# Electronic Supplementary Information

## Interface Engineering of Palladium and Zinc Oxide Nanorods with Strong Metal-Support Interaction for Enhanced Hydrogen Production from Base-free Formaldehyde Solution

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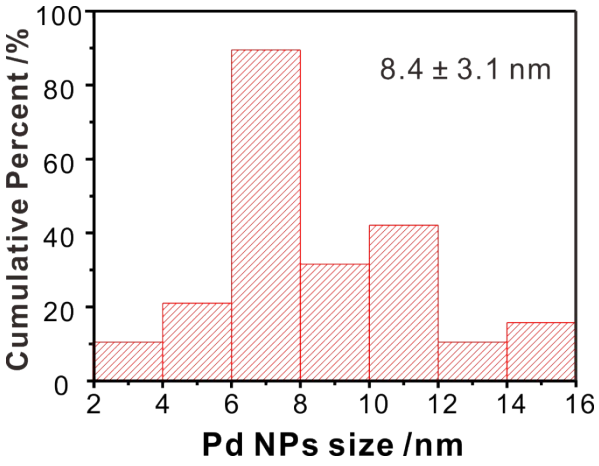


**Figure S1.** The size distribution of Pd NPs.

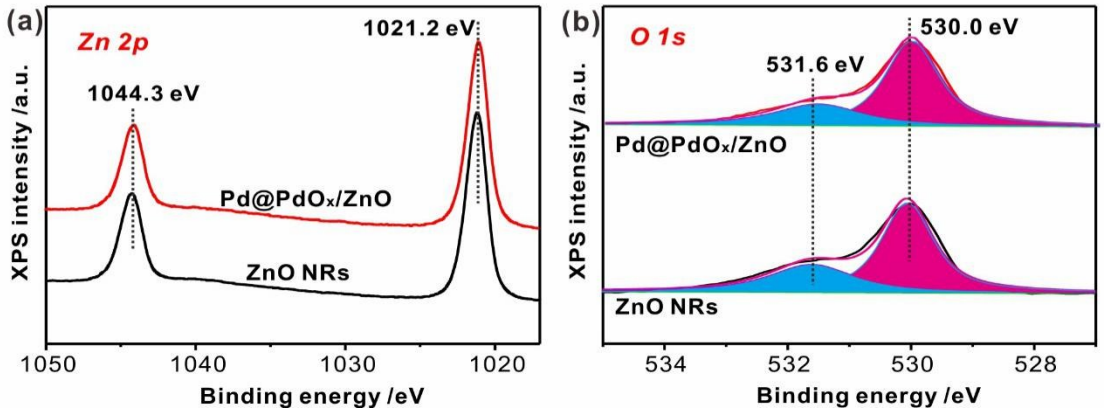


**Figure S2.** (a) Zn 2p and (b) O 1s XPS spectra of ZnO nanorods and Pd@$PdO_x$/ZnO.

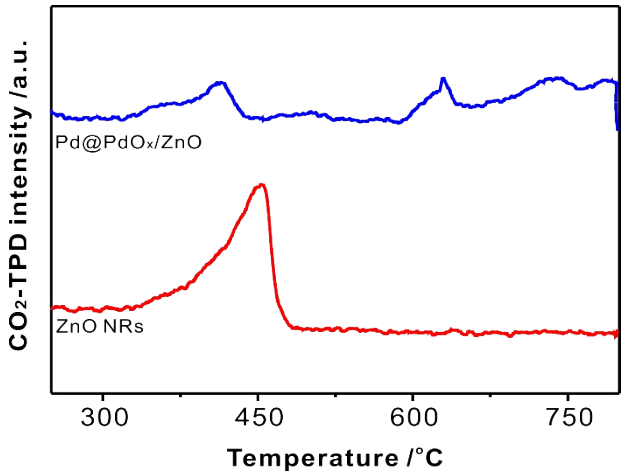


