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# pH response of zwitterionic polydopamine layer to palladium deposition in the microchannel

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## HIGHLIGHTS

- Polydopamine layer exhibits potentially ampholyticity or zwitterionicity.
- pH response of zwitterionic polydopamine to palladium deposition is studied.
- Synergy of electrostatic interaction and ion transfer determines palladium deposition.
- Relation between catalytic performance and palladium deposition is summarized.

## ARTICLE INFO

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## ABSTRACT

In this study, the pH-response of the zwitterionic polydopamine layer to the palladium deposition in a capillary microchannel and the resultant catalytic performance for the nitrobenzene hydrogenation were explored. Experimental results showed that the polydoapmine layer exhibited the switchable surface charge from positive to negative with increasing the pH value. Under low $K_2PdCl_4$ concentration, the intrinsic low pH not only allowed most palladium to be deposited at the inlet region of the microchannel, but also provided more accessible sites for the anion $PdCl_4^{2-}$ deposition. Such property resulted in less palladium deposited at the outlet region because of the limited supply of the precursor and poor mass transfer, while an excellent size distribution of the deposited palladium nanoparticles at both the inlet and outlet of the microreactor was obtained. With the increase of the $K_2PdCl_4$ concentration, the increased pH value of the precursor solution aggravated the dispersity of the deposited palladium species and led to large palladium particles at the upstream of the microreactor. The gradually lowered pH value of the precursor solution along the microchannel and the large concentration gradient could directly intensify the anion $PdCl_4^{2-}$ deposition. Thus, an inverse palladium distribution between the inlet and outlet regions was observed due to the shift of surface potential from negative to positive along the microchannel. Such feature influenced both the catalytic activity and the durability for the nitrobenzene hydrogenation. The obtained results in this work are beneficial for not only the controllable metal catalyst preparation but also the improvement in the economy utilization of catalyst.

## 1. Introduction

Mussel-inspired adhesive and coating technique, which was firstly proposed by Messersmith et al. in 2007, has attracted extensive attraction in recent years as a result of its intrinsic advantages, in that it is simple, environmental-friendly, multifunctional, etc [1–3]. As a readily accessible synthetic analogue of the naturally adhesive proteins secreted by mussels, polydopamine has been widely employed due to the coexistence of both amine and catechol groups, which is crucial for the adhesion and coating [1,4]. It shows the excellent ability of forming versatile layer on both organic and inorganic substrates with a wide variety of functionalities, including surface coatings, biotechnology and biomedicine, water purification membranes and electroless deposition [3–6].

Among these functional uses, the polydopamine modified surface has been widely used for electroless deposition [1,2]. For example,

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Wang et al. [7] fabricated a highly conductive Ag-coated glass fiber used for the electromagnetic shielding field in this manner. Hu et al. [8] developed a simple strategy to visualize latent fingerprint by interfacial separation of polydopamine film coated with Ag. Nugen et al. [9] proposed a polydopamine functionalized pillar substrate for Ag deposition to create Ag nucleation sites applied for the surface-enhanced Raman Scattering. Chen et al. [10] in-situ immobilized Cu nanoparticles on the polydopamine coated graphene oxide for the $H_2O_2$ determination. Besides, previous works have also demonstrated that adhesive polydopamine layer can be used as a polymer support prepared on the inner surface of a microchannel for the noble metal nanocatalysts (such as Pd, Pt, Au) deposition applied for various multiphase catalytic reactions with excellent catalytic activity [11–15]. Using this approach, the preparation process could be simplified and the manufacturing costs could be reduced [11,15].

It should be pointed out that the polydopamine layer itself exhibits potential ampholyticity or zwitterionicity because of the coexistence of amine groups and phenolic hydroxyl groups [16–18]. When the polydopamine layer is placed under low pH conditions, it shows positively charged as a result of the amine groups. While it shows negatively charged under high pH conditions due to the deprotonation of the phenolic hydroxyl groups [3,17–19]. Obviously, the potential zwitterionicity of polydopamine will directly affect the deposition behavior of the metal ions, which depends on the precursor solution property. Subsequently, the amount and the dispersity of the deposited metal species and the catalytic performance will be affected. Considering that the loading, size and dispersion of the deposited metal catalyst play significant roles in the catalytic performance [20–22], a deep understanding of the interaction between the polydopamine zwitterionicity and the precursor property is essential for not only the controllable metal catalyst deposition but also the promotion of the diversified applications.

Right now, however, regarding utilizing the zwitterionicity of polydopamine, most researchers paid their attention on the potential usage of governing the selective ion permeability for the selective uptake and release [17,18] or forming electrostatic repulsion to the molecules for anti-fouling [23,24]. Few researches have been reported on the potential influence of the zwitterionicity with pH response on the metal deposition and thereby the catalytic performance. Aiming at this target, the zwitterionic polydopamine layer with pH-response for the palladium deposition in a capillary microchannel and its catalytic performance was studied in this work. Zeta potential and electrochemical impedance spectroscopy (EIS) were performed to characterize the zwitterionicity and ion transfer on the polydopamine surface, respectively. Both the morphology and the chemical composition as well as the palladium loading deposited on the polydopamine layer were also investigated using FESEM, XPS and UV–Vis spectrum analysis, respectively, to characterize the synergy between the electrostatic interaction and ion transfer. Hydrogenation of nitrobenzene was utilized as a reference reaction to reflect the catalytic performance of the prepared catalyst layers.

