

## Electronic Supporting Information

### Highly efficient redox-driven reversible color switching of dye molecules via hydrogenation/oxygenation

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## **S1 Experimental section**

### **1.1 Materials**

Sodium hydroxide (NaOH) and absolute ethanol were obtained from Sinopharm Chemical Reagent and used as obtained. Cerium (III) nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), sodium tetrachloropalladate ( $\text{Na}_2\text{PdCl}_4$ ), thionine ( $\text{TH}^+$ ) and hydroxyethyl cellulose (HEC) were bought from Aldrich and used without further purification. Water was purified using ion exchange (MilliQ, Millipore, 18 M $\Omega$  cm), and used as deionized water.

### **1.2 Synthesis of $\text{CeO}_2$ nanorods**

Briefly, 47 mL of 9.5 M NaOH aqueous solution was added dropwise into 28 mL of 0.14 M  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  solution under vigorous stirring. Then, the mixture was kept stirring under room temperature for 30 min to form a milky slurry. Subsequently, the mixture was transferred into a 100 mL Teflon-lined steel autoclave which was heated to 100 °C and the reaction proceeded for 24 h. After cooling down to room temperature naturally, the white precipitates were collected by centrifugation and then washed several times with deionized water and absolute ethanol, followed by drying at 60 °C in a vacuum oven. Finally, the resulting solids were calcined at 400 °C in the air for 2 h with a heating rate of 2 °C min<sup>-1</sup>, and pale yellow  $\text{CeO}_2$  nanorods were obtained.