**Figure S3.** The $CO_2$-TPD spectra of ZnO nanorods and Pd@$PdO_x$/ZnO..

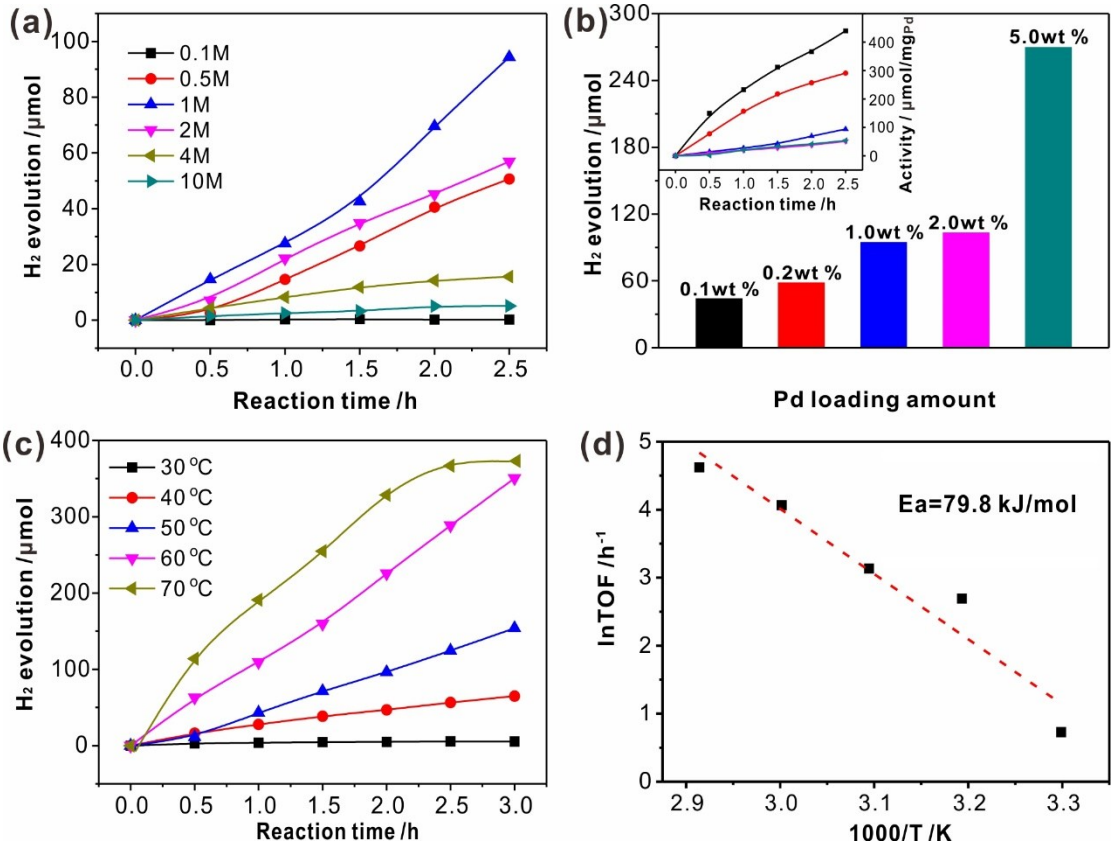


**Figure S4.** The effect of (a) formaldehyde concentration, (b) Pd loading amount (inset shows the Pd@$PdO_x$/ZnO mass activity, t = 50 °C) and (c) reaction temperature on the rate of $H_2$ evolution; (d) corresponding Arrhenius plots. All catalytic $H_2$ production experiments were carried out in $N_2$ atmosphere.

