

Supplementary information

A new type of gasochromic materials: Conducting polymers with catalytic nanoparticles

Chih-Wei Hu,* Yasusei Yamada and Kazuki Yoshimura

Structural Materials Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 2266-98, Anagahora, Shimo-Shidami, Moriyama-ku, Nagoya, Aichi 463-8560, Japan.

*Corresponding Author:

E-mail: chih-wei.hu@aist.go.jp

Supporting information

1. Materials

Aniline (99.0 %), hydrogen chloride (HCl, 37.0 %), ammonium persulfate (APS, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 98.0 %), hydrogen hexachloroplatinate(IV) hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 98.5+ %), isopropyl alcohol (IPA, 99.7 %), propylene carbonate (PC, 99.5 %), toluene (99.0 %), potassium trifluorosulfonimide (KTFSI, $\text{K}(\text{CF}_3\text{SO}_2)_2\text{N}$, 98 %) were purchased from Wako Pure Chemical Industries. Tetra(decyl)ammonium bromide ($\text{C}_{40}\text{H}_{84}\text{BrN}$, >98.0 %), dodecylamine ($\text{C}_{12}\text{H}_{27}\text{N}$, >97.0 %), sodium borohydride (NaBH_4 , >95.0 %) were obtained from Tokyo Chemical Industry co. Ltd, Japan (TCI). Poly(sodium 4-styrenesulfonate) (Na:PSS, $M_w \sim 70,000$) was obtained from Aldrich Chemicals. All chemicals were used without any additional purification.

2. Characterisation

The nanoparticle size distribution was recorded by dynamic light scattering instrument from Otsuka Electronics (ELSZ-1000). X-ray photoelectron spectroscopy (XPS) analysis was done using a Thermo Scientific™ Sigma Probe Spectrometer system. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4300. Atomic force microscopy (AFM) images were available by using Keyence VN-8010, nanoscale hybrid microscope). Cyclic voltammetry (CV) analysis was performed with a potentiostat (Solartron Analytical, model 1280C), using a three-electrode cell. The

working electrode for CV measurements was ITO/PANI:PSS/PtNPs and the counter electrode was a platinum sheet (1.0 cm × 3.0 cm). An Ag/AgCl electrode (RE-1B, ALS Co., Ltd, Japan) was used as the reference electrode. UV-vis-NIR spectra (wavelength 370 ~ 2500 nm) were obtained using a Hitachi U-4100, *in situ* UV-vis spectra were obtained using a spectrometer from Ocean Optics (USB-4000) and a light source from Ocean Optics (DH-2000). A Perkin Elmer (Frontier) spectrometer was used to obtain FTIR spectra. H₂ gas (100%) was obtained directly from a hydrogen generator (H-TEC education, electrolyser 65; the hydrogen production speed was 65 cm³/min). Ozone generator (Soec V350) was produced by Maruco, Japan and ozone gas output was set to be 20 mg/h, gas flow was 5 L/min. 4% H₂ gas is composed of 4% hydrogen and 96% argon gas.

3. Preparation of PANI:PSS

Aniline (1 mL) was added to a flat-bottomed flask containing HCl (4 mL) and deionized water (DIW) (10 mL) at 25 °C, and was stirred for 3 h for the aniline functionalisation reaction. Then, DIW (10 mL) containing Na:PSS (2 g) was added into the functionalized aniline solution, and stirred for 6 h to complete the electrostatic interaction between SO₃⁻ and NH₃⁺ groups. Finally, a solution of APS (10 mL, 0.1 M) was added into the reactor, and the solution changed colour from transparent and colourless to light green and finally became deep blue after 10 min (Scheme S1). Stirring was continued for 3 h to ensure complete reaction of the aniline. After the reaction, the resulting green precipitate was centrifuged at 15,000 rpm for 30 min and washed with DIW three times. The PANI:PSS slurry was obtained and then added of 30 mL DIW to form a PANI:PSS ink. This ink was used directly for spin-coating.