### **1.3 Preparation of $\text{CeO}_{2-x}$ supported palladium catalyst**

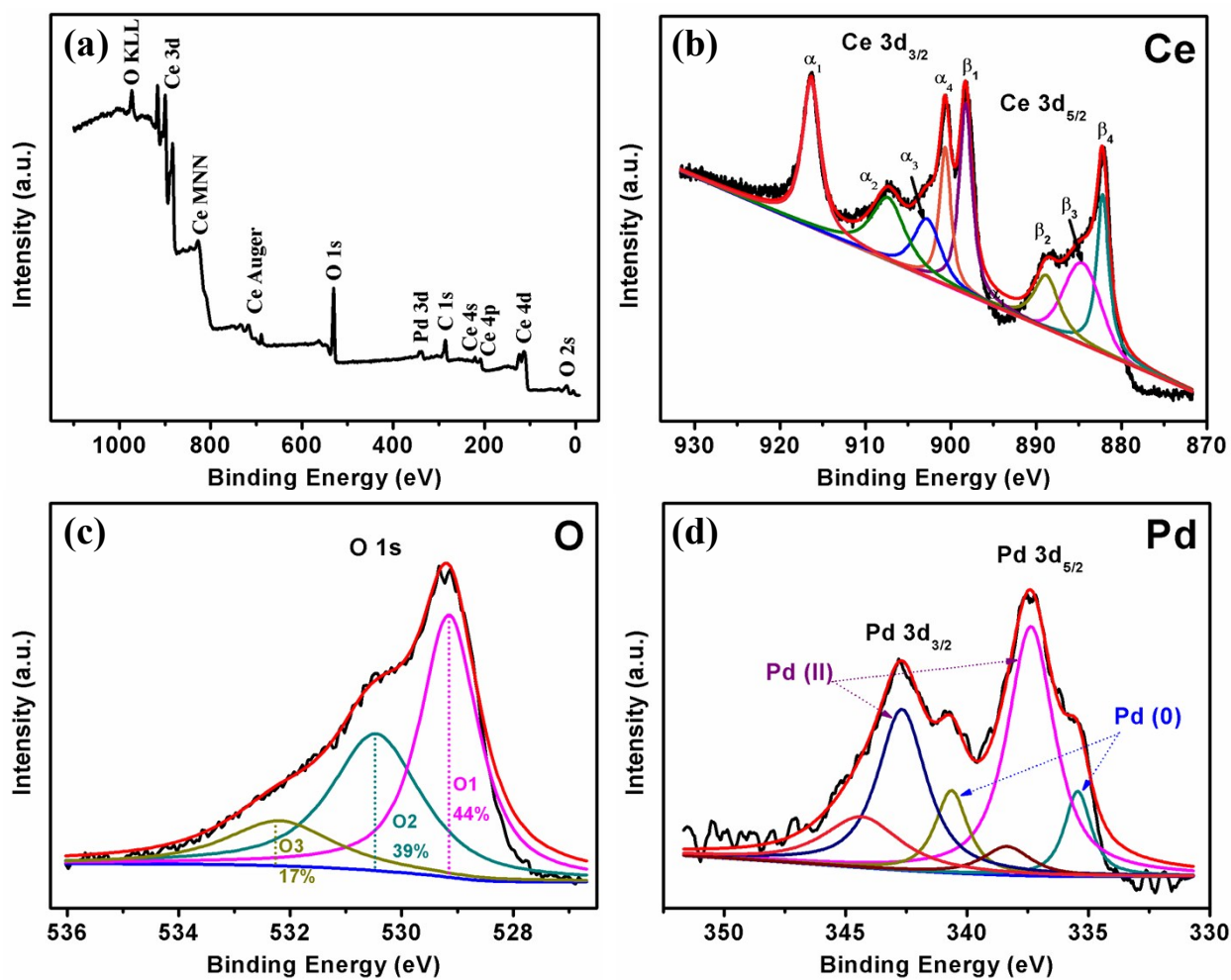
The  $\text{CeO}_{2-x}$  supported palladium catalyst was fabricated using  $\text{CeO}_2$  nanorods as supports and  $\text{Na}_2\text{PdCl}_4$  as the palladium source by aqueous impregnation and calcination method. Typically, 100 mg of  $\text{CeO}_2$  nanorods was dispersed in 50 mL deionized water by stirring and ultrasonic treatment. Then, 2.8 mL of  $\text{Na}_2\text{PdCl}_4$  (10 mM) was added dropwise to the above solution under constant stirring, and the mixture was stirred for 10 h at room temperature. The products were centrifuged from the suspension solution and washed three times with deionized water and absolute ethanol, then dried at 60 °C in a vacuum oven overnight. Finally, the solid products were calcined at 250 °C for 2 h in a tubular furnace, with a heating rate of 5 °C min<sup>-1</sup> under (5%)  $\text{H}_2/\text{Ar}$  atmosphere. After cooling to room temperature, the resulting dark brown catalyst was collected.

#### **1.4 The hydrogenation/oxidative dehydrogenation reversible color switching of TH<sup>+</sup>/LTH over Pd/CeO<sub>2-x</sub>**

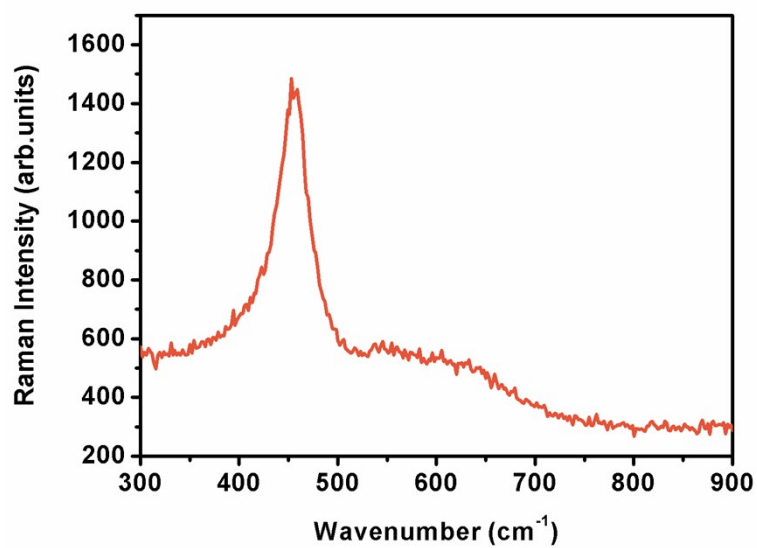
The HEC solution was prepared by dissolving 2 g of HEC in 100 mL H<sub>2</sub>O under stirring. Typically, 1 mL Pd/CeO<sub>2-x</sub> nanorods dispersion (0.5 mg mL<sup>-1</sup>), 4 mL thionine solution (1 mM) and 35 mL HEC solution were mixed together under stirring to form a mixture solution. Prior to the measurements, the above solution was degassed by bubbling nitrogen for at least 20 min. The hydrogenation/oxidation reactions typically started with a hydrogen/oxygen flow rate of 10 mL min<sup>-1</sup> controlled by a mass flow meter (D07-19B, sevenstar electronics Co., Ltd. Beijing). UV-vis spectrometry was applied to monitor the color switch reaction progress of thionine, by measuring the solution absorbance from 700 to 400 nm as a function of time.