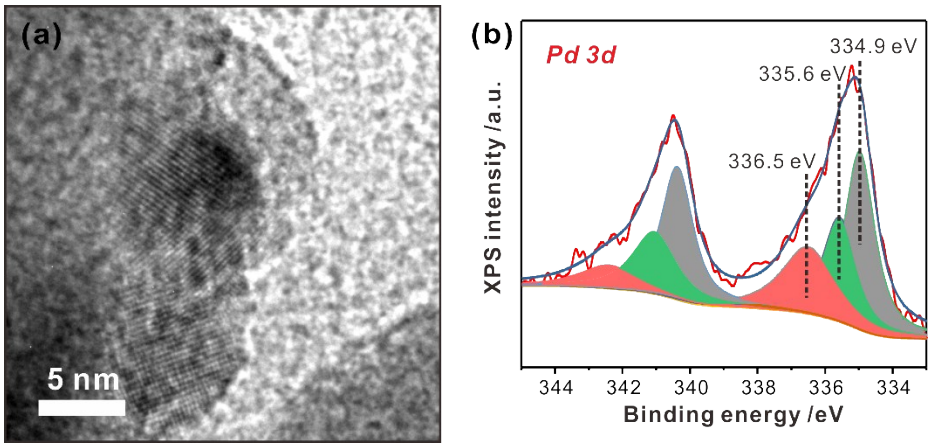


**Figure S5.** (a) HR-TEM image and (b) Pd 3d XPS spectrum of the Pd@$PdO_x$/ZnO catalyst after reaction.

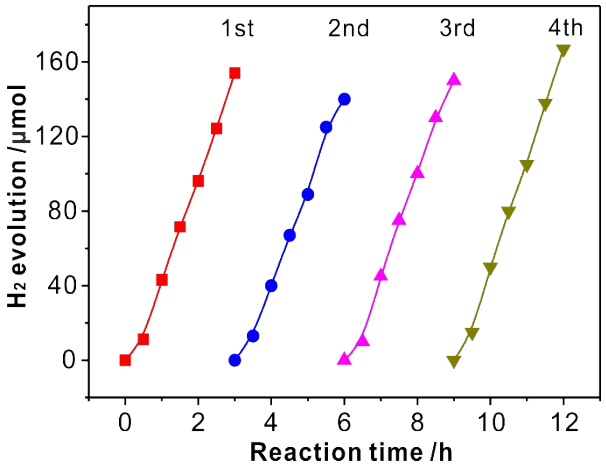


**Figure S6.** The cycle performance of the Pd@$PdO_x$/ZnO catalyzes the hydrogen production of formaldehyde solution.

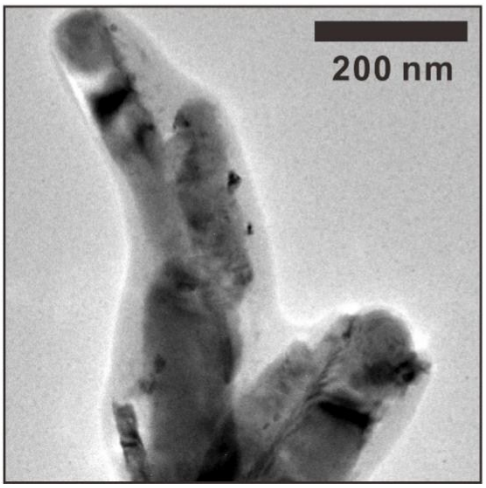


**Figure S7.** TEM image of ZnO/Pd@$PdO_x$/ZnO.

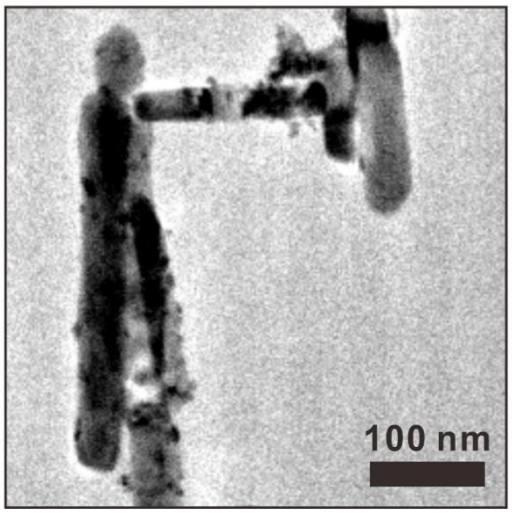


**Figure S8.** TEM image of PdPt@$PdO_x$/ZnO.

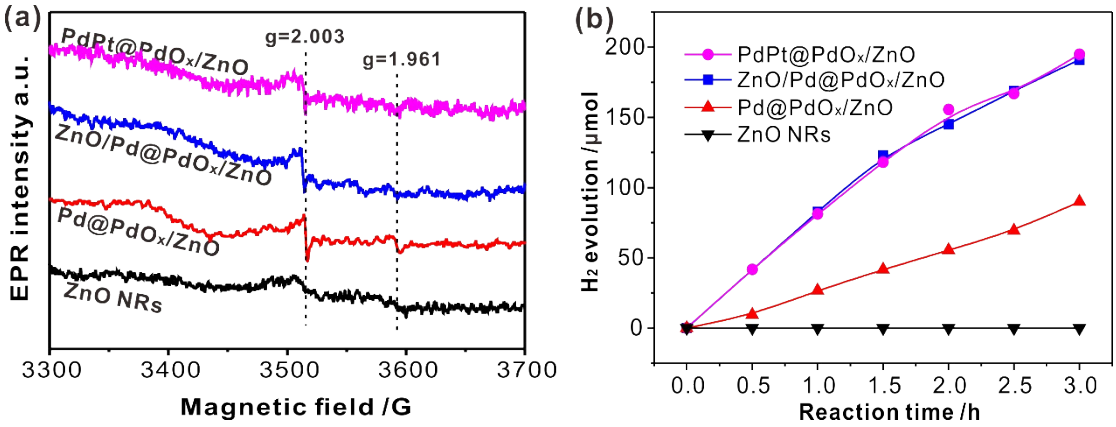


**Figure S9.** (a) Solid EPR spectra of different samples carried out at 25 °C in open air and (b) corresponding samples catalyzed $H_2$ evolution from HCHO solution.

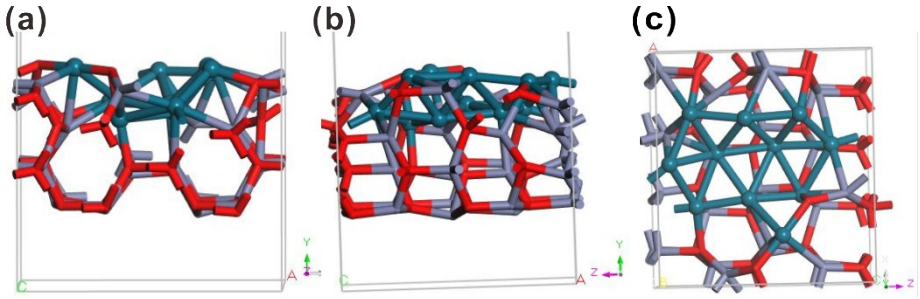


