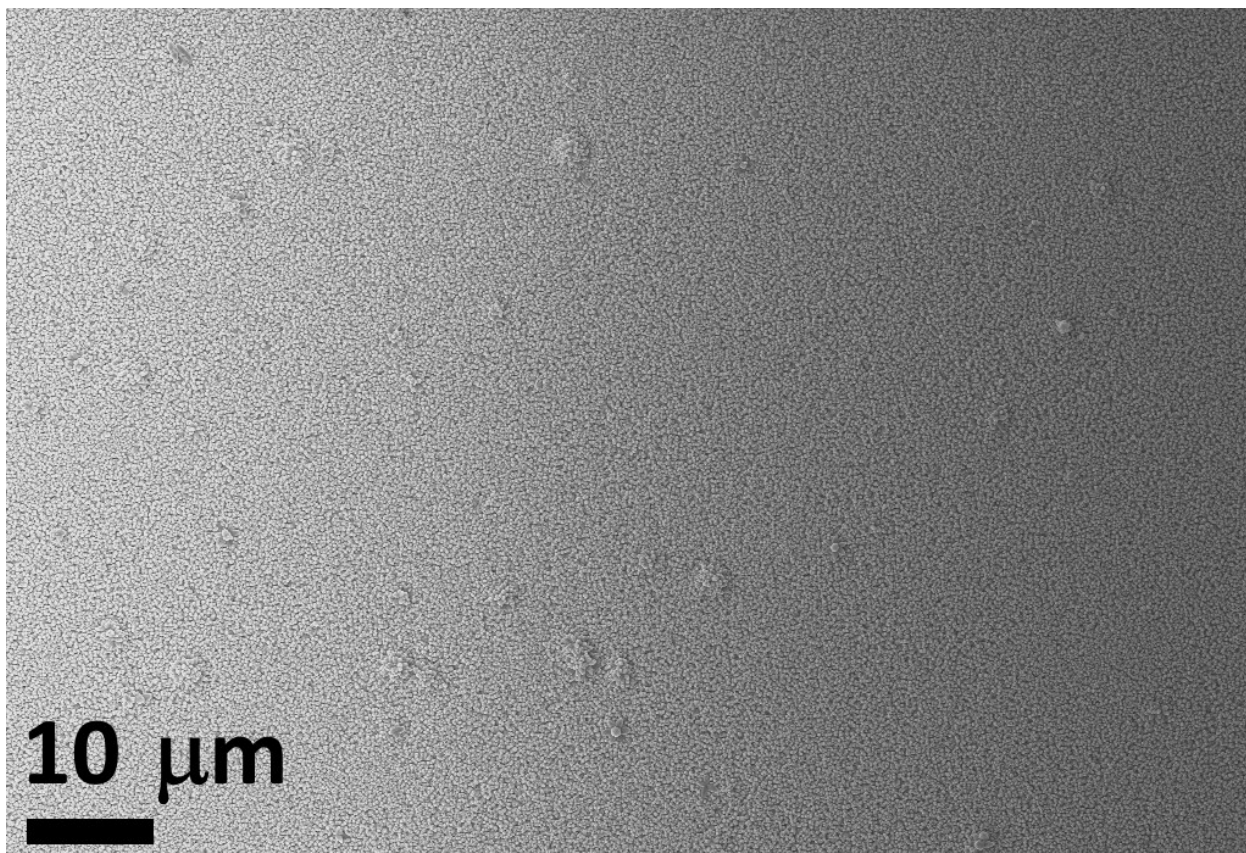


Figure S1. SEM image at low magnification of as-grown Pd-doped ZnO nanostructured films grown using 13.5 mM of PdCl₂.

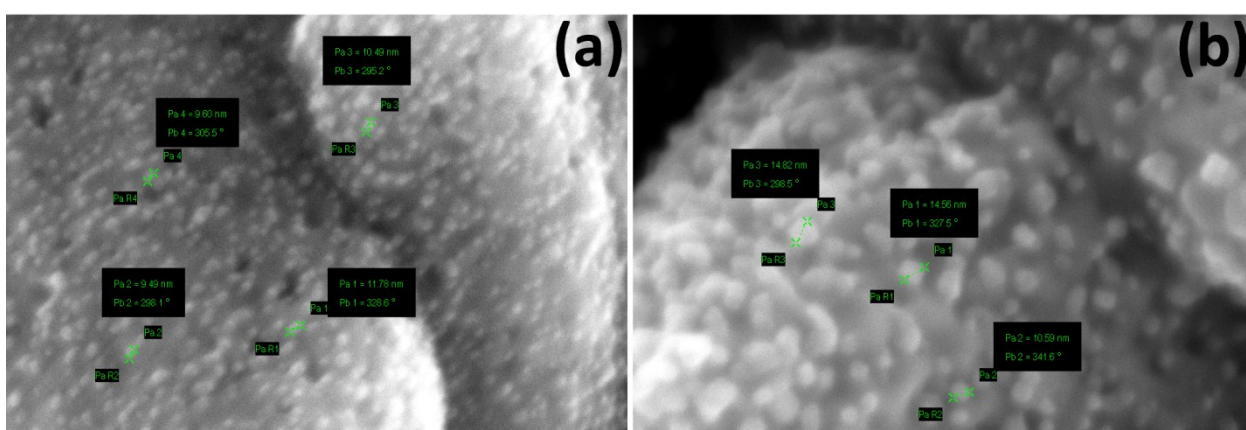


Figure S2. SEM images of as-grown and PdCl₂-functionalized ZnO: Pd nanostructured films (grown using 45 mM of PdCl₂).

