

Electronic Supplementary Information

High contrast gasochromism of wet processable thin film with chromic and catalytic nanoparticles

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1. Experimental section

Synthesis of Prussian blue nanoparticles and related analogues. Water-dispersible Prussian blue (PB) nanoparticles and related analogues was prepared using a previously reported method.¹ PB was synthesized by mixing iron nitrate and sodium ferrocyanide. Subsequent purification of the obtained blue precipitate, the indispensible PB nanocrystals, was achieved by decantation. After purification, surface modification to enhance the dispersibility in aqueous solution was performed by reacting with sodium ferrocyanide. The obtained ink was directly used for spin coating to prepare a thin film without additives. The molar ratio of iron nitrate, sodium ferrocyanide for nanocrystal synthesis and sodium ferrocyanide for surface modification was 4:3:1.05. The Ni-substituted Prussian blue analogues-nanoparticles (NiPBA-NP) and Cu-substituted Prussian blue analogues-nanoparticles (CuPBA-NP) inks were prepared in the same manner with different mixing ratios of the raw materials. For NiPBA-NP, nickel nitrate and potassium ferricyanide were mixed to obtain nanocrystals, and sodium ferrocyanide was added prior to surface modification. The molar ratio of nickel nitrate, sodium potassium ferricyanide, and sodium ferrocyanide was 3:2:0.6. The CuPBA-NP ink was prepared with the copper sulfate and potassium ferrocyanide to obtain nanocrystals, and potassium ferrocyanide for surface modification in a molar ratio of 3:2:1.

Synthesis of PtNPs. 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%), and 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%), and sodium borohydride (NaBH_4 , >95.0%) were obtained from Tokyo Chemical Industry Co. Ltd., Japan (TCI). All chemicals were used without additional purification. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (104 mg, 0.2 mmol) was added to a flat-bottomed flask containing 30 mL of toluene and 10 mL of deionized water (DIW). The solution formed two layers, the upper layer was a transparent organic layer composed primarily of toluene and the lower layer was the aqueous layer composed of yellow 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 solution turned orange and the lower DIW became transparent. Dodecylamine (690 mg, 4.4 mmol) was dissolved in advanced in 3.5 mL of toluene, then added to the flask as a stabilizer for the nanoparticles. The color of the solution showed was uniformly white. NaBH_4 (125 mg, 3.3 mmol) was dissolved in 10 mL of DIW and subsequently added to the flask as an initiator for PtNPs synthesis. The solution became brown in a short time and was left under continuous stirring for 1 h. All processes and reactions were performed under a N_2 purged environment. The brown toluene solution was washed with 300 mL of DIW three times, then added to 400 mL of ethanol and stored at $-18\text{ }^\circ\text{C}$ for 24 h. The brown precipitate was

centrifuged (5000 rpm, 10 min) three times with ethanol solvent. Finally, the resulting brown precipitate was dried in a vacuum oven overnight, and the PtNPs were obtained.

Preparation of metal hexacyanoferrate/PtNPs thin films. A flat glass ($3 \times 3 \text{ cm}^2$) was cleaned using IPA and a plasma cleaning machine prior to use. For preparation of the PBNP thin film, 150 μL of PBNP ink (9 wt%) was dropped on the glass surface and spun at various spin-rate (1000 and 3000 rpm) for 10 s, and then added 500 rpm based on previous rate for 5 s (1500 and 3500 rpm). Subsequently, the PBNP films were stored at 25°C for 30 min. Next, 100 μL of PtNPs ink (dissolved in toluene, 0.01, and 0.2 wt%) was dropped on the PBNP surface and spun at 500 rpm for 30 s, and then 1000 rpm for 5 s. The PBNP/PtNPs/glass thin films were stored in air and the active area was confined to a $2 \times 2 \text{ cm}^2$ area using a cotton bud to remove the excess. For NiPBA-NP/PtNPs and CuPBA-NP/PtNPs thin films, 30 μL of the respective inks (6 wt% for both NiPBA-NP and CuPBA-NP) was dropped on the glass surface and left for 1 h to allow the DIW to evaporate. The subsequent steps were identical to that of the PBNP/PtNPs thin film preparation. For cyclic voltammetry (CV) measurement, ITO coated (thickness $\approx 100 \text{ nm}$, 20 ohm/square) glass was used in place of the flat glass, but the rest of the process remained unchanged.

