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Supporting Information

Superfast and efficient hydrogen gas sensor by using $PdAu_{alloy}$@ZnO core-shell nanoparticles

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Experimental Section

Chemicals. All chemicals were commercially sourced at analytical grade and used without further purification. Hexadecyltrimethylammonium bromide (CTAB, $C_{19}H_{42}BrN$, 99%), hexadecyltrimethylammonium chloride (CTAC, $C_{19}H_{42}ClN$, 98%), palladium chloride ($PdCl_2$, 99%), tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.99%), ascorbic acid ($C_6H_8O_6$, 99%), zinc nitrate ($Zn(NO_3)_2.6H_2O$, 98%), hexamethylenetetramine (HMTA, $C_6H_{12}N_4$, 99%) were supplied by Sigma Aldrich; and sodium citrate ($C_6H_5Na_3O_7.2H_2O$, 98%) was purchased from Showa Chemicals.

Synthesis of PdAu Alloy NPs. The PdAu nanoparticles (NPs) were prepared based on previous literature with few modifications [30]. Initially, 44.0 mL of CTAB (15 mM) and 5.0 mL of CTAC (15 mM) aqueous solutions were mixed with each other in a 100 mL glass vessel. Then, 0.625 mL of Pd^{2+} (10 mM) and 0.625 ml of Au^{3+} (10 mM) precursors were added to above solution and stirred for 20 min at room temperature. 237.5 µL of Na_3-citrate (100 mM) was next added to the obtained solution and stirred for 10 min. After that, the glass was carefully sealed and heated at 90°C in oven. Three different chemical composition of PdAu alloy NPs ($Pd_{20}Au_{80}$, $Pd_{35}Au_{65}$, $Pd_{50}Au_{50}$) were obtained by setting up the reaction times for 16, 24 and 32 h.

Synthesis of PdAu_{alloy}@ZnO CSNPs. Firstly, 0.1465 g CTAB were wholly dissolved in 60 ml of distilled water in a 100 mL glass vessel. Secondly, 5 ml of obtained PdAu colloid and 0.0354 g of ascorbic acid were added to above solution with stirring. Thirdly, 0.12 g of Zn $(NO_3)_2 \cdot 6H_2O$ and 0.0564 g of HMTA were also introduced and stirred for 15 min at room temperature. Finally, the above glass was carefully sealed and heated at 86°C for 8 h in oven. After the reaction completion, the precipitates were centrifuged at 15,000 PRM for 20 min, washed with distilled water for several times to wholly delete the surfactants, and dried at 60°C for overnight. The selected powders were calcined at 500°C for 2 h in air to obtain $PdAu_{alloy}$@ZnO core-shell sensing materials with the different cores composition such as $Pd_{20}Au_{80}$@ZnO, $Pd_{35}Au_{65}$@ZnO, $Pd_{50}Au_{50}$@ZnO, respectively. Pure ZnO was also prepared using above method without adding PdAu colloids.

Characterizations. Sensing materials morphologies were observed using high-resolution transmission electron microscopy (TEM, JEOL, JEM-2010) with 200 kV accelerating voltage. The materials were dropped onto a carbon coated copper grid and dried at 100°C overnight. Their crystalline structures were measured using X-ray diffractometry (XRD, D/Max 2005, Rigaku) with CuK_{α} radiation ($\lambda = 1.54178$ Å). The Pd/Au molar ratio was measured by inductively coupled plasma mass spectrometry (ICP-MS-7500, Shimadzu) after the samples were treated with aqua regia at 100 °C for 10 h and were carefully filtered to remove solid components. UV-vis transmission spectroscopy (Agilent/HP 8453 UV-vis Spectrophotometer, Agilent Technologies, USA) was recorded at room temperature in the range of 350–750 nm using water as a blank reference sample. X-ray photoelectron spectroscopy (XPS; Multilab 2000, Thermo Fisher Scientific, USA) was carried out by using monochromated Al Kα X-ray photon (hν = 1,486.6 eV) sources to investigate the surface chemical states of the elements existing in the prepared catalysts. The binding energies of the adventitious carbon (C 1s) peak located at around 285 eV were used for calibration of the other peaks.