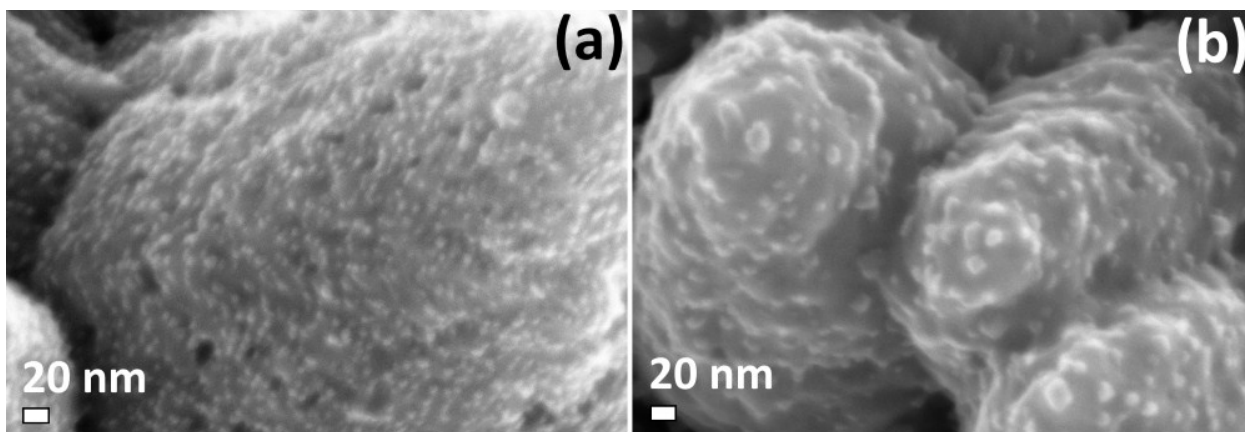


Figure S3. SEM images of PdCl₂-functionalized ZnO:Pd nanostructured films (grown using 45 mM of PdCl₂): (a) treated TA at 650 °C; (b) treated RTA at 650 °C.