Characterizations. The chemical compositions of PB-NP and NiPBA-NP were evaluated using microwave plasma-atomic emission spectrometry (MP-AES, Agilent 4100; Agilent Technologies Japan Ltd.) by standard addition with prior decomposition by a microwave sample preparation system (Multiwave3000; PerkinElmer Corp.) as well as CHN-analysis (EA-1110; CE Instrument Ltd.). MP-AES was used to determine the Fe, Cu, and K concentrations. CHN analysis was used for C and N in the PB-NP sample. The crystal structures of the prepared samples were investigated using an X-ray diffractometer (XRD, D2 Phaser; Bruker Corp.) with Cu K α radiation ($\lambda=0.154$ nm) at 30 kV and 10 mA. The sample images were obtained by field emission scanning electron microscopy (FE-SEM, S-4800; Hitachi High Technologies Corp.). The secondary nanoparticles in the ink were recorded using Otsuka electronics (ELSZ-1000). X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Scientific™ Sigma Probe Spectrometer system. CV analysis was performed with a potentiostat (Solartron analytical, model 1280C), using a three-electrode cell. The working electrode was composed of ITO/metal hexacyanoferrates/PtNPs and the counter electrode was a platinum sheet (1.0 cm \times 3.0 cm). An Ag/AgCl electrode (RE-1B, ALS Co., Ltd, Japan) was used as the reference electrode. Ultraviolet-visible (UV-vis) spectra (wavelength 400–800 nm) were obtained using a Hitachi U-4100 spectrometer, and *in-situ* UV-Vis spectra were obtained using a spectrometer (USB-4000) and a light source from Ocean Optics (DH-2000). A Perkin Elmer (Frontier) spectrometer was used to obtain *in-situ* Fourier transform infrared (FT-IR)

spectra. H₂ gas (100%) was produced directly from a hydrogen generator (H-TEC education, electrolyzer 65, hydrogen production rate 65 cm³/min).

FT-IR measurement. Reflectance measurements were taken in this study and the PBNP/PtNPs/ITO thin films were used for line (i)–(iv) in Fig. 4(b). For line (i), the fresh film was investigated without any treatment. For line (ii), thin film was exposed to 100% H₂ and measured *in-situ*. For line (iii), thin film was placed in a 0.1 M KTF SI/PC electrolyte in the 3-electrode system and a voltage of –0.3 V (vs. Ag/AgCl) was applied for 60 s to reduce the PB thin film to transparent Prussian white (PW) status. Subsequently, the thin film was removed from the electrolyte, to perform the FTIR measurements. For line (iv), same process was used as for line (iii), only changing the electrolyte to a 0.1 M HCl/DIW electrolyte.

CV measurements. A 3-electrode system was used in this study, 0.1 M KTF SI/PC was used as the electrolyte, and the scan rate was set to 1 mVs⁻¹. The CV scan started at –0.5 V and ended at +0.8 V.

