Chemical Engineering Journal 351 (2018) 959–966

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

# Coenzyme A-regulated Pd nanocatalysts for formic acid-mediated reduction of hexavalent chromium

Shengdong Dai, Xitian Wu, Jinli Zhang, Yan Fu*, Wei Li*

*School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, PR China*

## HIGHLIGHTS

- Highly soluble CoA-Pd NPs were synthesized by a facile one-pot reduction method in aqueous solution.
- CoA plays a significant role in regulating the grain boundaries during the growth of Pd NPs.
- CoA-Pd NPs are superior to recently reported Pd-based catalysts in the formic acid-mediated reduction of Cr(VI).
- CoA-Pd NPs have been successfully applied in a variety of hydrogenation reactions.
- Improved activity originates from the grain boundaries formed on CoA-Pd NPs.

## ARTICLE INFO

*Keywords:*
Pd nanocatalyst
Coenzyme A
Hexavalent chromium
Reduction
Hydrogenation

## ABSTRACT

Coenzyme A (CoA), as a cofactor of enzymes in bacteria, is involved in various reactions of intermediary metabolism owing to its thiol groups. Herein we develop a facile CoA-assisted approach for the green synthesis of nonspherical Pd nanoparticles (NPs) with grain boundaries, which potentially serve as the catalytic hot spots. As-prepared CoA-Pd nanocomposites were applied for the catalytic reduction of highly toxic chromium (VI) by using formic acid (FA) as the reductant with the highest reduction rate of 2.45 mmol mg$^{-1}$ min$^{-1}$ (50 °C), which is superior to recently reported homogenous and heterogeneous Pd-based catalysts. Through the characterizations by UV–vis, FTIR, TEM, XRD and XPS in combination with DFT calculations, CoA plays an essential role in regulating the growth of Pd NPs, resulting in the formation of nonspherical morphology at high [$Na_2PdCl_4$]/[CoA]. The catalytic activity of CoA-Pd was also assessed for the hydrogenation reduction of p-nitrophenol and the degradation of trichloroethylene (TCE) in the presence of formic acid. This strategy expands eco-friendly synthetic techniques to design highly efficient nanocatalysts to meet the requirement of catalytic reduction of Cr (VI) and other types of FA-mediated hydrogenation reactions.

## 1. Introduction

Hexavalent chromium (Cr(VI)) has wide industrial applications in metal finishing, wood products, electroplating and dye production [1–3]. However, Cr(VI) is also one of the most toxic pollutants and is proved to be hazardous to human and animals, especially to respiratory system, kidneys, liver, skin and eyes [4]. Therefore, the World Health Organization (WHO) has defined the maximum allowable limit of 0.05 mg L$^{-1}$ in drinking water [5]. Until now, a variety of approaches have been developed to eliminate Cr(VI) from environments, including precipitation [6], solvent extraction [7], membrane filtration [8], and ion exchange [9]. However, most of them involve high cost and time-consuming operation, and are also limited by other considerable factors including mixing time, pH and inevitable secondary wastes [10,11]. It is noticeable that a trace amount of nontoxic trivalent chromium (Cr (III)) can be recognized as an essential nutrient for humans and other animals [12,13]. Therefore, it is highly desirable to explore eco-friendly methods for reducing Cr(VI) to Cr(III) with mild reaction condition and low energy consumption, of which the core is the development of highly efficient catalysts.

To date, Pd-catalyzed reduction of Cr(VI) has attracted considerable attention owing to high efficiency, operational simplicity and long-term stability [14–16]. Extensive studies have shown that Pd-catalyzed reduction of Cr(VI) possesses at least one order of magnitude higher efficiency as compared to other reduction methods mainly involving non-noble metal-catalyzed reduction [17,18], photocatalytic reduction [19,20] as well as biological reduction [21,22]. For example, the graphene oxide immobilized Pd NPs possesses the turnover frequency (TOF) of

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* Corresponding authors.
*E-mail addresses:* fuyan@tju.edu.cn (Y. Fu), liwei@tju.edu.cn (W. Li).

https://doi.org/10.1016/j.cej.2018.06.138
Received 8 March 2018; Received in revised form 2 June 2018; Accepted 21 June 2018

