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Palladium nanoparticles supported by amyloid fibrils: From size controllable synthesis to extremely high catalytic performance

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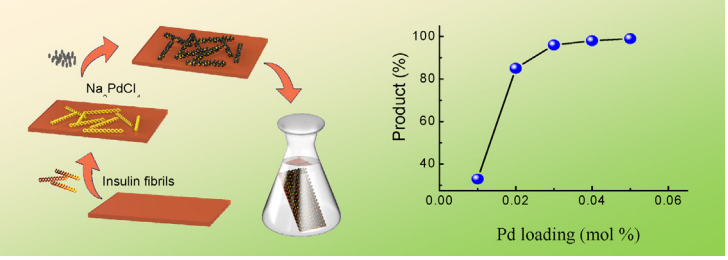
HIGHLIGHTS

- Biotemplated synthesis of Palladium Nanoparticles (Pd NPs).
- The size-controlled Pd NPs are very uniform.
- The Pd-insulin demonstrates extremely high catalytic activity at a very low Pd loading.

GRAPHICAL ABSTRACT



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ABSTRACT

Palladium nanoparticles (Pd NPs) play an important role as catalysts in various chemical reactions. In this paper, a new strategy is developed to synthesize thin films of biomolecule-supported metallic palladium nanoparticles by the alternative deposition of insulin fibrils and aged sodium tetrachloropalladate (II) on a solid substrate in the absence of any external reducing agents. The formation of metal Pd NPs was confirmed by high resolution transmission electron microscopy and X-ray photoelectron spectroscopy. The unique Pd-insulin exhibits extremely high catalytic activity in Suzuki coupling reactions at a very low Pd loading of 5.0×10^{-2} mol%.

1. Introduction

Palladium nanoparticles (Pd NPs) play a significant role in the catalysis of a variety of organic reactions including hydrogenation and C—C coupling reactions [1–5]. In industry, heterogeneous catalysts are widely used instead of homogeneous catalysts because of their relatively easy separation and stability. However, on the industrial scale, high catalyst concentrations are often required (normally 0.5–5 mol%) [6,7], which increases the cost and makes it difficult to purge the ligands that are usually employed to stabilize Pd NPs [8–10]. Moreover, substantially smaller, uniform, and well-dispersed nanoparticles are required for high-yield catalytic applications [11,12]; however, the synthesis of such Pd NPs under mild conditions in a controlled manner still remains a fundamental challenge.

Recently, biological supramolecules have attracted dramatic attention as template materials for the controlled synthesis of metallic Pd NPs as a consequence of their well-defined structures [13–18]. For example, in their pioneering work, Nguyen et al. fabricated Pd clusters along DNA molecules by reducing PdO precipitates with gaseous hydrogen [19]. Particularly, tobacco mosaic virus (TMV) has been frequently used to direct the controllable formation of NPs [20–22]. Very recently, Lim et al. reported a synthetic strategy enabling highly controlled aqueous-phase

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palladium crystallization on genetically engineered mutant TMV coupled with extra cysteines (TMV1cys) without the addition of any external reducing agents [21]. Yang et al. further applied the TMV1cys-templated Pd NPs in the dichromate reduction reaction [22]. However, the size and uniformity of Pd NPs coated on TMV1cys still cannot be well controlled, and it is also complicated to genetically engineer TMV to carry thiol groups on the exposed surface. Notably, amyloid fibrils provide another green alternative as scaffolds for nanostructure assembly [23–28]; their internal structures comprise a cross-β sheet core with rich hydrogen bonds formed between the amino and carbonyl groups of the polypeptide chain, thus making them remarkably stable even in harsh conditions [29]. Importantly, amyloid fibrils are rich in functional groups that can specifically interact with desired nanoparticles. Herein, we describe a facile and reproducible approach to fabricate Pd-insulin thin films on a solid substrate with size controllable Pd NPs. The Pd-insulin films were further demonstrated to promote the Suzuki coupling reaction with very low Pd loadings and high catalytic activity.

2. Materials and methods

2.1. Materials

Frozen powdered insulin peptide was purchased from ProSpec (ProSpec-Tany TechnoGene Ltd.) with a purity of 98%. The insulin powder was dissolved in Milli-Q water (18.2 MΩ cm) to achieve a final concentration of 1.0 mg/ml, and the solution pH was adjusted to 2.0 with diluted HCl. The solution was stored at −20 °C before use. 3-Aminopropyltriethoxysilane (APTES) and sodium tetrachloropalladate (II) (Na_2PdCl_4) were purchased from Sigma Co., Ltd. (Shanghai, China). 4-Iodophenetole, 4-methylphenylboronic acid, potassium carbonate (K_2CO_3) and EtOH were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All these chemicals were used in our experiments without further purification.