4. Preparation of PtNPs

H₂PtCl₆ · 6H₂O (104 mg, 0.2 mmol) was added to a flat-bottomed flask containing toluene (30 mL) and DIW (10 mL). The solution showed two layers; an upper transparent layer of toluene, and a yellow lower layer of DIW. Tetra(decyl)ammonium bromide (330 mg, 0.5 mmol) was added to the flask as a phase transfer catalyst and stirred for at least 6 h. After 6 h, the upper layer had become orange, and the lower DIW was colourless and transparent. Dodecylamine (690 mg, 4.4 mmol) was dissolved in toluene (3.5 mL), then added to the flask as a stabiliser for the nanoparticles. The colour of the solution was a uniform white. NaBH₄ (125 mg, 3.3 mmol) was first dissolved in DIW (10 mL) and added into the flask as an initiator for the synthesis of PtNPs. The solution quickly became brown, and stirring was continued for 1 h. All processes and reactions were carried out under an inert N₂ atmosphere.

The brown toluene solution was washed three times with DIW (300 mL) before it was added into ethanol (400 mL) and stored at -18 °C for 24 h. The brown precipitate was centrifuged (5000 rpm, 10 min) three times with ethanol. Finally, the brown precipitate was dried overnight in a vacuum oven to give the PtNPs product.

5. Preparation of PANI:PSS/PtNPs thin films

A flat glass slide (3 x 3 cm²) was cleaned in advance using isopropyl alcohol and a plasma cleaning machine. The PANI:PSS ink (150 μL) was dropped on the glass surface, and spun at 1000 rpm for 10 s and then 1500 rpm for 5 s. Then, the as-prepared glass/PANI:PSS films were placed on table at room temperature for 30 min. Next, the PtNPs ink (PtNPs in toluene, several of concentrations was used: 0.1, 0.05, 0.025, 0.01, 0.001 wt. %, 100 μL) was dropped on the PANI:PSS surface and spun at 500 rpm for 10 s, then 1000 rpm for 5 s. The glass/PANI:PSS/PtNPs thin films were stored in air, and the active area was restricted to 2 x 2 cm² by wiping away the excess material using a cotton bud.

For Fig. 2a and 2b, the PANI:PSS thin film was made by spray-coating method (supporting movie 2). Except that, all the other PANI:PSS thin films for characterization were made by spin-coating method as described above.

Except Fig. 4c, all the other measurement are depending on the PtNPs concentration of 0.1 wt. %.

ITO coated glass (thickness ~100 nm, 20 Ω □⁻¹) was used instead of a flat glass slide for CV measurements, but all other fabrication procedures remained the same.