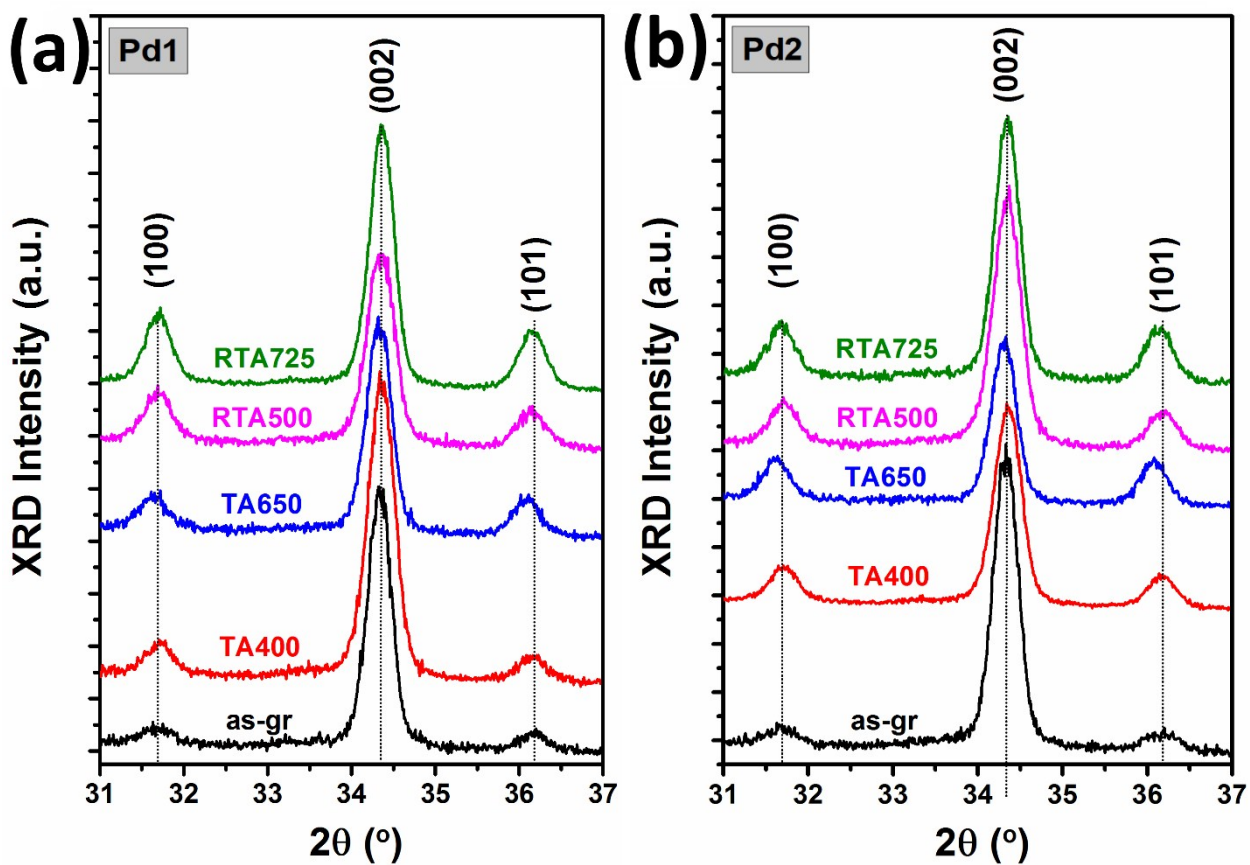


Figure S4. XRD patterns in the range 2θ from 31° to 37° of Pd doped ZnO nanostructured films treated TA and RTA at different temperatures: (a) with 0.3 at% Pd and (b) with 0.5 at% Pd. Where Pd0 stands for the undoped, Pd1 for the synthesis solution with 13.5 mM and Pd2 for the solution with 45 mM content of PdCl_2 .

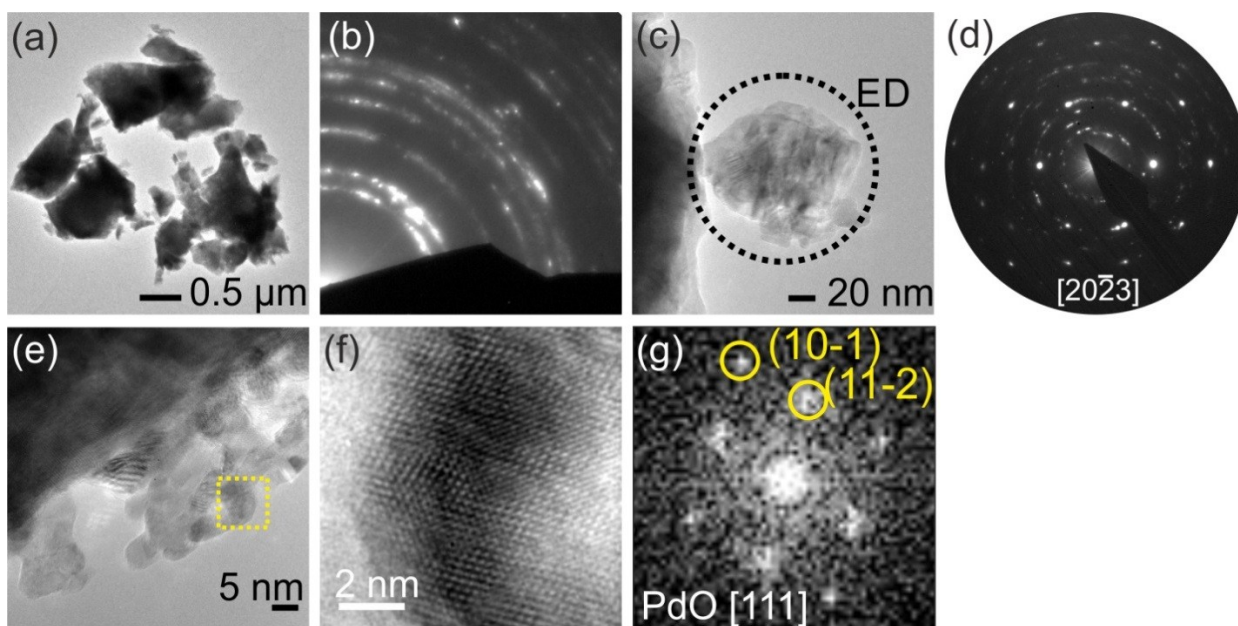


Figure S5. (a) TEM bright field image of ZnO:Pd crystals scratched onto the TEM grid. (b) Polycrystalline electron diffraction pattern of ZnO. (c+d) ZnO nanocrystal in [20-23] orientation (e) HRTEM image of PdO_x nanoclusters on the ZnO surface. A noise filtered image of a PdO particle with its FFT showing the [111] orientation is shown in (f+g).