## 2. Experimental

### 2.1. Preparation of the zwitterionic polydopamine layer

In this work, zwitterionic polydopamine layer was prepared on the inner surface of a commercial PTFE capillary microchannel with the inner diameter of 0.6 mm and the length of 0.5 m through the self-polymerization of dopamine [1,11]. Firstly, 30 mL Tris buffer solution with the concentration of 10 mM was prepared, which was followed by dissolving 60 mg dopamine hydrochloride in the Tris buffer solution to obtain the slight brown dopamine solution. Secondly, the dopamine solution was introduced into the microchannel with the flow rate of 1 mL/h for 30 h, then 10 mL deionized water was fed into the microchannel for 20 min to remove the residual polymers. After drying at 60 °C for 1 h under nitrogen atmosphere, the color of the inner surface of the PTFE microchannel turned into dark brown, indicating the successful fabrication of the zwitterionic polydopamine layer inside the microchannel.

### 2.2. Palladium deposition on the zwitterionic polydopamine layer

In this step, $K_2PdCl_4$ aqueous solution, prepared by dissolving $PdCl_2$ and KCl with the molar ratio of 1:2 in deionized water, was used as the precursor solution. For the palladium deposition, the precursor solution was supplied into the microchannel modified with the polydopamine layer with a flow rate of 6 μL/h for 12 h. After that, excess amount of deionized water was fed into the microchannel at a flow rate of 0.3 mL/h for several times to remove the residual ions. Considering the weak reduction ability for the complete reduction of the adsorbed palladium ions [7,11], the microchannel was then placed into a tube furnace for the further reduction under 200 °C with hydrogen as the reduction agent. Based on the concentration of the palladium concentration in the precursor solution, a series of precursor solutions with different pH values ranging from 2.6 to 3.6 could be obtained and the pH value was measured by a pH meter (FE28, Mettler Toledo, Switerland).

### 2.3. Material characterization

In this work, the surface chemical compositions of the catalyst layer were carried out by a Thermo ESCALAB 250Xi XPS system with Al Kα radiation ($h\nu = 1486.6$ eV) at a power of 150 W. The topography of the catalyst layer was characterized by using FESEM (S4800, Hitachi High Technologies, Japan) fulfilled at an accelerating voltage of 3 kV. UV–Vis spectral analysis was adopted to estimate the catalyst loading in the microreactor by a UV–visible spectrophotometer (T6-1650E, Persee, China) with the wavelength ranging from 190 nm to 1100 nm at 1-nm resolution. Through measuring the absorbance difference of palladium precursor solution before and after deposition, the catalyst loading could be estimated. The zeta-potential was measured using a Zetasizer (Nano S, Malvern, Britain) at 25 °C to characterize the surface charge of the polydopamine particles in response to the pH value, where the polydopamine was dispersed in deionized water and the pH was adjusted using 1 M HCl solution.

Besides, to characterize both the ion transfer and interfacial resistance of the polydopamine layer in response to pH, EIS measurement was carried out by an electrochemical workstation (VMP3, Bio-Logic, France) with the frequency swept from 100 kHz to 10 mHz and a perturbation of 10 mV in a three-electrode testing system. In the measurement, the polydopamine layer was prepared onto a glassy carbon electrode with a diameter of 3 mm, $[Fe(CN)_6]^{3-/4-}$ was used as the probe and 1 M HCl aqueous solution was used to adjust the pH value.

### 2.4. Nitrobenzene hydrogenation

Nitrobenzene hydrogenation to aniline was used to evaluate the performance of the deposited palladium nanoparticles in a capillary microchannel. Nitrobenzene (Aladdin, Shanghai, China) solution, used as the liquid reactant, was prepared by dissolving nitrobenzene into ethanol aqueous solution with the volume ratio of 7:3 for ethanol to water. High purity hydrogen gas (Chaoyang, Chongqing, China) was used as the gas reactant. The liquid and gas reactants were delivered into the microreactor using a syringe pump (LSP01-1BH, Longer-Pump, China) and a gas mass flow controller (FMA-2602A-I, Omega, USA), respectively. For fair comparison, both the gas and liquid flow rates as well as the nitrobenzene concentration were kept the same under each condition, where they were set at 0.15 sccm, 0.9 mL/h and 60 mM, respectively. And the hydrogenation of nitrobenzene was conducted at room temperature of about 25 °C.

During the test, the concentrations of nitrobenzene and the desired product of aniline collected from the outlet of the microreactor were