6. Supplementary Information

Scheme S1: The synthetic mechanism of PANI:PSS

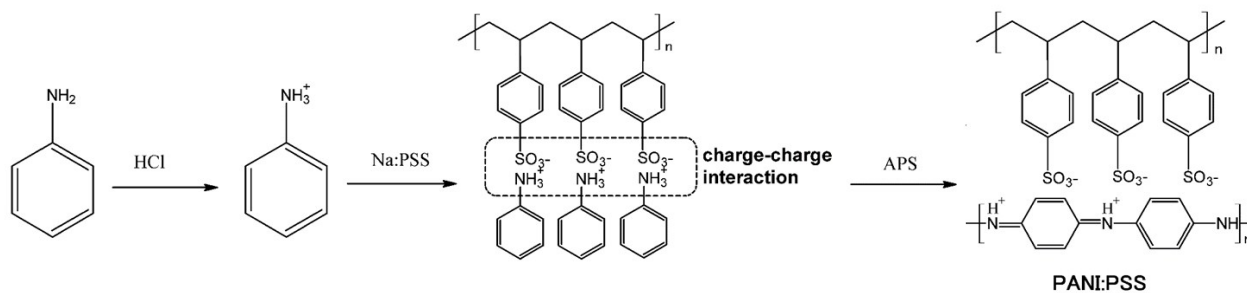


Figure S1: Size distribution of PtNPs

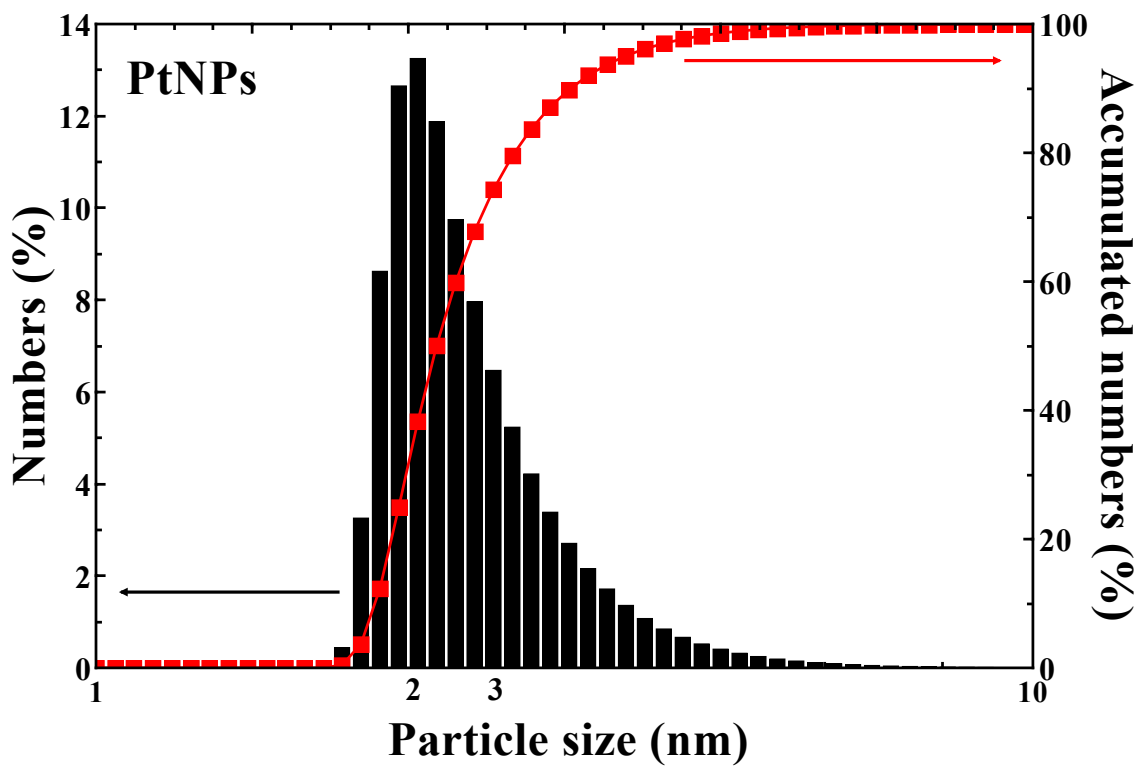


Fig. S1 Size distribution of the PtNPs. The average diameter was 2.6 ± 0.7 nm. The x-axis is displayed on a logarithmic scale. Most of the particles had diameters between 1–5 nm.