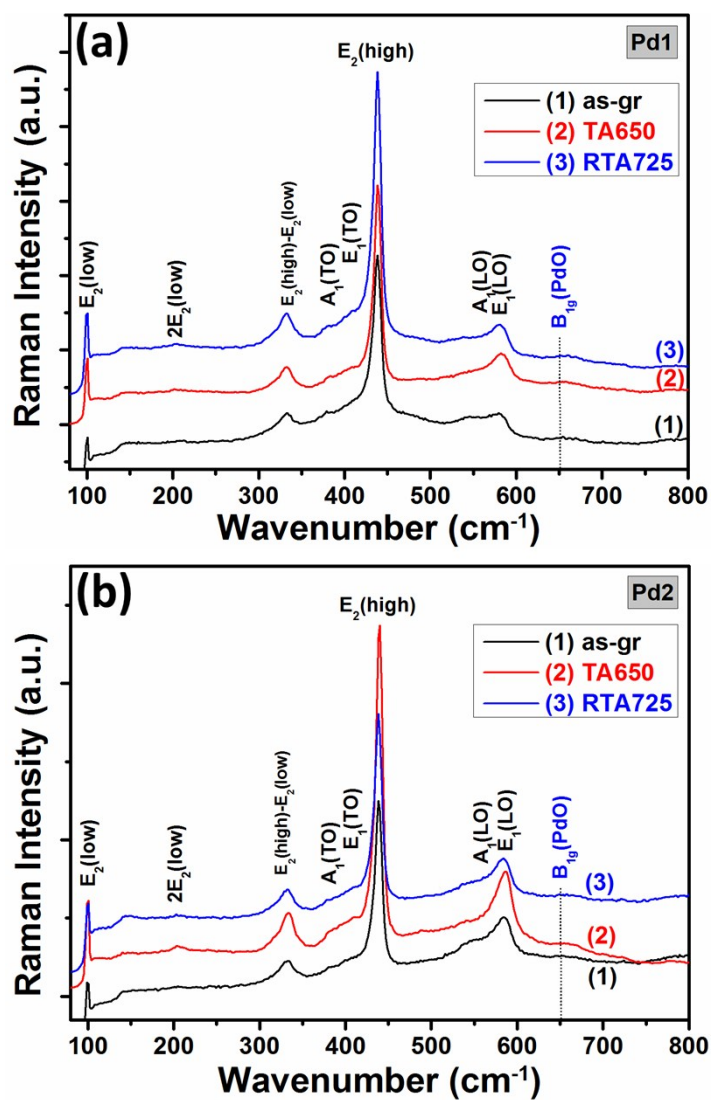


Figure S6. The room temperature Raman spectra of the ZnO:Pd nanostructured films with (a) 0.3 at% Pd and (b) 0.5 at% Pd.

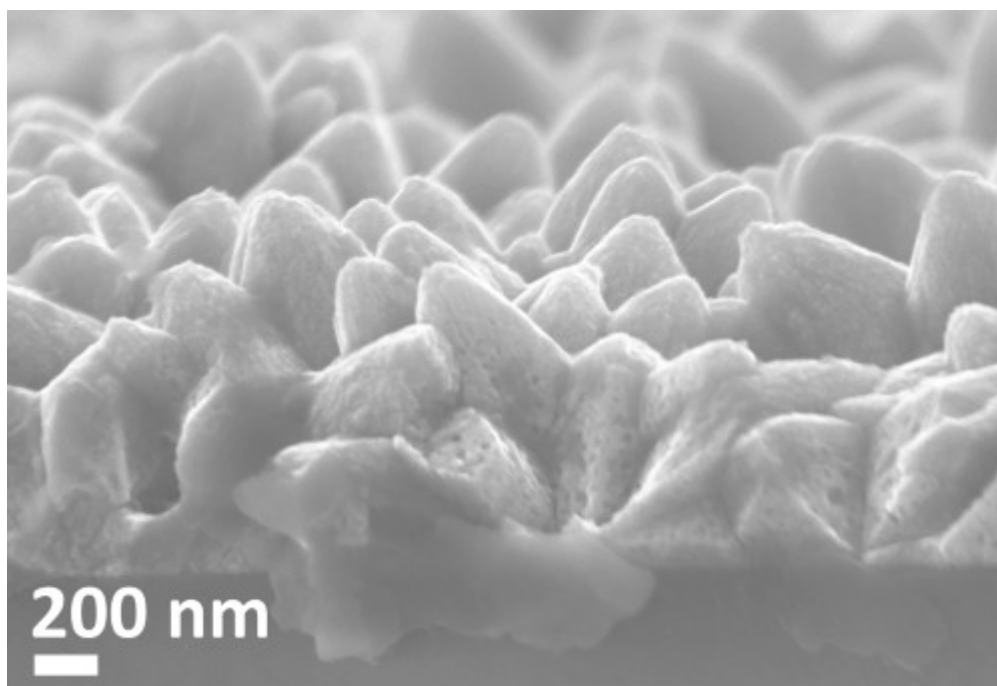


Figure S7. SEM image of ZnO:Pd sample in cross section.