2.2. Surface modification

To immobilize the insulin and Pd NPs on the surface, the silicon substrates were coated with a 5-nm adhesion layer of Ti followed by a 100-nm layer of Au using an e-beam evaporator at a rate of 5 nm/min. To examine the effect of Au on the coupling reaction, control experiments were conducted where silicon surfaces were modified with APTES to immobilize the insulin fibrils. Briefly, a drop of 0.5% APTES was put on a silicon surface. After 10–15 min of incubation, the sample was carefully rinsed with Milli-Q water and dried with N_2 gas. The sample was then heated at 100 °C for 1 h. After cooling to room temperature, the sample was stored in a desiccator for use. The two substrates were termed as "Au-silicon" and "APTES-silicon."

2.3. Preparation of Pd-insulin catalyst

To prepare insulin fibrils in solution, ~200 μL of insulin peptide (1.0 mg/mL, pH 2.0) was incubated at 70 °C for three days. A 20 μL drop of the as-prepared insulin fibrils was deposited on the Au-silicon or APTES-silicon surface followed by an addition of 20 μL of Na_2PdCl_4 solution (5 mM) aged at room temperature for two days. The samples were then dried in air. The deposition of insulin fibrils and aged Na_2PdCl_4 solution was alternately repeated for a certain number of times to increase the loading amount of Pd NPs. Subsequently, the samples were dried under nitrogen stream. The insulin fibril-supported Pd NPs, termed Pd-insulin, were then utilized for the Suzuki coupling reaction.

2.4. Physical characterization of catalysts

A Multimode 8/Nanoscope V system (Bruker AXS, Germany) was used to characterize the surface morphologies of all samples at room temperature and ~35% RH. RTESP silicon cantilevers (Bruker) with resonance frequencies of ~260 kHz were used for AFM imaging. AFM data were analyzed with the NanoScope Analysis V1.20 software.

A Thermo Scientific Nicolet infrared microscope (Nicolet 6700) equipped with a liquid nitrogen-cooled MCT detector and continuum infrared microscope accessory was used to examine the secondary structures of the as-prepared insulin fibrils. A drop of solution (2–3 μL) was deposited on a diamond sample holder and dried under infrared light at room temperature. The absorbance spectra of different samples were collected, and a total of 200 scans were performed to improve the signal-to-noise ratio.

The samples for high resolution TEM (HRTEM) characterization were prepared as follows: 5 μL of well-dispersed Pd-insulin solution was placed onto 300 mesh copper grid carbon TEM grids and left to dry before examination. The TEM images were obtained using a JEOL 2100 at 200-keV.

X-ray photoelectron spectroscopy (XPS) spectra were obtained on an Axis Ultra DLD spectrometer (Kratos Analytical, Ltd.) with a monochromated Al Ka X-ray source (1486.7 eV of photons) to determine the quantities of C, N, Au, and Pd atoms present on the sample surfaces.

2.5. Suzuki coupling reaction

Suzuki reactions between aryl halides and 4-methylphenylboronic acid were catalyzed by Pd NPs. Briefly, 15 mL vessels were first loaded with aryl halides (1.0-mmol), 4-methylphenylboronic acid (1.2-mmol), K_2CO_3 (3.0-mmol) and the Pd-insulin catalyst. Subsequently, EtOH (4.0 mL) and H_2O (3.0 mL) were added, the reaction mixtures were heated to 90 °C under ambient atmosphere for 10 h and cooled to room temperature. The crude products were purified with silica gel column chromatography using a mixture of ethyl acetate and petroleum ether as an eluent to afford the pure product. ^1H NMR (400 MHz) spectra were recorded in $CDCl_3$ to examine the final product. Pd mol% refers to the molar ratio of the catalyst (Pd) to the reactant (aryl halides) and was used to characterize the amount of catalyst in the reaction. Product yield was calculated as the molar ratio of the final product to the original amount of aryl halides.

3. Results and discussion

3.1. Biosynthesis of palladium nanoparticles

As illustrated in Fig. 1, our biosynthetic approach consists of the following two steps. First, 1.0 mg/mL of insulin peptide solution was incubated at 70 °C for three days to form insulin fibrils. The long and uniform fibrils were clearly visualized by AFM, and the formation of β-sheet structures was confirmed by the presence of a characteristic peak around 1629.5 cm^{-1} in the FTIR spectrum (Fig. 2) [29]. Second, 20 μL of the as-prepared insulin fibrils and an equal volume of 5.0 mM Na_2PdCl_4 solution aged at 25 °C for two days were alternatively deposited on a 1 × 2 cm^2 Au-coated silicon substrate for a certain amount of time. After drying in air, the Pd-insulin films were ready to be used as catalysts in the coupling reaction.

Palladium precursors such as Na_2PdCl_4 have been reported to hydrolyze to form colloidal particles in an aged solution [19,30]. After mixing with the Cys-rich insulin fibrils, these particles could precipitate onto the insulin fibrils and gradually self-reduce to metallic palladium. Fig. 3a clearly illustrates a highly dense cov-