Figure S2: XPS analysis

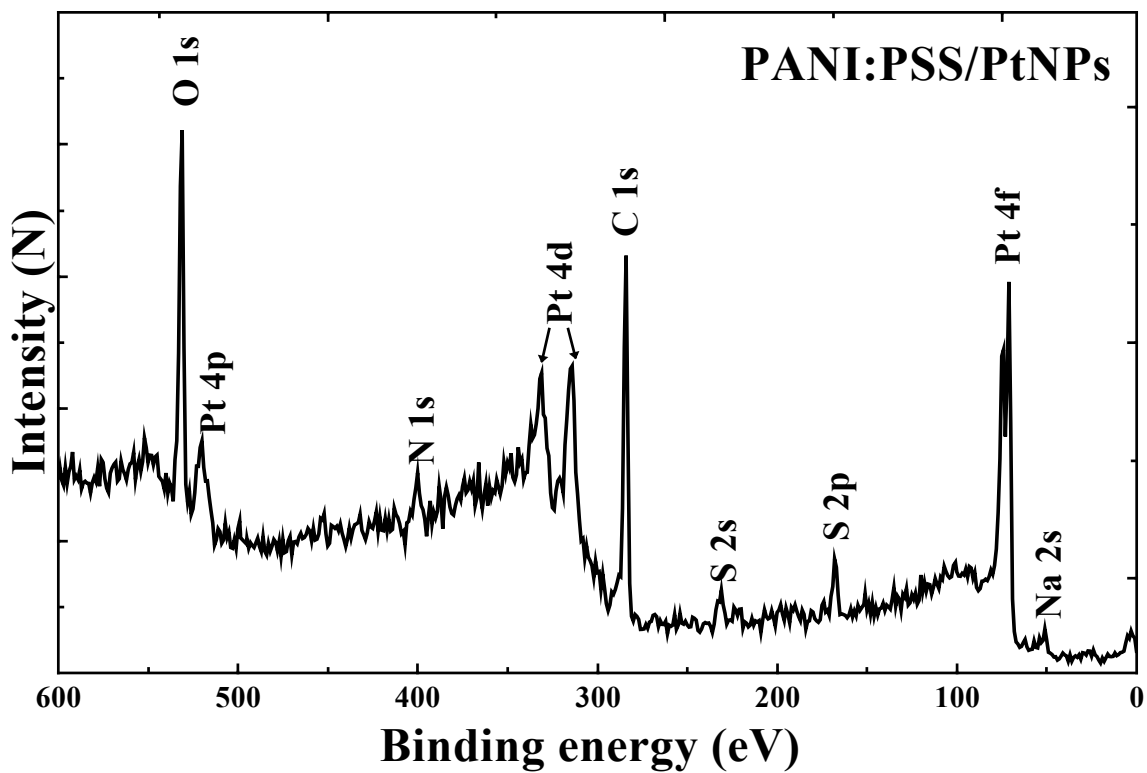


Fig. S2. Strong peaks corresponding to PtNPs were observed at various energies (Pt 4p, Pt 4d, Pt 4f). Peaks corresponding to PANI (N 1s and C 1s) and Na:PSS (Na 2s, S 2s, S 2p, and O 1s) were also observed.

Figure S3: Thickness of the PANI:PSS/PtNPs thin film

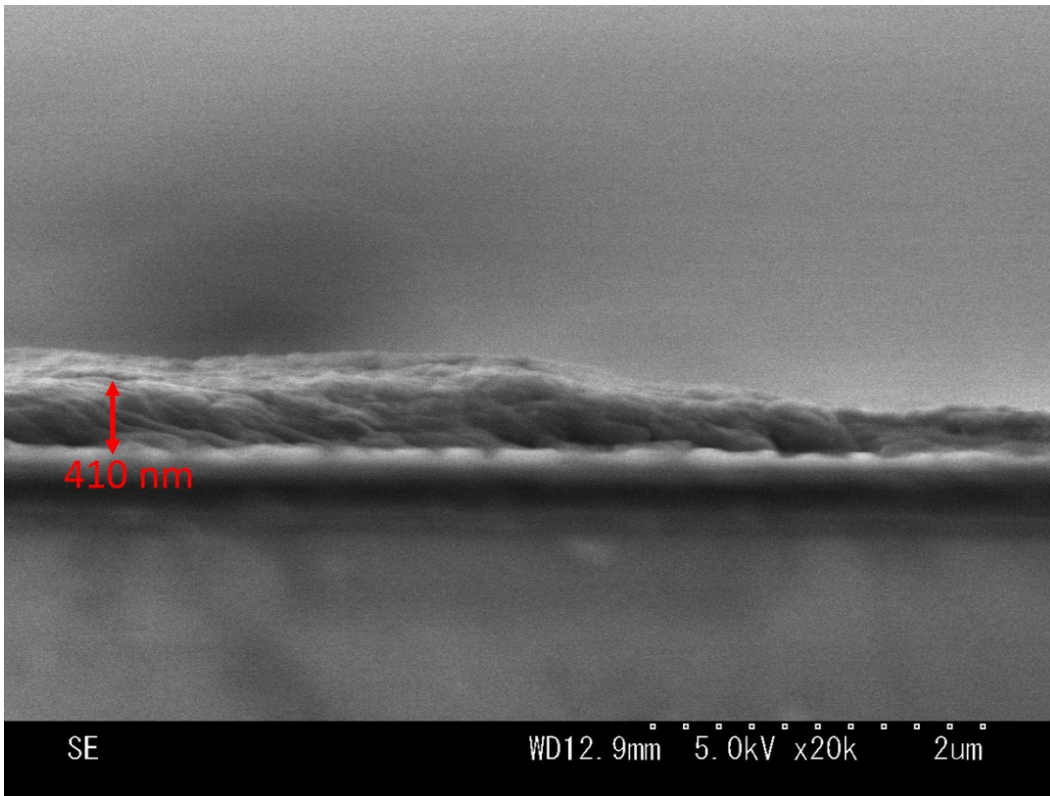


Fig. S3. The thickness of PANI:PSS/PtNPs thin film is about 410 nm.