2. Supplementary figures

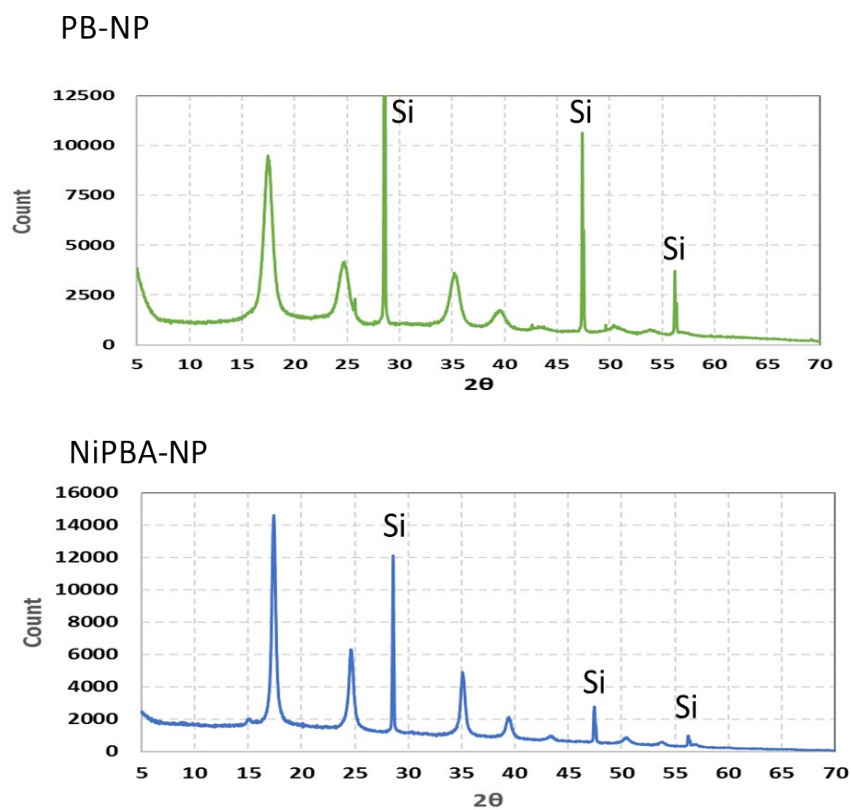


Figure S1. XRD patterns for the powder obtained after drying the PBNPs and NiPBA-NP inks.

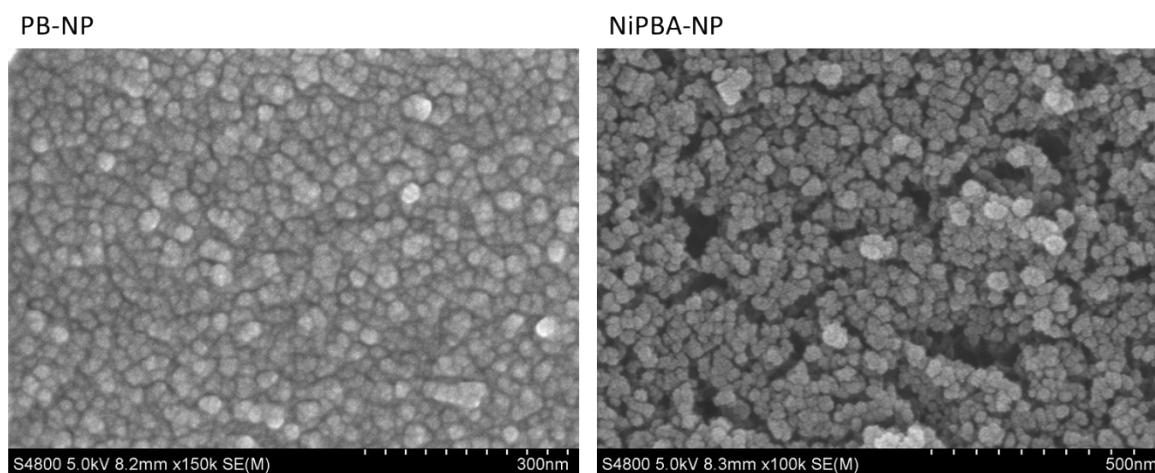


Figure S2. FE-SEM images of the PB-NP and NiPBA-NP thin films.