**Figure S10.** (a-c) Three views of $Pd_{11}(ZnO)_{26}$ unit cell from different directions.

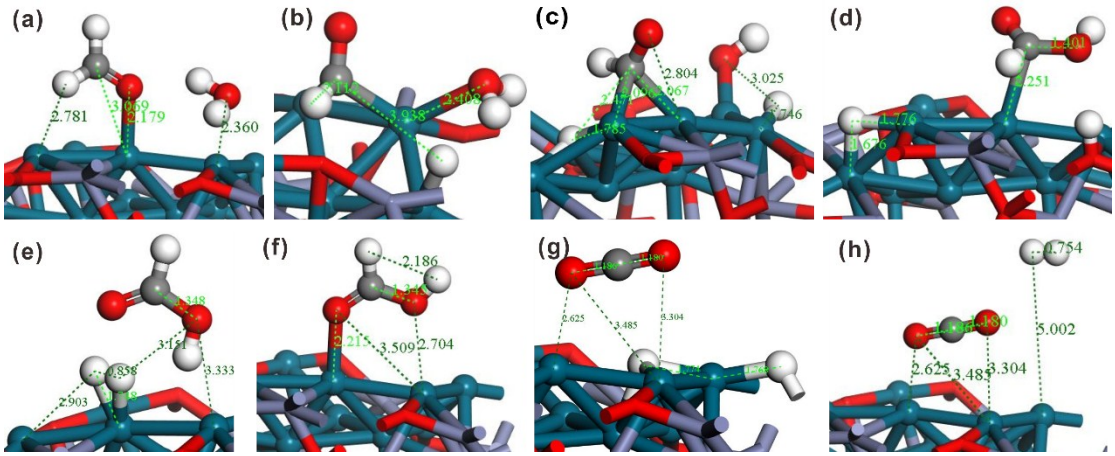


**Figure S11.** (a) Optimized structure for $H_2CO$ and $H_2O$ (Conf.#1). (b) Optimized structure for H, HCO, and $H_2O$ (Conf.#3). (c) Optimized structure for HCO, OH and two H (Conf.#5). (d) Optimized structure for two H and HCOOH (Conf.#7). (e) Optimized structure for $H_2$ formed from two adsorbed H atoms, and generated HCOOH (Conf.#9). (f) Optimized structure for HCOOH (Conf.#10). (g) Optimized structure for 2H and generated $CO_2$ (Conf.#12). (h) Optimized structure for weakly adsorbed $H_2$ and $CO_2$ (Conf.#14).