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Stabilization and decomposition of organic matters by nano-porous metals

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Abstract

Nanoporous (np-) metals affect chemical stability of various organic matters much more than their bulk counterparts. Self-assembly monolayers (SAMs) of 4-aminothiophenol are more stable on np-Au fabricated by dealloying Ag-Au alloy than on flat Au, which were elucidated by cyclic voltammetry (CV). The first-principles calculations indicate that atomic defect of Au surface, which is characteristic of ligament surface of np-Au, reduce the binding energy of thiol molecule.

The stabilized SAMs on np-Au are also effective for enzyme immobilization. When laccase was immobilized on np-Au surface, its thermal stability was improved compared with nonfixed laccase. The higher stability of immobilized laccase is due to the synergistic effect of reduced conformational flexibility of the enzyme in nanopores and SAMs stability. CV with the working electrode of enzyme-immobilized np-Au revealed that the electron transfer between enzyme and electrode is successfully enhanced by SAMs. These aspects of enzyme-immobilized and SAMs-decorated np-Au can be applied to the electrodes of biofuel cell.

Np-metals such as np-Au, np-Pd and np-Ni, on the other hand, remarkably decompose methyl orange (MO, a typical stable azo dye in the textile industry) in an aqueous solution, while MO is highly stable in aqueous solutions which include their bulk counterparts. Ultraviolet-visible light spectroscopy and high-performance liquid chromatography demonstrated that np-Au breaks the azo bond ($-N=N-$) in MO molecules. Defective surface of ligaments in np-metals plays an important role in this catalytic decomposition of MO.

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1. Introduction

Nanoporous (np-) metals fabricated by dealloying have various interesting properties including mechanical, catalytic, piezoelectrical ones (Ding and Chen (2009)). The three-dimensional np-structure induces surface lattice disorders such as lattice expansion/contraction and atomic defects. Here we demonstrate that np-metals have different influences from their bulk counterpart on surrounding organics (Hakamada et al. (2011), Hakamada et al. (2011), Hakamada et al. (2012), Hakamada et al. (2012)).

2. Experimental Methods

2.1. Self-assembled monolayers (SAMs)

Detailed experimental methods are described in the published paper (Hakamada et al. (2011)). In brief, Np-Au was synthesized by dealloying of the $\text{Au}_{0.35}\text{Ag}_{0.65}$ alloy (free corrosion) at 253 K for 15 h in 70 mass% HNO_3 . Some of the sample was freely corroded at room temperature and annealed at 423 K for 15 min under Ar atmosphere to coarsen the porous structure. The 4-aminothiophenol (4-ATP) thiolate monolayers were self-assembled on both dealloyed and coarsened samples. For the preparation of SAMs on np-Au, the samples were soaked in a 20 mmol/L ethanolic solution of 4-ATP for 65 h at room temperature.

Cyclic voltammetry (CV) was carried out at room temperature to determine the stability of the adsorbed SAMs on np-Au. A three-electrode electrochemical cell with a platinum wire as a counter electrode, the np-Au sample decorated with SAMs as a working electrode and the saturated calomel electrode (SCE) as a reference electrode were used. For comparison, smooth Au surface (polished Au plate) decorated with 4-ATP SAM is also used as a working electrode. The electrolyte was 0.1 mol/L NaOH and the scan rate was 5 mV/s from 0 to -1.2 V. Curves for the first scan are used for consideration.

2.2. Enzymes

Detailed experimental methods are described in the published papers (Hakamada et al. (2011), Hakamada et al. (2012)). In brief, np-Au samples (with and without a 4-ATP SAM) were stored quiescently in 2 mL of 7 mg/mL laccase solution (diluted by 0.1 mol/L citrate–0.2 mol/L phosphate buffer solution (PBS), pH=5.0) at 4 °C for 24 h. Np-Au samples were then rinsed five times with 10 mL of buffer solution to remove any excess or only weakly adsorbed enzyme. An appropriate amount of laccase was stirred with 3 mL of buffer solution and 300 μL of 10mmol/L 2,6-dimethoxyphenol (DMP) (Qiu et al. (2008)), and the activities of free and immobilized laccase were spectrophotometrically determined on the basis of the absorbance change at 470 nm. The effect of incubation time was examined by incubating free laccase and laccase-immobilized np-Au in buffer solution (pH=5.0) at 50 °C. At given time intervals, 5 μL of free enzyme solution or 20 mg of laccase-immobilized np-Au was removed and left to stand in the buffer solution for 1 h at room temperature. The residual activity was then assayed at 35 °C.

Cyclic voltammetry (CV) was carried out at room temperature to elucidate the electrochemical properties and stability of the enzyme-immobilized samples. A three-electrode electrochemical cell with Pt wire as a counter electrode, the laccase-immobilized np-Au electrode as a working electrode, and saturated calomel electrode (SCE) as a reference electrode was used. Potentials were documented vs standard hydrogen electrode (SHE) unless otherwise stated in this section. For the laccase-immobilized electrode, the electrolyte of 0.1 mol/L citrate-0.2 mol/L PBS was air-saturated with dry air bubbling for 1 h. CV was conducted at 100 mV/s from -0.15 to 0.7 V.

2.3. Azo dyes

Detailed experimental methods are described in the published paper (Hakamada et al. (2012)). In brief, methyl orange (MO), a typical azo dye used in the textile industry, is very stable and is commonly used as the probe for evaluating photocatalysts (Yen et al. (2009)) thus the catalytic activities of the np-Au for degradation of the MO was assessed at room temperature (≈ 298 K). Different samples (with nominal exposed areas of 2 cm^2) were immersed into 5 mL of MO solution (2×10^{-5} mol/L). The experiments were conducted under dark conditions to distinguish

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