Device Fabrication and Measurement. 0.02 g sensing powder was uniformly grounded and mixed with one drop α-terpineol, then was pasted over the interdigitated circuit alumina board (area = 10 mm ×10 mm) with platinum electrodes (Ogam Technology Co. Ltd.) as shown in **Fig. S10a**. The fabricated devices were dried at 60°C overnight and was then annealed at 500°C in argon atmosphere for 2 h with a heating rate of 1°C/min. The gas sensing properties for the prepared devices were investigated in the temperature range of 200–400°C. The gas sensing test is a system created to reproduce environmental conditions, in which the sensor devices are evaluated. Each sensor was separately evaluated using the same procedure in a high dynamic chamber, at which the target gas was mixed with nitrogen (background gas) and dry air (21% oxygen). **Fig. S10b** illustrates the experimental gas sensing setup. The whole gas flow rate in the mass flow controller (MFC) was constantly maintained at 100 sccm by the computer management. The resistance change of the sensors during gas testing was recorded using a high resistance meter (Agilent 34970A). The gas sensing response (R_s) was defined as R_a/R_g, where, R_a and R_g are the sensor resistance in dry air and target gas, respectively.

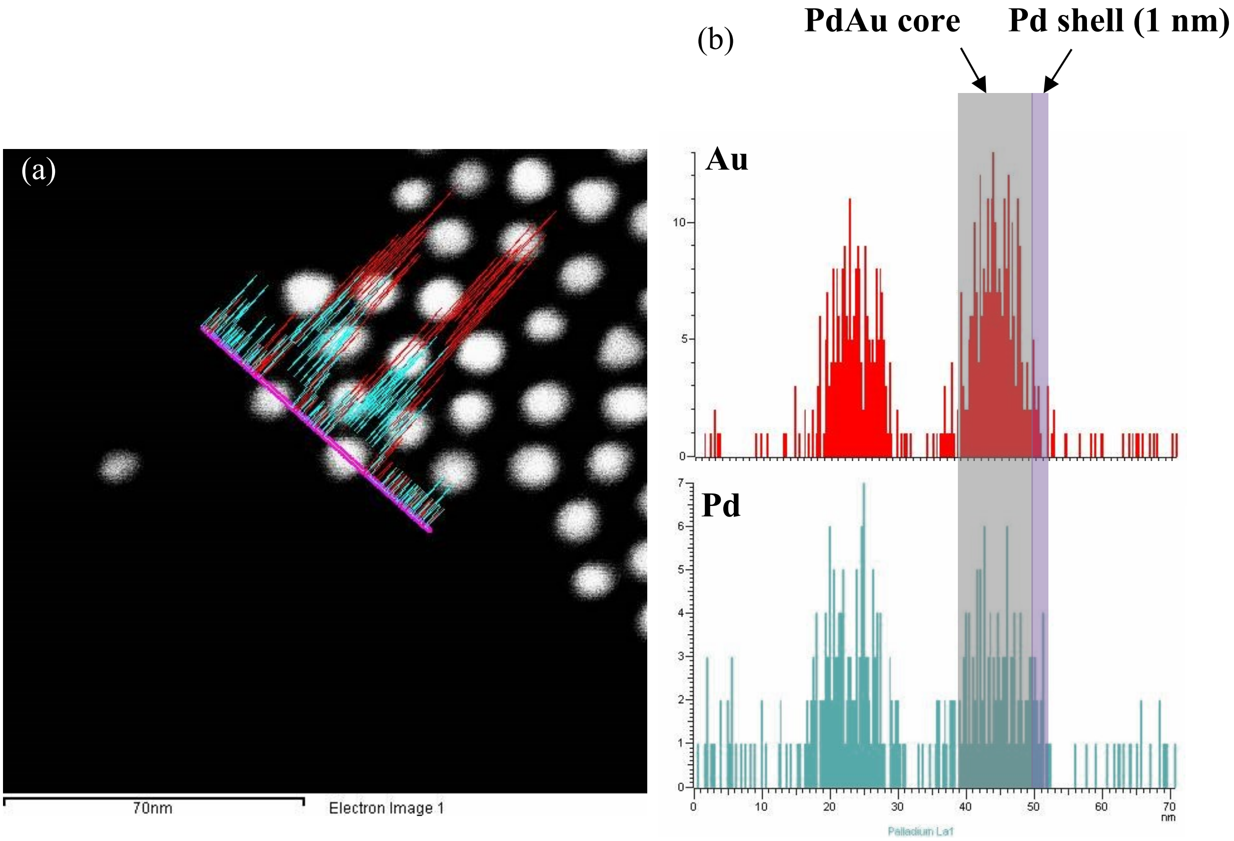

Fig. S1 (a) Dark field TEM and (b) EDS line-scanning profiles confirmation for $Pd_{50}Au_{50}$@ZnO core-shell nanostructure.

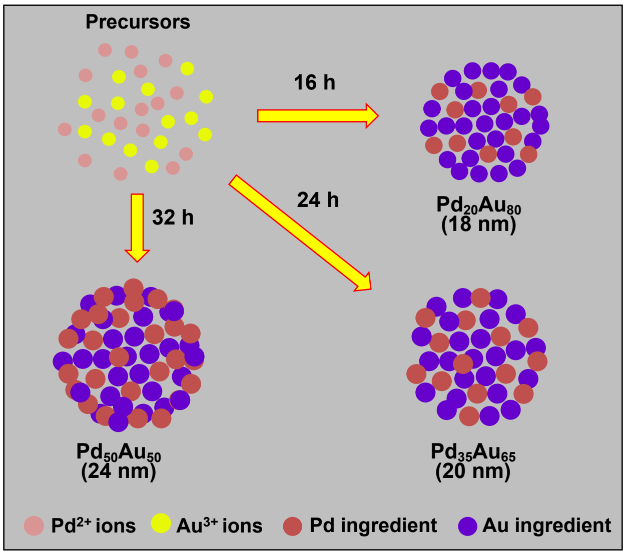

Fig. S2 Possible time-dependent formation mechanism of PdAu bimetallic compositions.

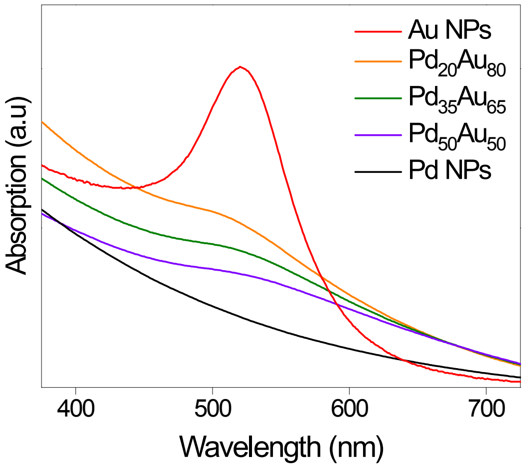

Fig. S3 UV-vis spectra of the synthesized PdAu colloids and its counterparts in water.