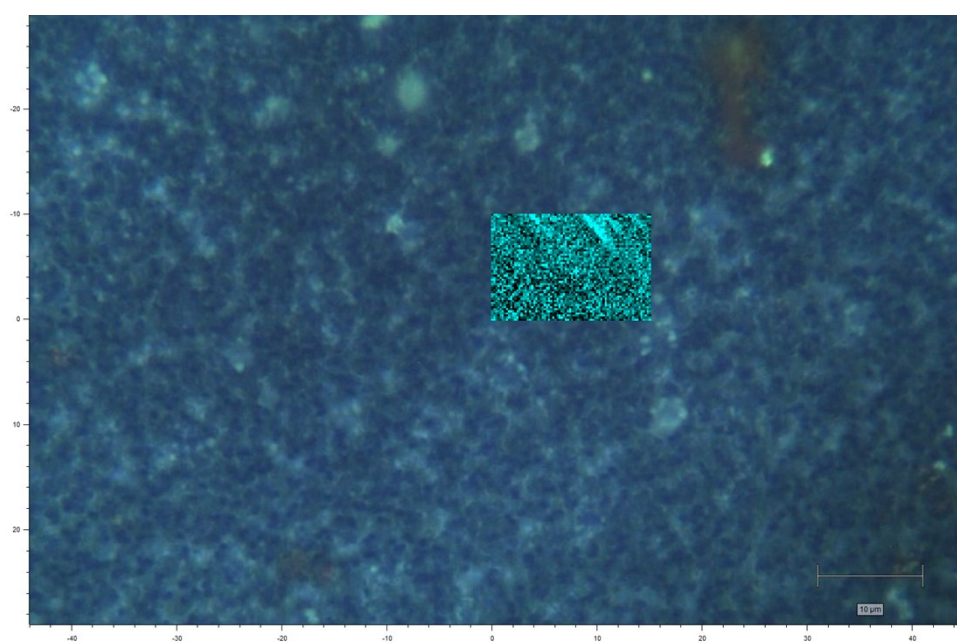


Figure S8. Spatial mapping of corresponding Raman intensities of the B_{1g} peak ranging from 630 to 664 cm^{-1} for PdO-functionalized ZnO:Pd samples from the top.

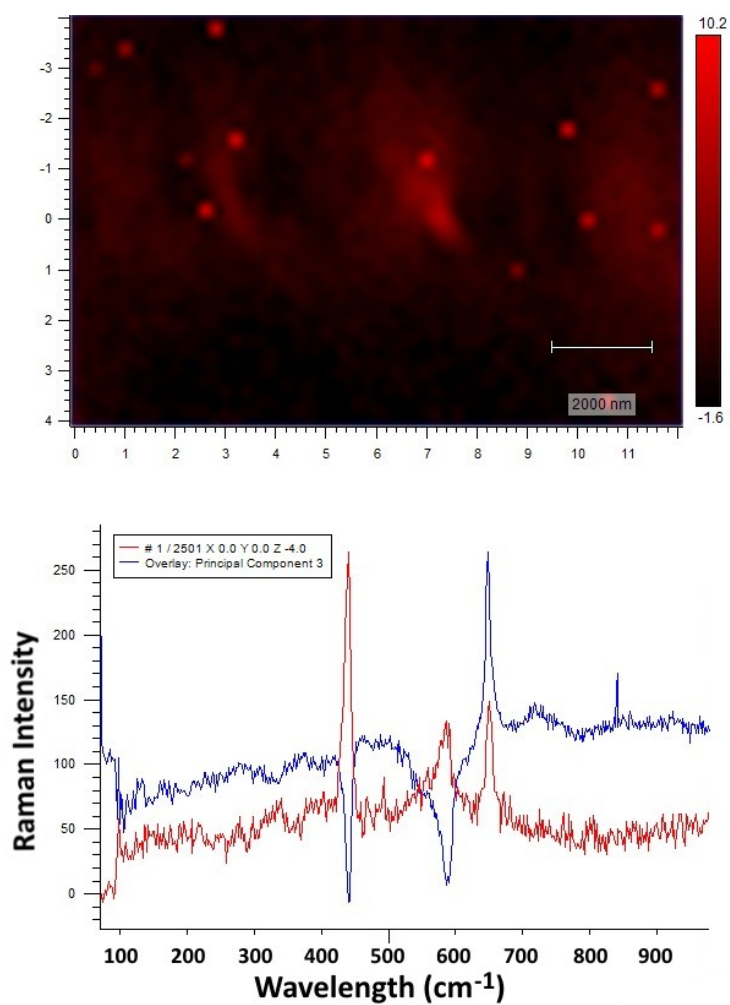


Figure S9. Spatial mapping of corresponding Raman intensities of the B_{1g} peak ranging from 630 to 664 cm^{-1} for PdO-functionalized ZnO:Pd samples in cross section.