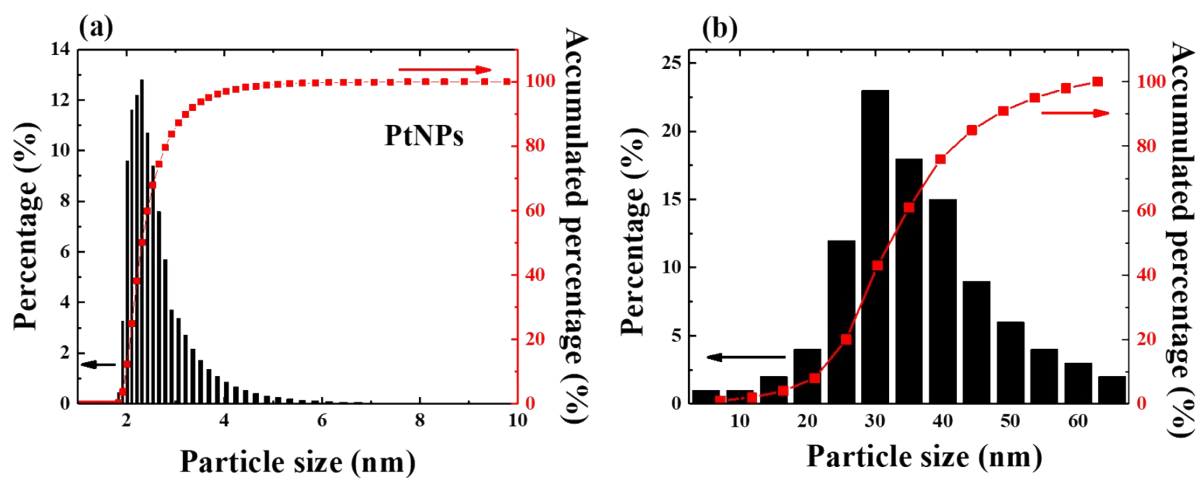


Figure S3. Secondary particles size of the (a) PtNPs ink and (b) PBNPs ink obtained using the dynamic light scattering (DLS) method.