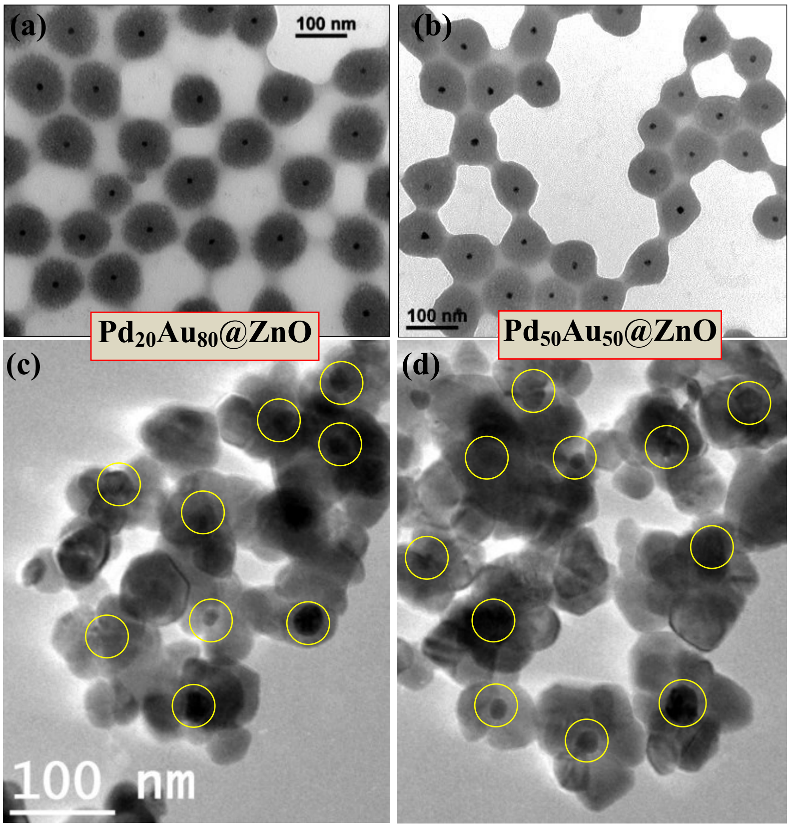

Fig. S4 TEM analysis of $Pd_{20}Au_{80}$@ZnO and $Pd_{50}Au_{50}$@ZnO (a, b) before and (c, d) after calcination.

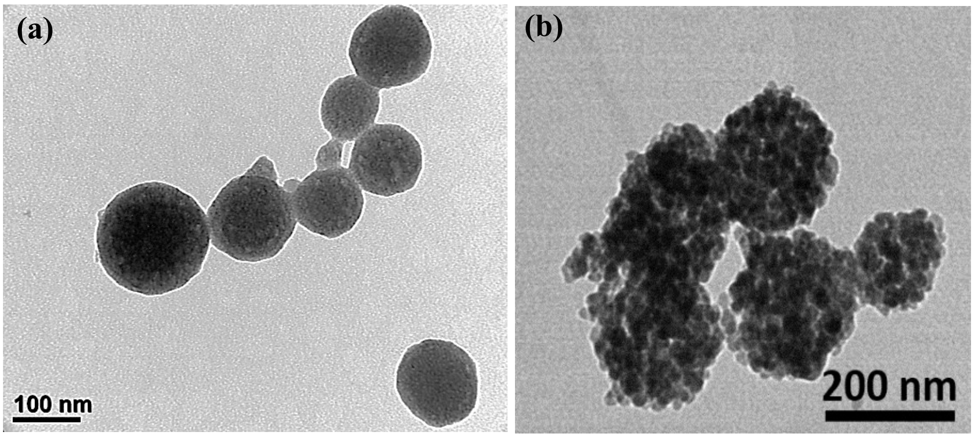

Fig. S5 TEM analysis of pure ZnO (a) before and (b) after calcination.