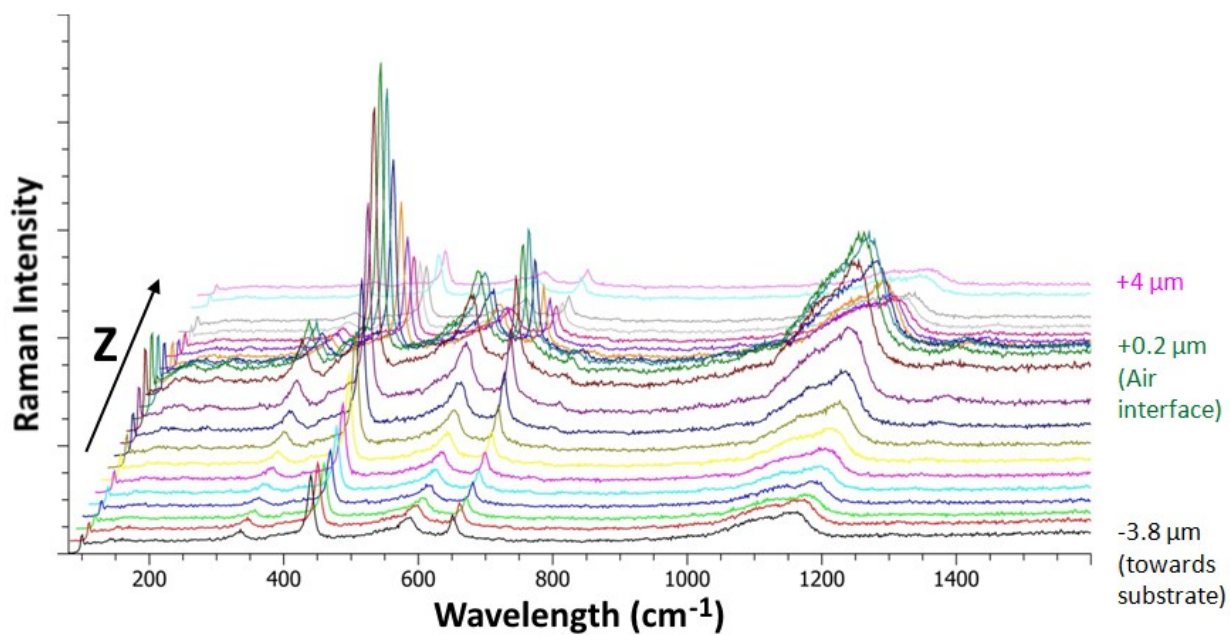


Figure S10. The room temperature Raman spectra for PdO-functionalized ZnO:Pd samples in cross section measured along Z-axis with a 0.4 μm step.