#### **S2 Characterization**

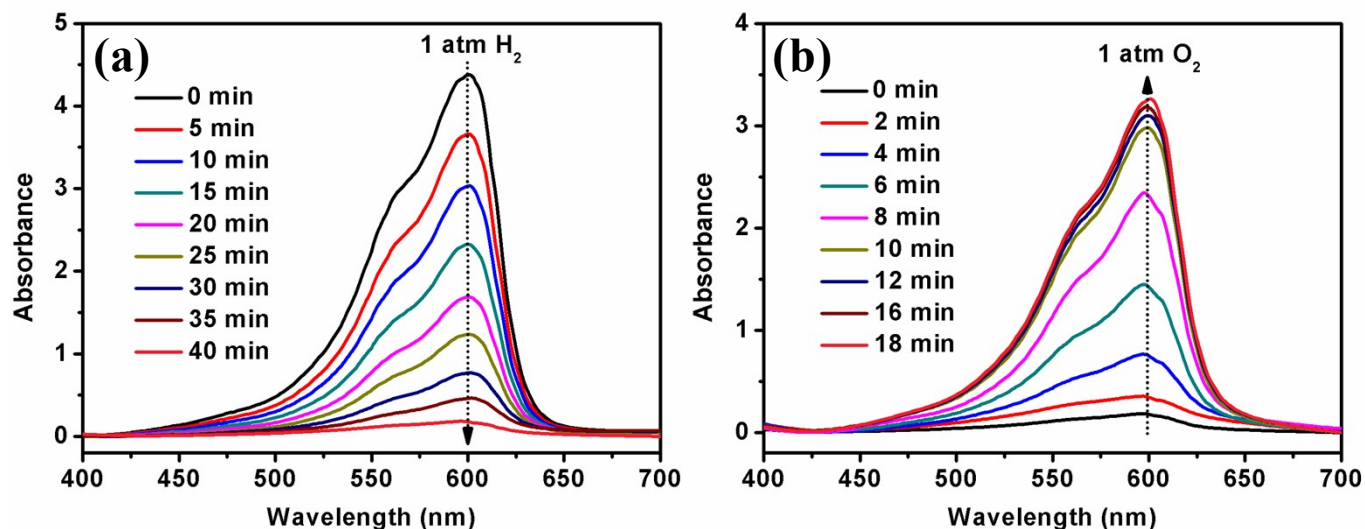
Powder X-ray diffraction (XRD) measurements of the prepared catalysts were done by a Philips X'Pert Pro Super X-ray diffractometer equipped with Cu K $\alpha$  irradiation ( $\lambda = 1.54178 \text{ \AA}$ ). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken on JEM-2010 microscope with an accelerating voltage of 200 kV. Energy disperse spectroscopy (EDS) analysis was performed on an environmental scanning electron microanalyzer (QUANTA 200) equipped with an Oxford EDS detector. The X-ray photoelectron spectroscopy (XPS) was measured using the Photoemission Endstation in the National Synchrotron Radiation Laboratory (NSRL, Hefei, P. R. China). The UV-vis absorption spectra were tested on a Shimadzu UV-2510 spectrophotometer in the region of 400 to 700 nm. The actual content of Pd in the Pd/CeO<sub>2-x</sub> was characterized by inductively coupled plasma-mass (ICP-MS) optical emission spectroscopy on the optima 7300 DV, PerkinElmer.