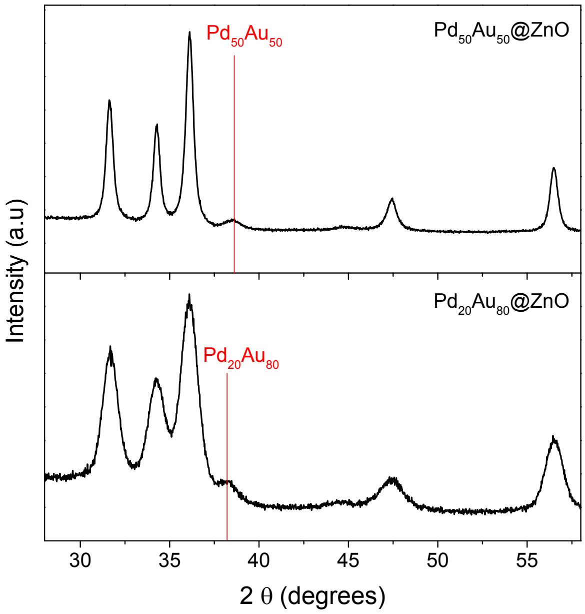

Fig. S6 XRD of as-calcined $Pd_{20}Au_{80}$@ZnO and $Pd_{50}Au_{50}$@ZnO core-shell materials.

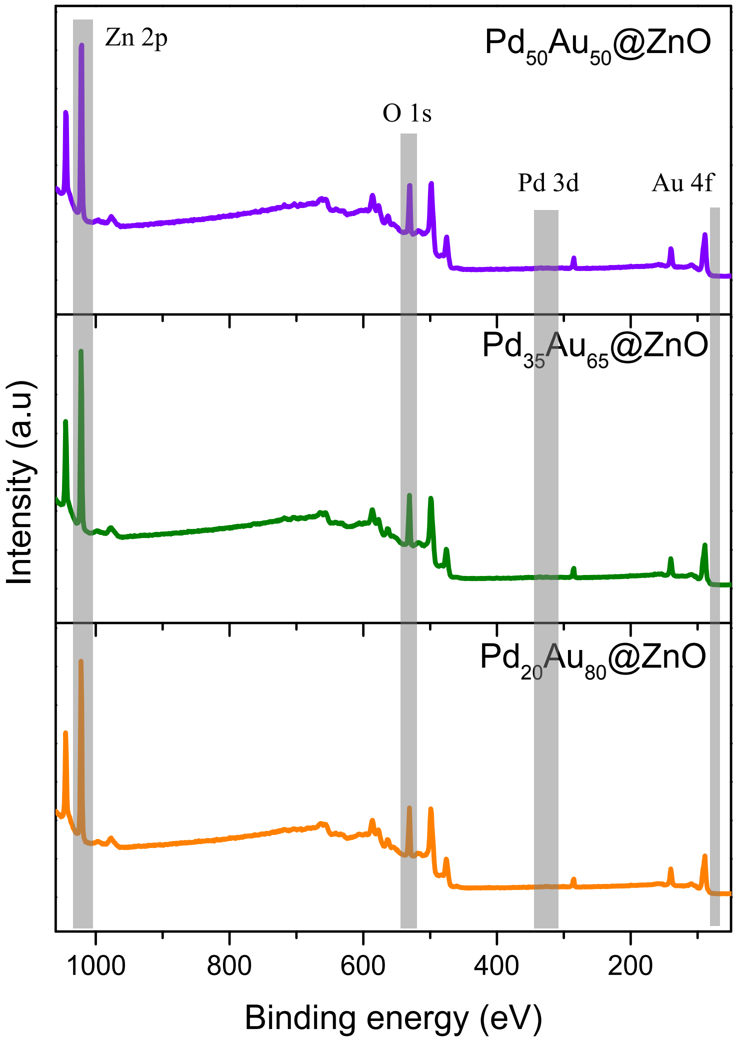

Fig. S7 XPS full range of as-calcined $Pd_{20}Au_{80}$@ZnO, $Pd_{35}Au_{65}$@ZnO and $Pd_{50}Au_{50}$@ZnO samples.