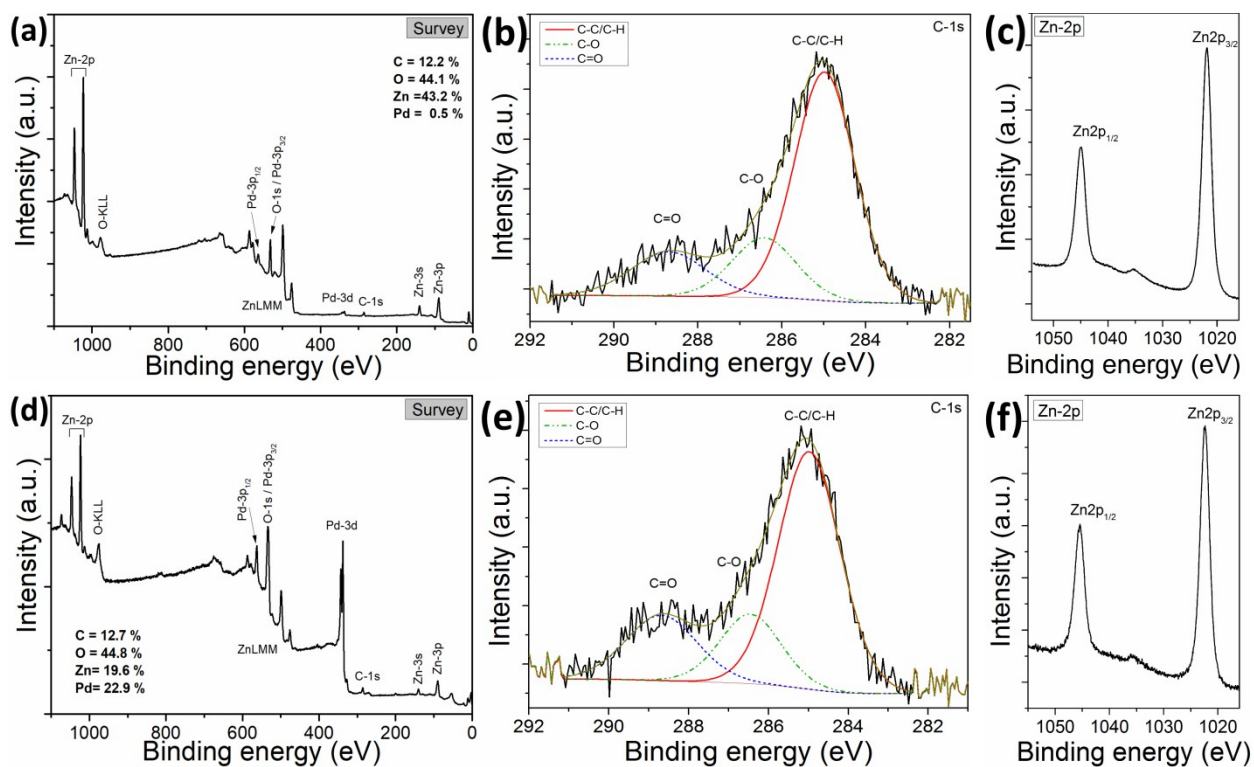


Figure S11. XPS spectra of ZnO:Pd nanostructured films: (a) survey spectra; higher resolution XPS spectrum of: (b) C-1s and (c) Zn-2p core level. XPS spectra of ZnO:Pd nanostructured films functionalized with PdCl₂: (d) survey spectra; higher resolution XPS spectrum of: (e) C-1s and (f) Zn-2p core level.

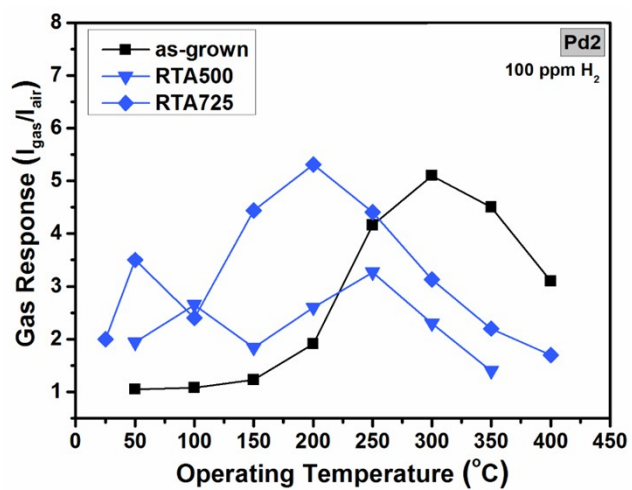


Figure S12. Gas response to 100 ppm of H₂ gas versus operating temperature of ZnO:Pd with 0.5 at% Pd and treated RTA at different temperatures.

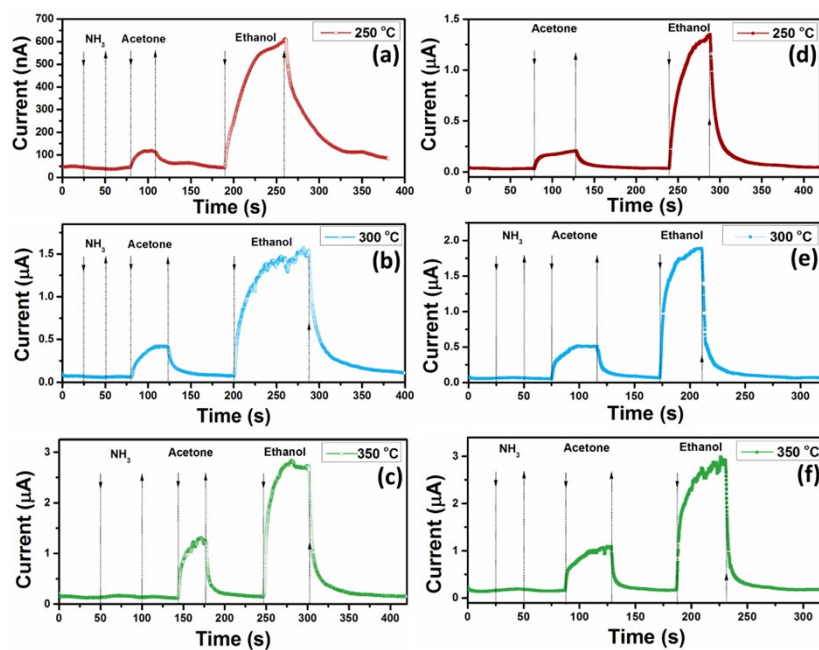


Figure S13. Dynamic gas response to 100 ppm of different vapors (ammonia, acetone and ethanol) of ZnO:Pd nanostructured films with (0.5 at% Pd): (a,b,c) as-grown at 250 °C, 300 °C and 350 °C operating temperature, respectively; (d,e,f) RTA treated at 725 °C at 250 °C, 300 °C and 350 °C operating temperature, respectively.