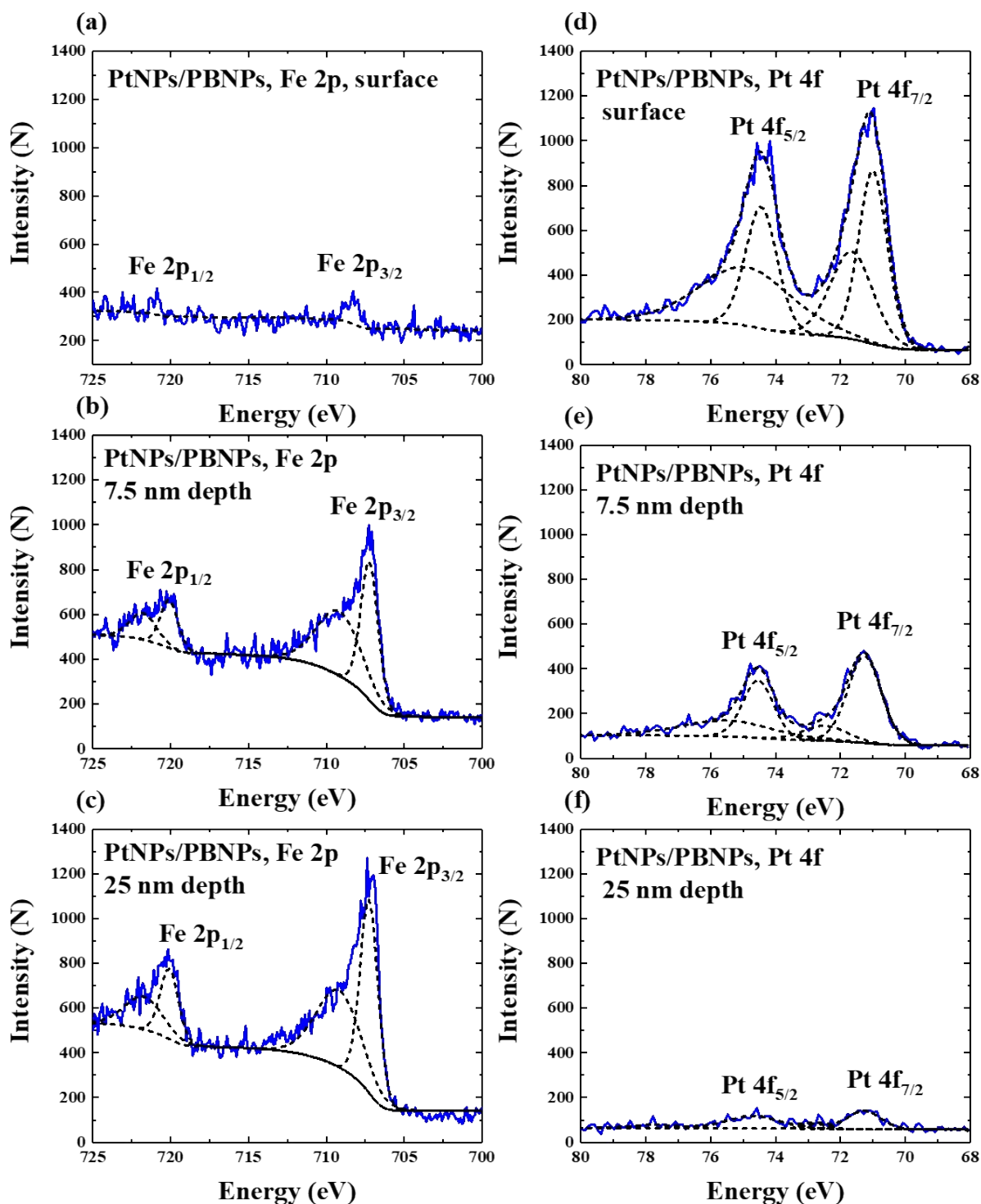


Figure S4. The XPS spectra of the PBNP/PtNPs thin film for Fe2p ((a)–(c)) and Pt 4f ((d)–(f)) at various depths. For the Fe 2p orbital, (a) surface, (b) 7.5 nm depth, and (c) 25 nm depth spectra are shown, and for the Pt 4f orbital, (d) surface, (e) 7.5 nm depth, and (f) 25 nm depth spectra are shown.