Table S1 Pd species contents in $PdAu_{alloy}$@ZnO core-shell materials

Samples	Pd species contents (%)		
	Metallic Pd^0	PdO*	Ionic Pd^{2+}
$Pd_{20}Au_{80}$@ZnO	73.20	9.52	17.28
$Pd_{35}Au_{65}$@ZnO	71.92	11.14	16.94
$Pd_{50}Au_{50}$@ZnO	63.52	23.53	12.95

* The content of PdO is calculated by normalizing its XPS peak areas for (Pd^0 + PdO + Pd^{2+}) peak areas.

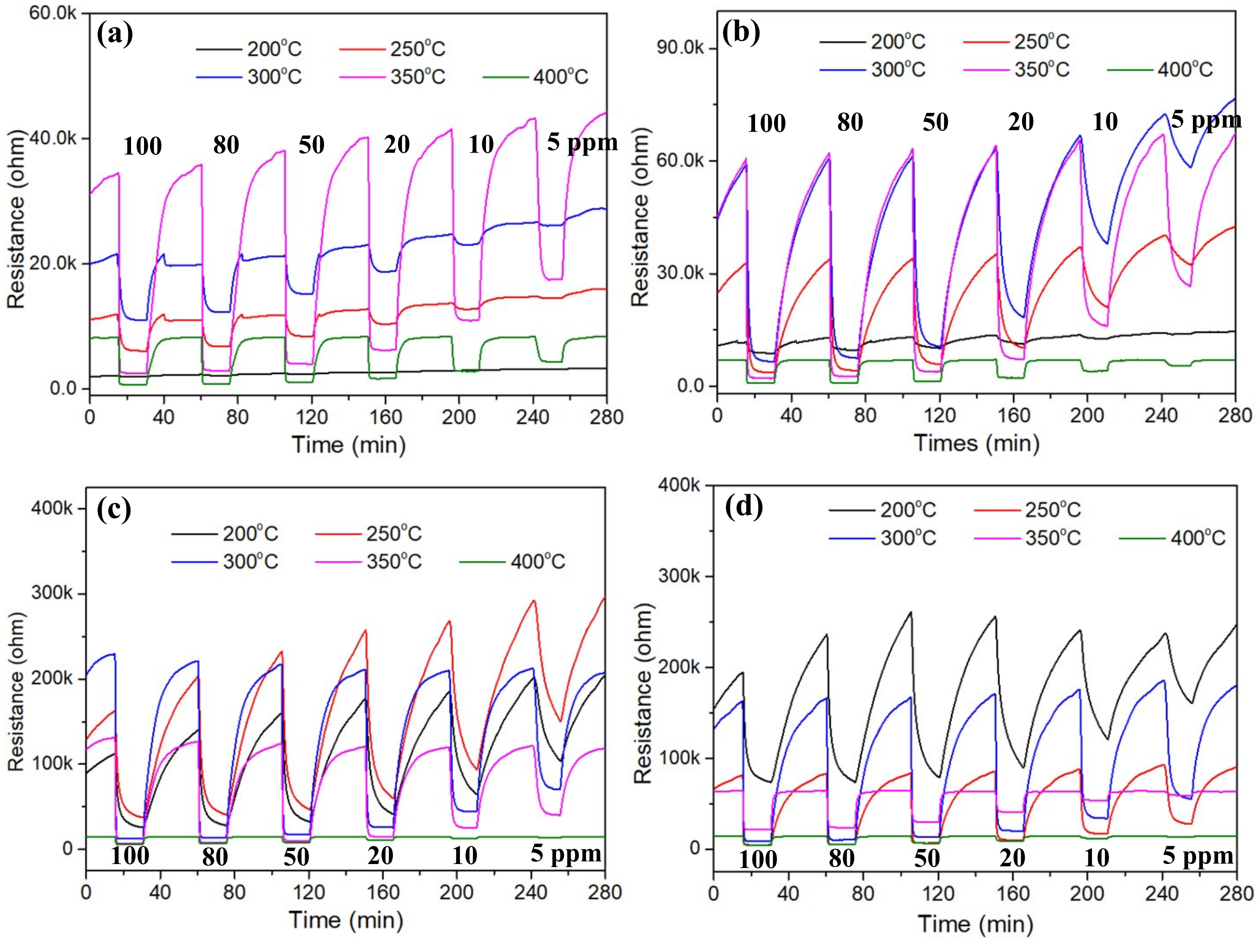

Fig. S8 Dynamic sensing curve to 5-100 ppm hydrogen at different working temperatures for (a) as-calcined ZnO, (b) $Pd_{20}Au_{80}$@ZnO, (c) $Pd_{35}Au_{65}$@ZnO and (d) $Pd_{50}Au_{50}$@ZnO sensors.