3.6 $mol_{K2Cr2O7}^{1}$ $mol_{Pd}^{-1}$ $min^{-1}$ for Cr(VI) reduction in the presence of FA at room temperature [23], which is two order of magnitude higher than those of Co-RGO (0.049 $mol_{K2Cr2O7}^{1}$ $mol_{Pd}^{-1}$ $min^{-1}$) [24] and Ni-RGO (0.014 $mol_{K2Cr2O7}^{1}$ $mol_{Pd}^{-1}$ $min^{-1}$) [1] under similar conditions. Wang et al. prepared a AuPd@Pd core–shell nanocrystals by using minoxidil as growth-directing agents, and the *k* value reaches up to 1.44 $min^{-1}$ for FA-mediated Cr(VI) reduction [25]. In contrast, the *k* was only 0.079 $min^{-1}$ for Cr(VI) reduction catalyzed by $TiO_2$ under UV light irradiation [26]. Compared with other developed catalysts, Pd-based catalysts have presented intriguing prospects in practical applications on Cr(VI) reduction.

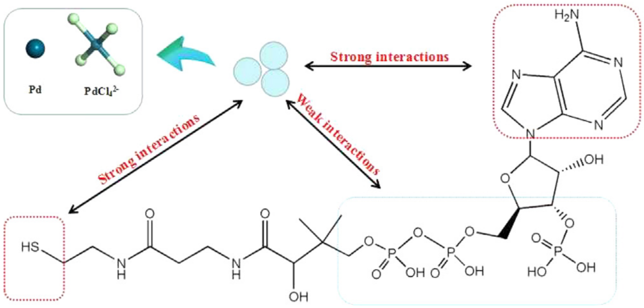
Up to now, a variety of methods have been developed for the synthesis of highly active Pd nanocatalysts through minimizing particle sizes, manufacturing defects, and generating dislocation lattices [27–29]. For example, Zhu and coworkers [30] employed a facile hydrothermal method to prepare $TiO_2$-supported Pd nanowires with high density of grain boundaries, in which Pd co-catalysts effectively reduce the $H_2$ evolution and greatly enhance the photocatalytic performance in $CO_2$ reduction. Remita and coworkers [31] utilized electron beam irradiation method to fabricate 1D Pd nanowires with twinning grain boundaries and stacking defaults, which serve as catalytic hot spots for electrocatalytic ethanol oxidation. Moreover, Liu and coworkers [32] adopted one-step reduction to synthesize nano-porous Pd catalysts with surface defects, which display high performance for the decomposition of FA. Aiming to lower the consumption of noble metal precursors, we are motivated to develop new methodologies for creating highly active sites on Pd-based catalysts.

CoA (as illustrated in Fig. S1), as a cofactor of enzymes in bacteria [33], is involved in reactions of intermediary metabolism. The thiol groups of CoA participate in the oxidation pathway of fatty acids and/or in calmodul-independent protein kinase activation, and maintain the reducing environments of cells [34,35]. CoA contains a variety of functional groups including thiol, amide, phosphate, etc., which show distinct binding affinities toward metal ions [36,37]. In this study, we are motivated to employ CoA as a growth-directing agent to synthesize nonspherical Pd NPs with grain boundaries for the reduction of Cr(VI) (as illustrated in Scheme 1). CoA-Pd NPs prepared at the $[Na_2PdCl_4]/[CoA]$ of 45, show the highest activity in the reduction of Cr(VI) by FA, with the reduction rate of 2.45 mmol $mg^{-1}$ $min^{-1}$ at 50 °C. Our proposed nanocatalysts were shown to be superior to most reported homogenous and heterogeneous Pd-based catalysts in catalytic reduction of Cr(VI).

## 2. Experimental section

### 2.1. Materials

Adenosine 5′-triphosphate disodium salt (ATP) was purchased from Tianjin Heowns technology co. Ltd. Potassium dichromate ($K_2Cr_2O_7$) were purchased from Shanghai Aladdin Chemical Reagent Company (Shanghai, China). Trichloroethylene (TCE) was purchased from J&K Scientific. Formic acid (FA, 88%) and *p*-nitrophenol (4-NP) were purchased from Tianjin Guangfu Fine Chemical Research Institute. $Na_2PdCl_4$ (99.9%) was purchased from Alfa Aesar. Coenzyme A (CoA) was purchased from Sangon Biotech (Shanghai) Co. Ltd. Dimethylamine borane (DMAB) was purchased from Sigma-Aldrich. All the chemical reagents were used without further purification. The water used in all the experiments was distilled for three times.