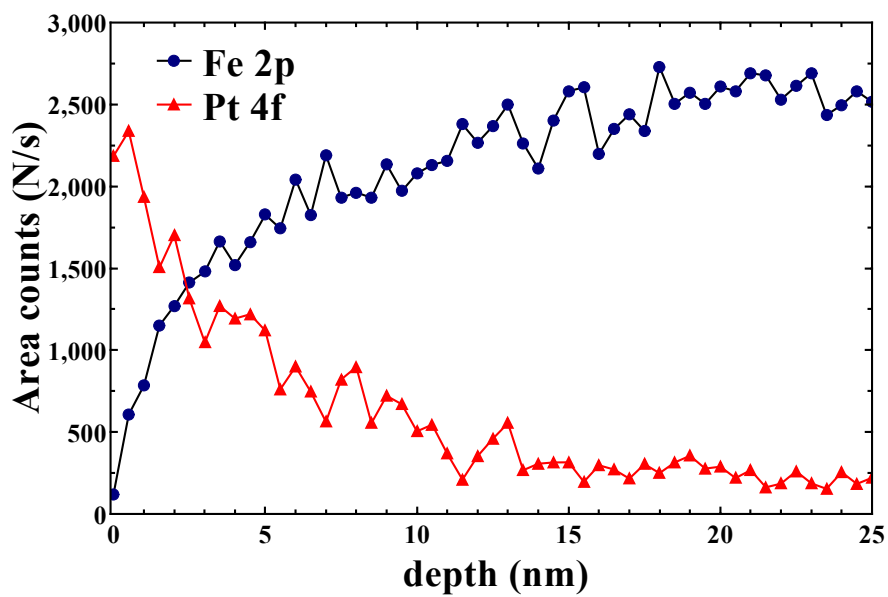


Figure S5. The area counts of the PBNP/PtNPs thin film for the Fe 2p and Pt 4f as a function of depth with an interval of 0.5 nm from surface to a final depth of 25 nm.

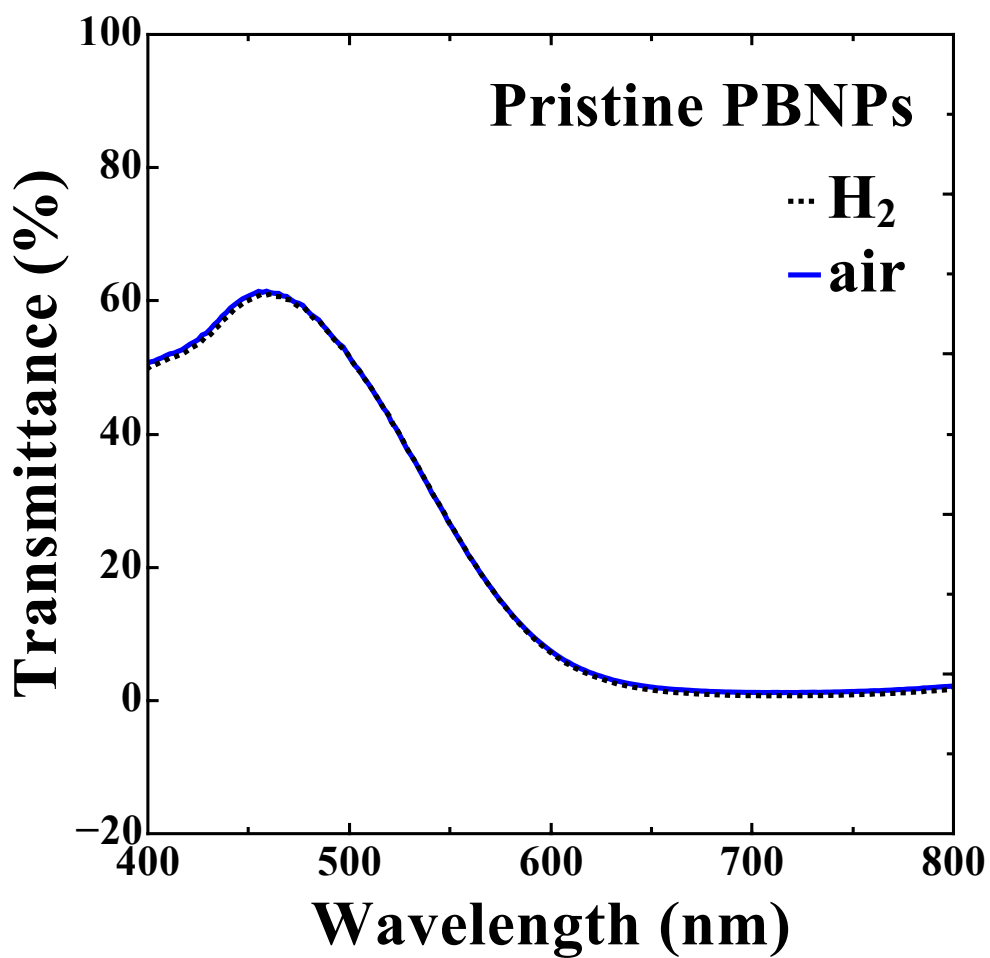


Figure S6. The optical transmission curve of pristine PBNPs in air (blue solid line) and after being exposed to 100% H₂ gas for 5 min (black dash line).

