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Green synthesis of palladium nanoparticles with carboxymethyl cellulose for degradation of azo-dyes

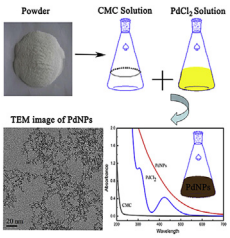
Gang Li, Yun Li, Zhengdong Wang, Huihong Liu*

College of Chemistry and Chemical Engineering, Wuhan Textile University, Wuhan, 430200, China

HIGHLIGHTS

- Green synthesis of palladium nanoparticles using carboxymethyl cellulose.
- The synthesis of palladium nanoparticles were performed easily.
- Carboxymethyl cellulose acts as both reducing and stabilization agents.
- The as-synthesized palladium nanoparticles show excellent catalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

Palladium nanoparticles (PdNPs) were synthesized through friendly environmental method using $PdCl_2$ and carboxymethyl cellulose (CMC) in an aqueous solution (pH 6) at controlled water bath (80 °C) for 30 min. CMC functioned as both reducing and stabilizing agent. The characterization through high resolution-transmission electron microscopic (HRTEM) and **X**-ray Fluorescence Spectrometry (XRF) inferred that the as-synthesized PdNPs were spherical in shape with a face cubic crystal (FCC) structure. The results from dynamic light scattering (DLS) suggested the PdNPs had the narrow size distribution with an average size of 2.5 nm. The negative zeta potential (−52.6 mV) kept the as-synthesized PdNPs stable more than one year. The PdNPs showed the excellent catalytic activity by reducing degradation of azo-dyes, such as p-Aminoazobenzene, acid red 66, acid orange 7, scarlet 3G and reactive yellow 179, in the present of sodium borohydride.

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1. Introduction

Given that palladium is one of the most efficient metals in catalysis, the study of palladium-based materials is hugely important and valuable [1–7]. Historically, the most common synthesis of palladium nanoparticles (PdNPs) has utilized chemical reducing agents such as hydrazine, sodium borohydride, sodium citrate and ascorbic acid to reduce Pd^{2+} ions in the presence of some stabilizers to create uniform suspensions [7–9].

For the development of green chemistry, utilization of nontoxic chemicals, environmentally friendly solvents, and renewable/biodegradable materials are the central tenants in the preparation of nanoparticle [10,11]. Recently, biological entities have been reported as serving as both reducing and stabilizing agents for green synthesis of metallic nanoparticles [12–16]. Among these methods, polysaccharides from nature have attracted significant attention due to the simple sampling and cost effectiveness. Moreover, polysaccharides have many functionalities including hydroxyl groups and a hemiacetal reducing end that are capable of reducing precursor salts or acting as supporters for catalytic applications [13]. Among the polysaccharides, chitosan [17,18], starch [19,20], alginate [21,22] and cyclodextrin [23,24] were used as the reducing agents, capping agents or nanoparticle supporters in synthesis of PdNPs catalysts.

* Corresponding author.
E-mail addresses: huihongliu@126.com, huihongliu@wtu.edu.cn (H. Liu).

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Cellulose is the most abundant renewable polysaccharide available on earth. carboxymethyl cellulose (CMC) is a water-soluble polysaccharide possessing both carboxylate and hydroxyl groups that allow this biodegradability, flexibility, non-toxicity and inexpensive polysaccharide for many practices in different areas of science. For example, CMCs have been used to immobilize Pd NPs and employed in organic transformations [25–28]. However, these reductions of the metallic precursors were carried out in the presence of reducing agents such as $NaBH_4$, a hazardous and dangerous compound. Few reports described the green synthesis of CMC-supported PdNPs by direct reduction of palladium species with CMCs as a green reductant [29,30]. Nevertheless, in one case, the cellulose nanocrystal-supported PdNPs were synthesized for a long time (12 h) in a higher temperature (100 °C) [29]. In another case, the cellulose microencapsulated PdNPs were synthesized in a cellulosic ionic liquid solvent [30].

Motivated by recent applications of green synthesis for PdNPs and the corresponding need to better understand the fundamental properties of biopolymers, our idea was to apply CMC to prepare PdNPs as both reducing and stabilizing agent. In this system, PdNPs would be physically enveloped by cellulose thin films and perhaps stabilized by the interaction by ligation of hydroxyl groups of the cellulose. The controllably synthesized PdNPs-CMC nanocomposites had several properties such as good stability and high catalytic activities.

2. Experimental

2.1. Reagents and materials

Carboxymethyl cellulose sodium salt (800-1200 cP) was received from Shanghai shanpu Chemical Co., Ltd. Palladium chloride ($PdCl_2$), sodium borohydride, Sodium hydroxide, Hydrochloric acid and p-Aminoazobenzene were all purchased from Sinopharm Chemical Reagent Co., Ltd. All the azo-dyes were obtained from local companies. All aqueous solutions were prepared using purity water (18.30 MΩ cm) produced by a Labpure Water System (Chendou, China).