Figure S4: SEM images

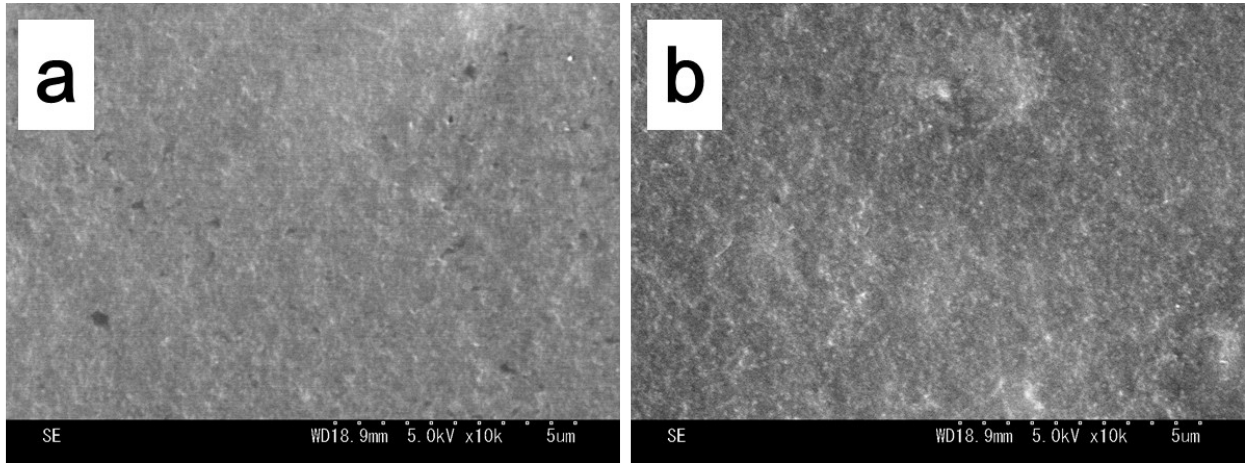


Fig. S4. The SEM images of (a) pure PANI:PSS thin film and (b) PANI:PSS/PtNPs thin film.