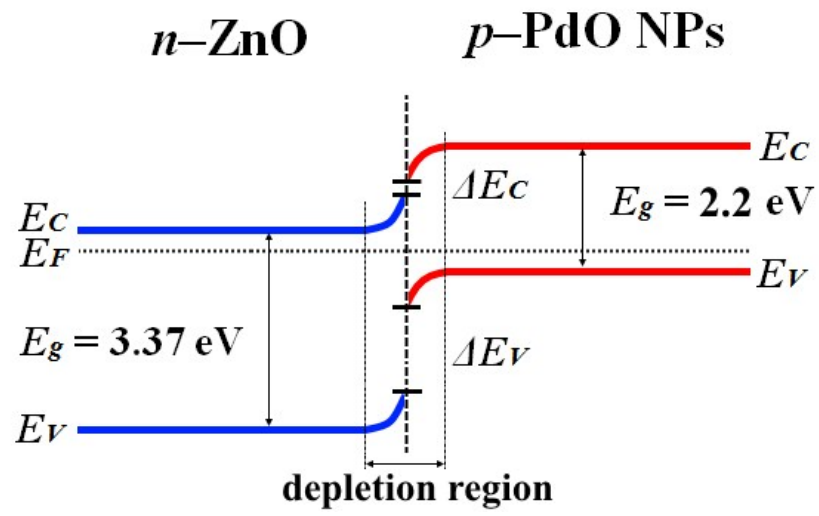


Figure S14. Energy band diagram for ZnO/Pd NP heterojunction.

Table S1. Structural parameters of Pd-doped ZnO nanostructured films

Pd content and type of treatment of ZnO films	Intensity of (002) peak relative to as-grown sample with 0.0 at% Pd content	XRD (002) peak position (2 θ)	FWHM for (002) peak (°)	The average crystallite size D (nm)	<i>d</i> (002), (Å)	<i>a</i> (100), (Å)	<i>c</i> (001), (Å)	Residual stress along <i>c</i> -axis σ (Pa)	Dislocation density δ ($\times 10^{14}$ line/m ²)
0.0 at% Pd, as-grown	1	34.391	0.3182	4.683	2.605	3.265	5.211	-0.205	0.035
0.0 at% Pd, RTA500	1.31	34.395	0.4053	4.027	2.605	3.251	5.210	-0.179	0.058
0.0 at% Pd, RTA725	1.56	34.398	0.3332	4.724	2.606	3.253	5.210	-0.159	0.039
0.0 at% Pd, TA400	1.27	34.392	0.3741	4.313	2.605	3.256	5.211	-0.198	0.049
0.3 at% Pd, TA650	1.42	34.394	0.3149	5.068	2.605	3.257	5.335	-0.185	0.035
0.3 at% Pd, as-grown	0.72	34.335	0.3585	4.683	2.609	3.268	5.219	-0.573	0.045
0.3 at% Pd, RTA500	0.51	34.349	0.4170	4.027	2.608	3.257	5.217	-0.481	0.061
0.3 at% Pd, RTA725	0.76	34.364	0.3555	4.724	2.607	3.257	5.215	-0.381	0.044
0.3 at% Pd, TA400	0.84	34.358	0.3894	4.313	2.608	3.256	5.216	-0.422	0.053
0.3 at% Pd, TA650	0.64	34.321	0.3312	5.068	2.610	3.259	5.221	-0.673	0.038
0.5 at% Pd, as-grown	0.84	34.332	0.3550	4.729	2.609	3.258	5.219	-0.588	0.044
0.5 at% Pd, RTA500	0.81	34.347	0.3999	4.199	2.608	3.256	5.217	-0.489	0.056
0.5 at% Pd, RTA725	0.82	34.349	0.3684	4.558	2.608	3.258	5.217	-0.478	0.048
0.5 at% Pd, TA400	0.64	34.359	0.3938	4.265	2.607	3.255	5.215	-0.412	0.054
0.5 at% Pd, TA650	0.54	34.312	0.3787	4.432	2.611	3.264	5.222	-0.720	0.050

Table S2. The estimated values of optical band gap.

Content of Pd (at%)	Treatment	Thickness (μ m)	E_g (eV)
0.3	As-grown	1.00	3.27
		1.25	3.27
0.3	TA at 400 °C	1.00	3.19
		1.25	3.22
0.3	TA at 650 °C	1.00	3.23
		1.25	3.2
0.3	RTA at 500 °C	1.00	3.22
		1.25	3.25
0.3	RTA at 725 °C	1.00	3.2
		1.25	3.23
0.5	As-grown	1.00	3.3
		1.25	3.29
0.5	TA at 400 °C	1.00	-
		1.25	3.21
0.5	TA at 650 °C	1.00	3.22
		1.25	3.2
0.5	RTA at 500 °C	1.00	3.18
		1.25	3.24
0.5	RTA at 725 °C	1.00	3.17
		1.25	3.23

Table S3. The calculated response and recovery time of ZnO:Pd nanostructured films.

	Temperature (°C)	Response time (s)	Recovery time (s)
As-grown (100 ppm of H₂)	50	110	200
	100	80	180
	150	72	155
	200	65	105
	250	54	59
	300	32	21
	350	28	8
	400	2	4
RTA500 (100 ppm of H₂)	50	55	105
	100	15	155
	150	34	24
	200	69	20
	250	8	10
	300	6	9
	350	5	8
	400	3	6