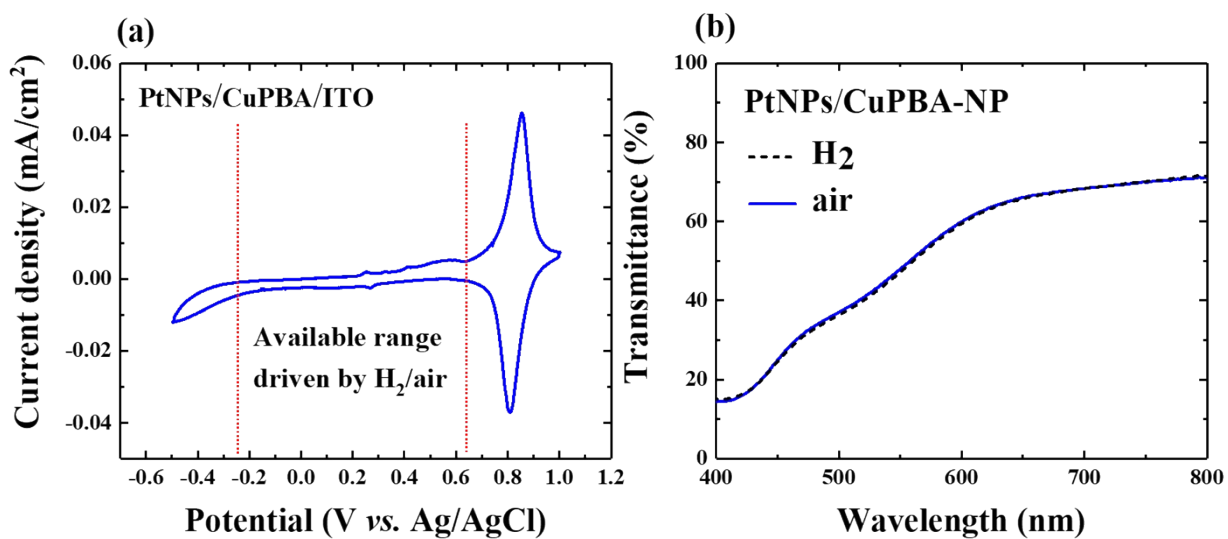


Figure S7. (a) Cyclic voltammogram of the CuPBA-NP/PtNPs thin film casted on ITO glass with an active area of $2.5 \times 2.5 \text{ cm}^2$. A 0.1 M KTFSI PC solution was used as the electrolyte, and the operation voltage was -0.5 to $+0.8 \text{ V}$ with a scan rate of 1 mVs^{-1} . (b) UV-vis-NIR transmittance of the CuPBA-NP/PtNPs thin film before/after exposure to H_2 .

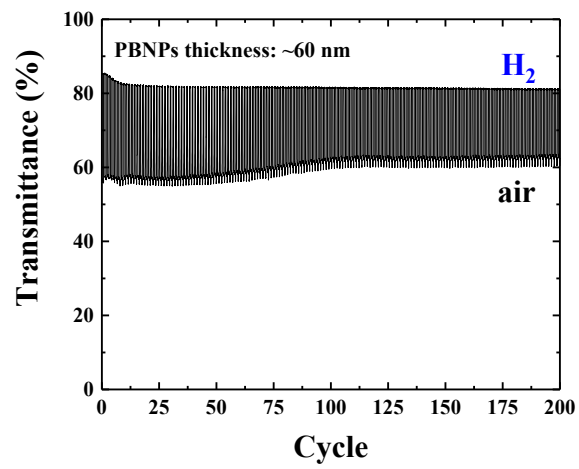


Figure S8. Cycle test for sequential exposure to 100%-H₂ gas and air with an interval time of 1 min, optical responses of PtNPs/PBNPs films with 60 nm during long-term test for 200 cycles.