Figure S5: AFM images

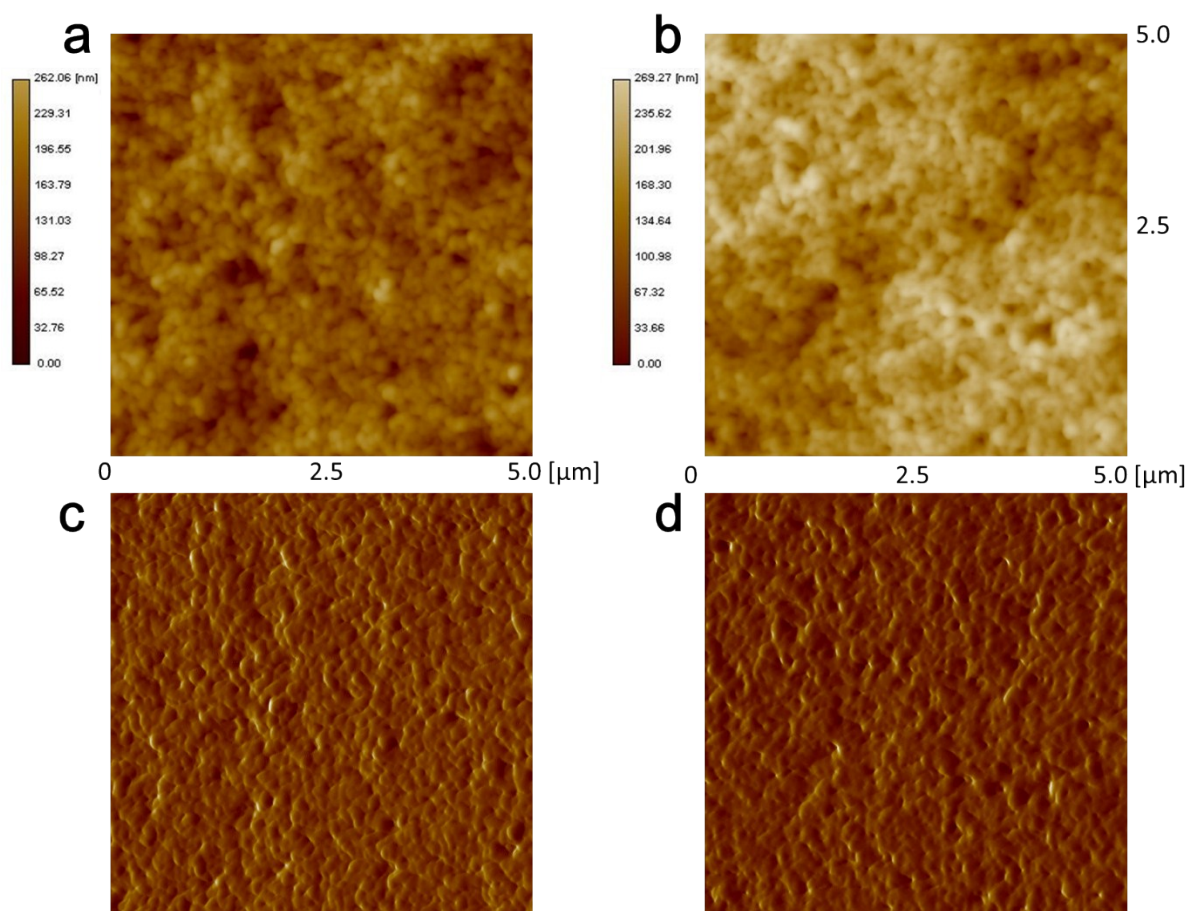


Fig. S5 The topographic images of (a) pure PANI:PSS and (b) PANI:PSS/PtNPs thin films. The phase-mode AFM images of (c) pure PANI:PSS and (d) PANI:PSS/PtNPs.