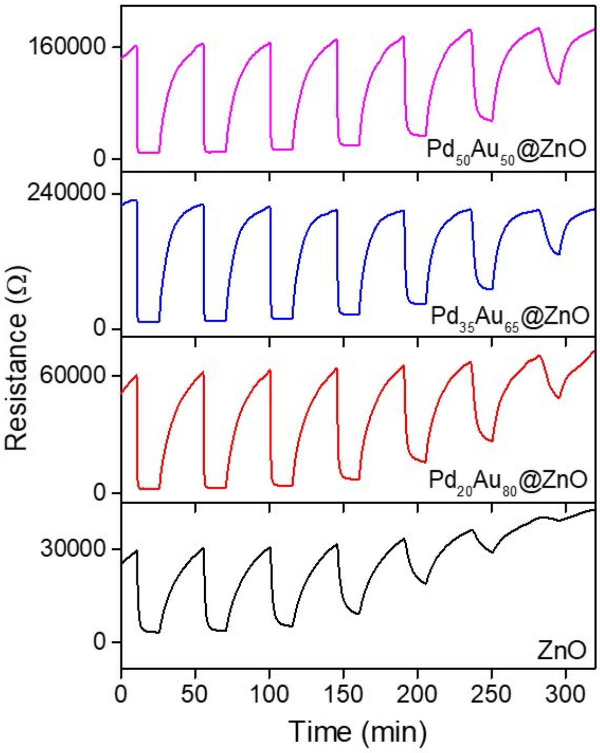

Fig. S9 Dynamic sensing curve to 5-100 ppm hydrogen for as-calcined ZnO, $Pd_{20}Au_{80}$@ZnO, $Pd_{35}Au_{65}$@ZnO and $Pd_{50}Au_{50}$@ZnO sensors at their optimal working temperatures.

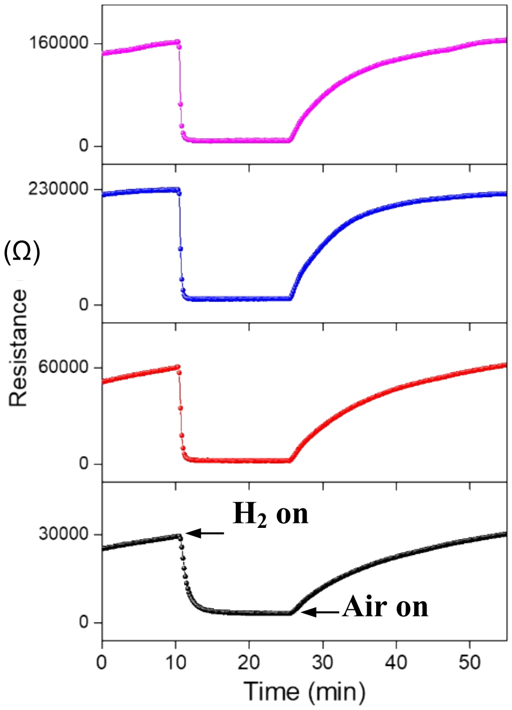

Fig. S10 Sensing response and recovery properties to 100 ppm hydrogen for as-calcined ZnO, $Pd_{20}Au_{80}$@ZnO, $Pd_{35}Au_{65}$@ZnO and $Pd_{50}Au_{50}$@ZnO sensors at their optimal working temperatures.