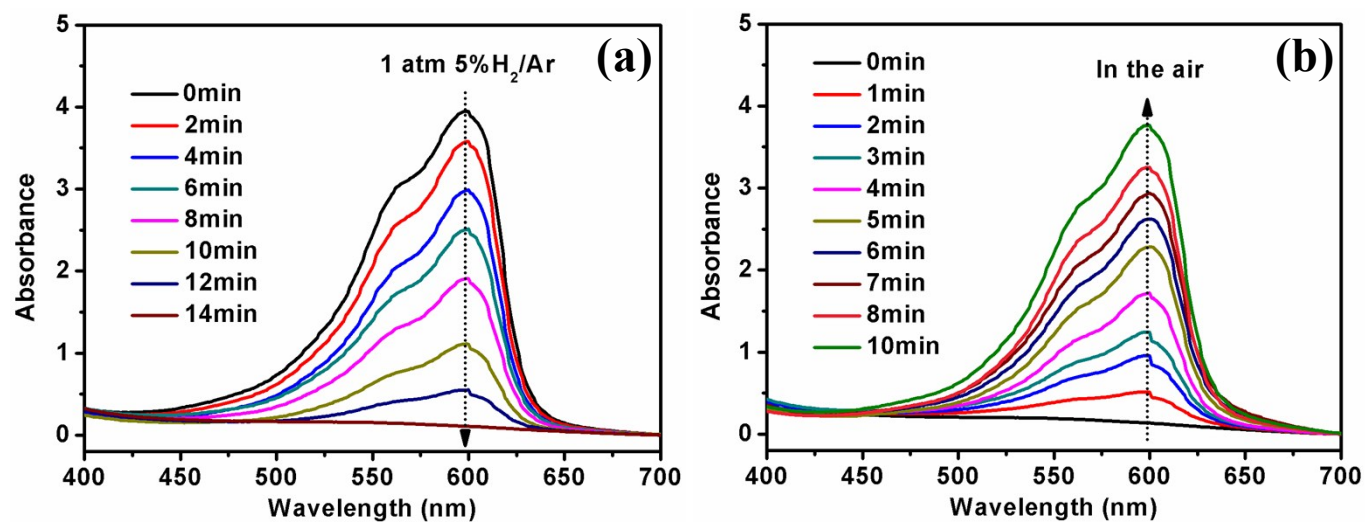
**Fig. S1** XPS spectra of 2.36 wt%Pd/CeO<sub>2-x</sub> sample: (a) survey spectrum, (b) Ce 3d XPS spectrum, (c) O 1s XPS spectrum and d) Pd 3d XPS spectrum.



**Fig. S2** The Raman spectrum of the 2.36 wt%Pd/CeO<sub>2-x</sub> sample measured at room temperature.



**Fig. S3** UV-vis spectra of Pd/commercial CeO<sub>2</sub>/thionine/HEC/water solution in response to 1 atm H<sub>2</sub> and O<sub>2</sub>: (a) UV-vis spectra of the decoloration process under 1 atm H<sub>2</sub> and (b) UV-vis spectra of the recoloration process under 1 atm O<sub>2</sub> at room temperature.



**Fig. S4** Color switching of 2.36 wt%Pd/CeO<sub>2-x</sub>/thionine/HEC/water system in response to 1 atm 5%H<sub>2</sub>/Ar and air: (a) UV-vis spectra of the decoloration process under 1 atm 5%H<sub>2</sub>/Ar and (b) UV-vis spectra of the recoloration process in the air.