Figure S6: UV-vis-NIR spectrum of pure PANI:PSS

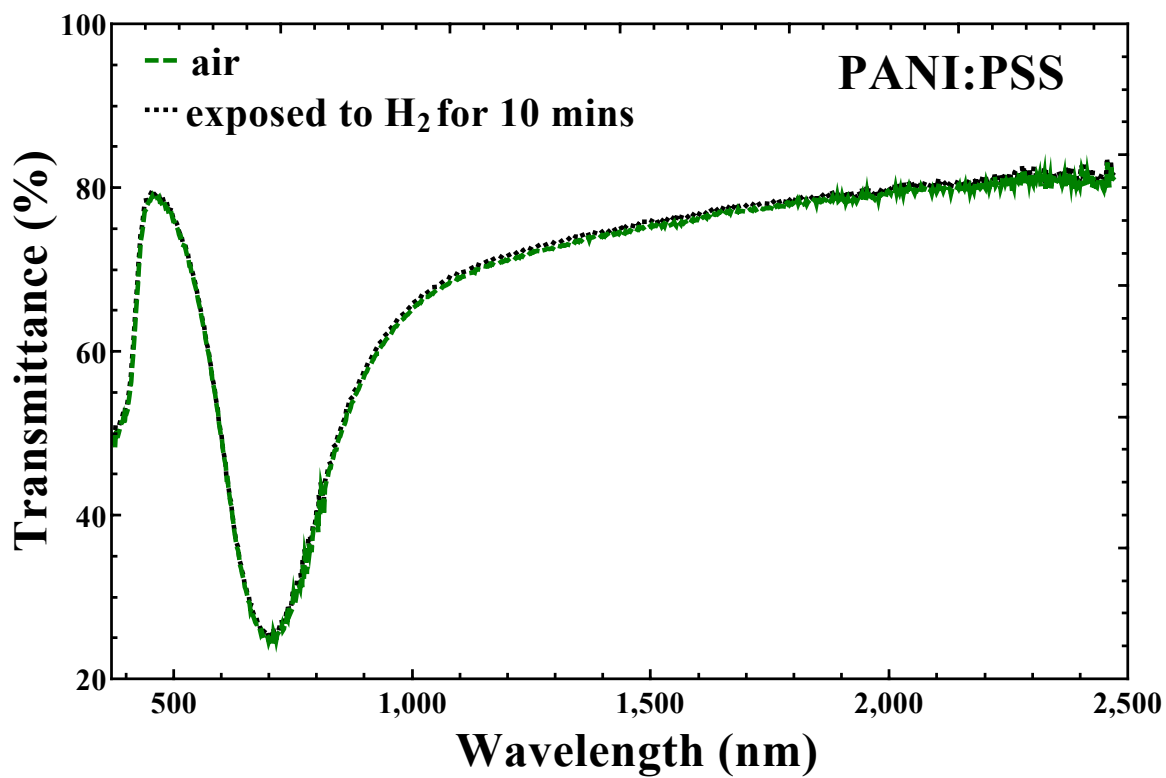


Fig. S6 UV-vis-NIR spectra showing the transmittance of pure PANI:PSS before and after exposure to H₂ for 10 min.

Figure S7: The UV-vis spectra of ITO/PANI:PSS/PtNPs

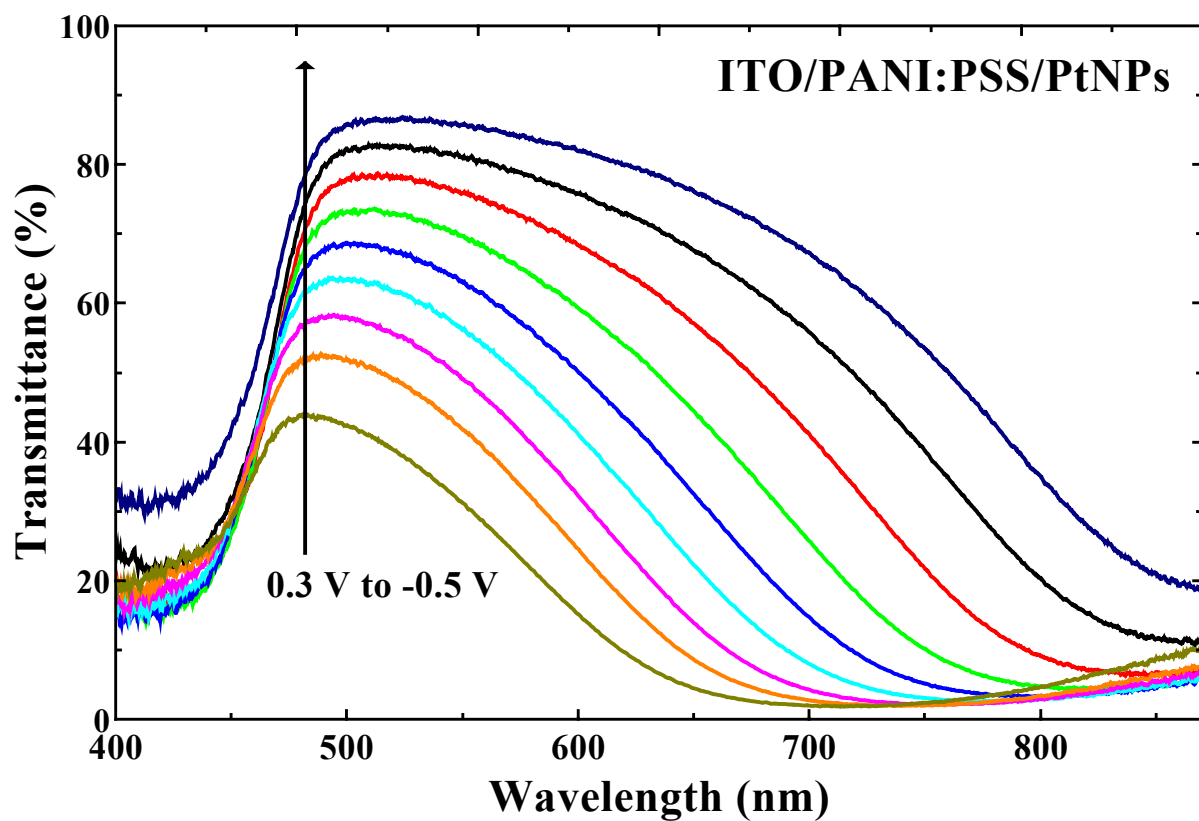


Fig. S7. UV-vis spectra showing the transmittance of ITO/PANI:PSS/PtNPs thin films at different applied potentials (-0.5 to $+0.3$ V, with an interval of $+0.1$ V, vs. Ag/AgCl).