

Electronic Supplemental Information

Hydrogen Peroxide as Sustainable Fuel: Combination of Production with a Solar Cell and Decomposition with a Fuel Cell

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Experimental Section

Materials. Silver nitrate (99.9 %), formalin (36-38 % HCHO), sodium hydroxide were obtained from Wako pure chemicals. Polyvinylpyrrolidone (PVP, Mw = 40,000) was supplied by Nakalai tesque. Lead acetate trihydrate (99.5%) was purchased from Kishida Chemicals. Oxo[5,10,15,20-tetra(4-pyridyl)porphyrinato]titanium (IV) was obtained from TCI. Cobalt porphyrins of [Co(TPP)] and [Co(OEP)] were purchased from Sigma-Aldrich and [Co(TCPP)] and [Co(DPP)] were synthesized by reported methods.^{1,2)} Pt wire (0.5 mm ϕ), Au electrode (1 mm ϕ) and glassy carbon electrodes (3 mm ϕ or 1.5 cm x 2 cm) were purchased from BAS. Purified water was provided by a Millipore MilliQ water purification system where the electronic conductance was 18.2 M Ω . Ag based nanoparticles were synthesized as follows.

Preparation of Ag Nanoparticles. To an aqueous solution of PVP (0.40 M in monomer unit, 7.5 mL) and silver nitrate (13 mg, 7.7×10^{-5} mol) was added an aqueous solution of NaOH (1 M, 0.875 mL) and formalin (0.25 mL) with vigorous stirring at room temperature for 5 min. The formed Ag nanoparticles were separated by centrifugation at 15,000 rpm for 5 min. The obtained particles were characterized by DLS and XRD.

Preparation of Ag-Pb Nanoparticles. To an aqueous solution of Ag nanoparticles prepared by the procedure above was added an aqueous solution of calculated amount of lead acetate trihydrate and PVP (0.40 M, 7.5 mL). To the solution was then added an aqueous solution of sodium hydroxide (1.0 M, 0.375 mL) following formalin (0.25 mL). The solution was magnetically stirred for 15 min at room temperature. The formed particles were separated by centrifugation at 15,000 rpm for 5 min. The obtained particles were characterized by DLS, XRD and/or TEM.

Electroreduction of Oxygen over Cobalt Porphyrins. Cobalt porphyrins were dissolved to benzonitrile to be 1 mM solution. The solution of 300 μ L was dropped on a glassy carbon electrode (3 cm²) and dried at 60 $^{\circ}$ C until complete drying. The electrochemical behavior of O₂ at several electrodes mounting cobalt porphyrins was examined using a BAS 100W electrochemical analyzer. A two-compartment H-type cell was used with an agar salt bridge. Saturated calomel electrode and platinum electrodes were used as a reference and a counter electrodes, respectively. Glassy carbon electrodes mounting cobalt porphyrins were used as working electrodes. The measurements were performed at 25 $^{\circ}$ C in 0.1 M sulfuric acid passed through oxygen more than 30 min. The counter electrode was immersed in the

solution containing 1M hydrazine to reduce anode polarization. The applied potential of 0.5 V by the solar cell was sufficient for H₂O₂ production because the onset potential observed for two-electron reduction of an O₂ molecule over [Co(TCPP)] was 0.3 V (vs. SCE) at pH 0.7 and the potential for hydrazine oxidation is 0.71 V. The H₂O₂ produced was quantified by a colorimetric titration with oxo[5,10,15,20-tetra(4-pyridyl) porphyrinato]titanium (IV) in a HClO₄ solution. For the reliable quantification, the concentration of HClO₄ is very important.³⁾

Electroreduction of Hydrogen Peroxide over Ag or Ag-Pb Nanoparticles. Ag based nanoparticles were loaded onto a small glassy carbon electrode (3 mm ϕ). The nanoparticles taken out from the as-prepared solution (200 μ L) was re-dispersed into water (500 μ L). A small portion of the dispersion (7 μ L) was dropped onto the glassy carbon electrode and dried at 60 °C overnight. The surface of nanoparticles was electrochemically cleaned by cyclic sweepings in the widest potential range of H₂O₂ reduction experiments for more than 50 times before electroreduction experiments. The electrochemical behavior of H₂O₂ at several electrodes was examined using an electrochemical analyzer. Saturated calomel electrode and platinum electrodes were used as reference and counter electrodes, respectively. Glassy carbon electrodes mounting Ag or Ag-Pb nanoparticles were used as working electrodes. The measurements were performed at 25 °C in 1 M NaOH solution containing 3 mM H₂O₂.

Evaluation of the Performance of a H₂O₂ Fuel Cell. An aqueous solution of H₂O₂ (300 mM) was placed in a one-compartment electrochemical cell. An Au electrode and glassy carbon electrode with Ag or Ag-Pb nanoparticles were immersed in the H₂O₂ solution. Cell performance was evaluated by a BAS 100W electrochemical analyzer. Measurements were performed at 25 °C in deaerated 1 M NaOH solution.

Physical Measurements. Dynamic laser scattering measurements were performed on a Malvern Zeta Sizer Nano ZS. Ag based nanoparticles were washed with water at least 4 times. The measurements were performed several times with changing the particles concentration. X-ray diffraction patterns were recorded by a Rigaku Ultima IV. Incident X-ray radiation was produced by a Cu X-ray tube, operating at 40 kV and 40 mA with Cu K_a radiation of 1.54 Å. The scanning rate was 4°/min from 30° to 50° in 2 θ . Transmittance electron microscope images of nanoparticles, which were mounted on a copper microgrid coated with elastic carbon, were observed by a JEOL JEM 2100 operating at 200 keV.

References

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Table S1. Average particles diameters and deviations of Ag and Ag-Pb nanoparticles determined by Dynamic Laser Scattering (DLS) measurements

Ag:Pb ratio	average diameter, nm	deviation, nm
10:0	21	4.4
9:1	21	4.7
7:3	24	7.8
6:4	24	8.0

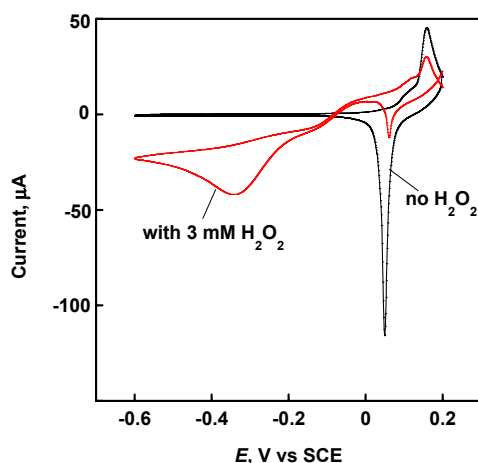


Fig. S1 Typical CV of H_2O_2 over Ag-Pb (9:1) nanoparticles. The measurements were performed in an aqueous solution containing 1M NaOH with or without 0.3M H_2O_2 . The scan rate was 20 mV/sec.