2.2. Synthesis of PdNPs

For a typical synthesis of PdNPs, an amount of $PdCl_2$ solution (10 mM) and CMC aqueous solution (1.0 wt %) were mixed in a 10 mL flask. After mixed thoroughly, NaOH (0.1 M) was added into the reaction mixture to adjust the solution pH. Then the mixture was heated on a constant temperature controlled by water bath for several minutes. PdNPs were finally synthesized at pH 6.0 at 80 °C within 30 min.

2.3. Characterization

2.3.1. UV–visible spectroscopy

Preliminary characterization of the PdNPs was carried out using UV–Visible spectroscopy. The reduction of palladium ions to the nanoparticle form was monitored by measuring the UV–visible spectra of the solutions after diluting the sample with deionized water. The UV–visible spectra of PdNPs colloid solution were recorded in a 1 cm path length quartz cuvette with a UV–vis 8000S spectrophotometer (Shanghai Metash Instruments Co. Ltd, Shanghai, China).

2.3.2. High resolution-transmission electron microscopic (HRTEM) and energy dispersive X-ray spectroscopy (EDX)

The HRTEM images were recorded in a JEOL-JEM-2100F. Composition of PdNPs was analyzed by the TEM instrument equipped with an energy dispersive X-ray spectroscopy (EDX). For the TEM and EDX analysis, a droplet of aqueous solution of synthesized PdNPs was spread onto a carbon coated copper grid (300 meshes) and dried under IR lamp.

2.3.3. Zeta potential measurement and particle size analysis

The zeta potential of the synthesized nanoparticles was determined by means of zeta potential analyzer (Malvern ZEN3600 Zetasizer, England). The measurement of zeta potential was based on the direction and velocity of particles under the influence of known electric field. The size of PdNPs was measured on the basis of the time dependent oscillations of the coherent laser light, e.g., dynamic light scattering (DLS), which were scattered by the nanoparticles subjected to the inherent Brownian movement.

2.4. Catalytic reductive degradation of azo-dyes

The decolorization of azo-dyes catalyzed by the PdNPs in the present of $NaBH_4$ was performed. The aqueous solution of $NaBH_4$ (100 μL, 0.1 M) was mixed with the aqueous solution of an azo-dye in a tube, and then a 20 μL mixture solution of CMC supported PdNPs was added. After mixed thoroughly by manual shaking, the UV/vis absorption spectra were recorded on the spectrophotometer immediately. The control experiments were carried out in the same condition without addition of PdNPs.

3. Results and discussion

3.1. Synthesis of PdNPs

The color change was noted by visual observation in the flasks that contained $PdCl_2$ and CMC solution. The color of the solution changed from pale yellow to dark brown depending on the $PdCl_2$/CMC ratio, solution pH, temperature and reactive time. This color change indicated the generation of PdNPs in the solution.

The formation of PdNPs was monitored by UV– visible spectroscopy in the 200–800 nm range. Fig. 1 displayed the absorption spectra of palladium colloidal suspensions (Fig. 1c) after 30min of reduction by 0.4% CMC at the temperature of 80 °C. The absorption spectra of CMC (Fig. 1a) and $PdCl_2$ solution (Fig. 1b) were used for comparison. The UV–vis spectrum of CMC displayed almost no absorbance bands over the spectral range tested (Fig. 1a). The absorption bands located at 422 nm and 305 nm were ascribed to the ligand-to-metal charge-transfer transition between Pd(II) and

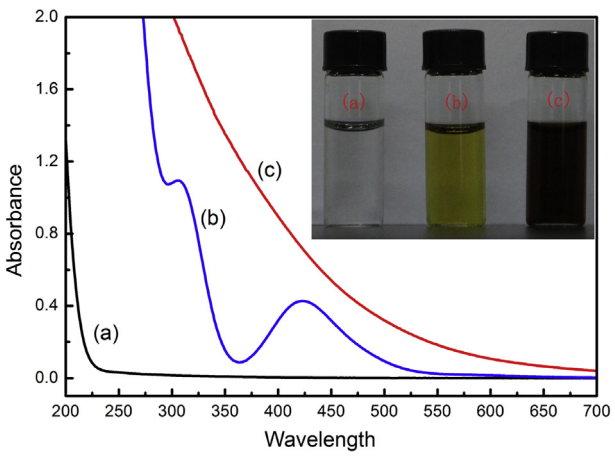

Fig. 1. UV–vis spectra of (a) CMC aqueous solution, (b) $PdCl_2$ and (c) PdNPs synthesized by CMC and $PdCl_2$.

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