**Scheme 1.** The growth schematic of nonspherical Pd NPs by different interactions between Pd atom or $PdCl_4^{2-}$ and CoA.

### 2.2. Preparation of CoA-Pd NPs

Pd NPs were synthesized through the reduction of $Na_2PdCl_4$ by DMAB in the presence of CoA. Firstly, different amount of CoA dissolved in 10 mM $NaH_2PO_4$-$Na_2HPO_4$ buffer (pH 5.0) were firstly incubated with $Na_2PdCl_4$ at the $[Na_2PdCl_4]/[CoA]$ ratio of 15, 30, 45 and 60, respectively. After incubation for 12 h at 25 °C, freshly prepared aqueous solution of DMAB was added to the mixture at the $[DMAB]/[Na_2PdCl_4]$ ratio of 3.33, to initiate the reduction at 25 °C. The obtained CoA–Pd NPs were used after a 24 h-reduction. Similar procedure was adopted to synthesize ATP-Pd NPs through replacing CoA by ATP.

### 2.3. Catalytic reduction of Cr(VI) assisted by FA

In our experiments, FA was chosen as the reductant for Cr(VI) reduction since it undergoes direct mineralization to $CO_2$ and $H_2$ in the presence of metal catalysts without the formation of intermediates. In addition, acidic pH facilitates the reduction process of Cr(VI). Typically, a certain amount of as-prepared CoA-Pd NPs was put into 14 mL of $K_2Cr_2O_7$ solution (5 mM) at 50 °C under vigorously magnetic stirring, followed by adding 1 mL of FA solution. At a regular time interval, 200 μL of the reactants was taken out and then diluted to 3 mL, and immediately analyzed by UV–vis spectra (260–530 nm). Control experiments were carried out by varying the reaction temperature or the concentration of FA.

The rate constant (*k*) was calculated according to $\ln(C_t/C_0) = -k\,t$, where *t* is the reaction time, $C_0$ and $C_t$ are the concentration of Cr(VI) in the reaction system at the start and *t*, respectively. The reaction rate was calculated by $M_{K_2Cr_2O_7}/(m_{\mathrm{Pd}} \times t)$, where $M_{K_2Cr_2O_7}$ is the mole number of $K_2Cr_2O_7$, $m_{\mathrm{Pd}}$ is the quality of Pd in the reaction system, *t* is total reaction time. The turnover frequency (TOF, defined as the number of reactant that 1 mol of Pd catalyst can convert into products per unit time, the unit is $mol^1$ $mol^{-1}$ $min^{-1}$) is calculated according to $\mathrm{TOF} = \Delta M_{K_2Cr_2O_7}/(n_{\mathrm{Pd}} \times \Delta t)$, where $\Delta M_{K_2Cr_2O_7}$ is the change of $K_2Cr_2O_7$ (mol), $n_{\mathrm{Pd}}$ is the amount of Pd based on the precursor (mol), $\Delta t$ is the change in time (min).

Recycling experiments were performed to test the catalytic stability of CoA–Pd NPs in the reduction of Cr(VI). 14 mL of $K_2Cr_2O_7$ solution (5 mM) containing a certain amount of CoA-Pd NPs was heated to 50 °C under vigorously magnetic stirring. After addition of 1 mL FA solution, the maximum absorbance around 350 nm was monitored at different time intervals. After completing the reduction reaction, fresh $K_2Cr_2O_7$ solution was added to keep the initial concentration of 5 mM. The recycling tests were repeated according to the above procedures.

### 2.4. Catalytic reduction of 4-NP and degradation of TCE

For the reduction of 4-NP by FA, a certain amount of CoA-Pd NPs was added into 3 mL aqueous solution containing 60 mM FA and 0.1 mM 4-NP. Then time-dependent UV curves were recorded at 316 nm at 50 °C. For the degradation of TCE, a 5 mL mixture of CoA-Pd NPs and FA was firstly added into a 10 mL headspace bottle. Then 0.38 mM TCE solution was added, and the bottle was sealed immediately by using aluminum crimp caps with Teflon-limed septa. All the reactions were carried out on a shaking table. At an interval of 30 min, the concentration was measured by injecting 1 mL of the headspace sample directly into a gas chromatography (SP-3420A) with a flame ionization detector (FID) and a FFAP column. The detector temperature was set at 523 K. Based on the Henry's law constant, the changes of the