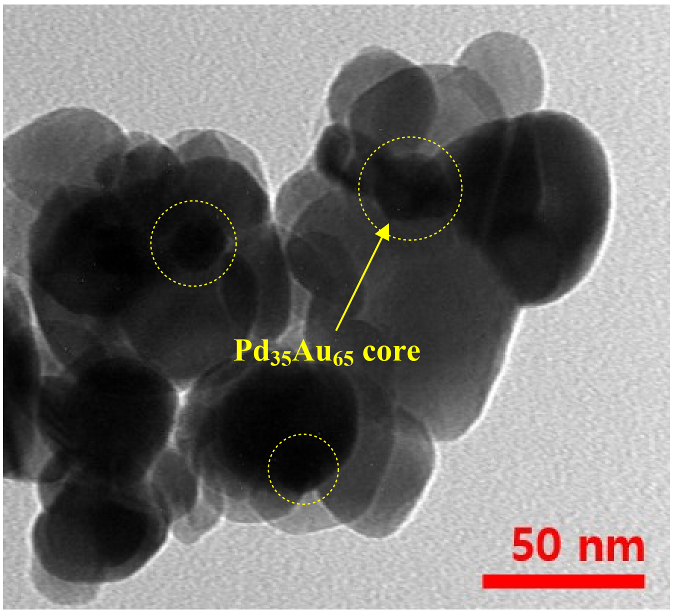

Fig. S11 TEM analysis of used $Pd_{35}Au_{65}$@ZnO materials after sensing activity.

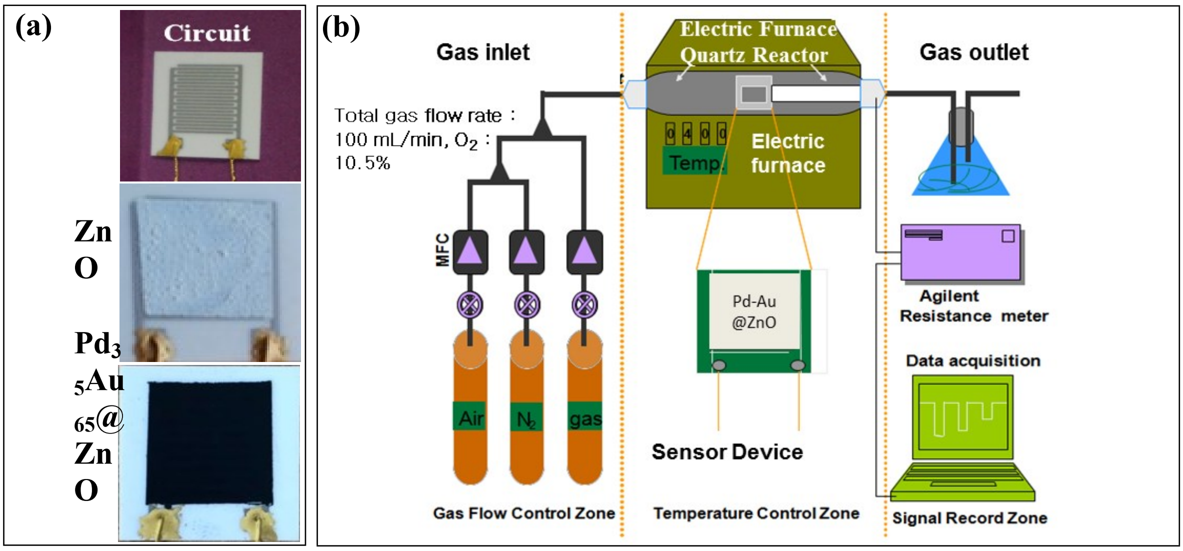

Fig. S12 (a) Circuit and prepared sensors, and (b) sensing system setup.