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Facile and Green Cinchonidine-Assisted Synthesis of Ultrafine and Well-Dispersed Palladium Nanoparticles Supported on Activated Carbon with High Catalytic Performance

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Abstract

We report the facile and green synthesis of activated carbon-supported palladium (Pd/AC) containing homogeneously dispersed Pd nanoparticles (Pd NPs) by using eco-friendly and naturally available cinchonidine (CD) as the capping agent. The Pd NPs in the synthesized Pd/AC hybrid are uniform with sizes predominantly in the range 4 to 7 nm. The synthesized Pd/AC was characterized with various methods, such as TEM, XRD, and XPS, and the influence of the synthetic conditions on its properties were investigated. The advantages of CD over conventional capping agents include its easy depletion after the synthesis with a simple rinsing process. Owing to the ultrafine, well-dispersed and purified Pd NPs, the synthesized hybrid exhibits excellent catalytic activities in the reduction of 4-nitrophenol and methylene blue. These findings further the development of novel stabilizing agents from naturally available sources for the preparation of heterogeneous catalysts with enhanced performance.

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1. Introduction

Palladium nanoparticles (Pd NPs) are among the most intensively used noble metals in catalysis owing to their excellent catalytic performance in a variety of reactions.[1-3] Nonetheless, there are difficulties inherent in the use of colloidal Pd NPs in homogeneous systems, particularly in separation and subsequent recycling. Moreover, to meet the demand of high performance catalytic applications, synthesized Pd NPs require a sufficiently small particle size with a homogeneous distribution; however, these properties are impeded by inter-particle aggregation due to the increase in the total surface energy as the size of Pd NPs decreases. One of the most common and effective strategies to overcome these shortcomings is the solution-phase deposition of Pd NPs onto a pre-existing nanostructured support.[4-6] Although there have been many attempts to improve the synthetic method, several problems still persist. Firstly, many harmful chemical compounds, ranging from organic solvents (DMF, ethylene glycol, *etc.*) to inorganic reagents ($NaBH_4$, hydrazine, *etc.*) are conventionally employed, which pose environmental risks and threaten human safety. Next, the synthetic process generally requires multi-step preparation under heat treatment, which results in high production costs and asynchronous yields that limit commercial applications. Lastly, the presence of capping agents severely limits the catalytic activities of the metal NPs. Therefore, the development of state-of-the-art synthetic methods that can produce high performance supported Pd catalysts and address the abovementioned disadvantages is highly desirable.

Pd NPs supported on carbon-based nanomaterials have been paid intensive attention due to their potential applications in various fields.[7,8] Many previously reported works related to Pd/carbonaceous material based nanocatalysts have showed high efficiency in catalytic performance. Z. Zhang *et. al.* reported a unique Pd NPs loaded hierarchically porous graphene network obtained by multiple synergistic interactions.[9] The synthesized architecture showed excellent activity and durability in ethanol oxidation due to the ultrafine monodispersed Pd NPs, the strong interaction between Pd NPs and the support, and the unique hierarchically porous network structure. Z. Wang *et. al.* reported a highly efficient hydrogen generation from formic acid/sodium formate aqueous solution catalyzed by *in situ* synthesized Pd/Carbon with citric acid.[10] The presence of citric acid during the formation and growth of the Pd NPs on carbon can

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drastically enhance the catalytic property of the resulted Pd/Carbon. Among the most commonly employed carbon materials as supports for metal-based catalysts in industrial applications is activated carbon (AC) because it is cheap and it has a large surface area as well as high resistance to acidic and basic media.[11]

The recent tremendous advances in nanoscience and nanomaterials have led to robust developments in chemical industries and manufacturing, but pose serious problems for the preservation of the environment and the protection of human health. To establish sustainable nanotechnologies, the design and usage of environmentally friendly chemicals and processes that minimize the consumption as well as the generation of hazardous substances in every technological area have been essentially emphasized.[12] Typically, a "green" synthesis of metal-based catalysts involves the employment of products from natural or environmentally benign sources, such as vitamins,[13] tea and coffee,[14] or sugars[15] in nontoxic media under mild reaction conditions. Hence, a particularly exciting challenge is to search for facile synthetic pathways and novel eco-friendly chemicals that can achieve high catalytic efficiencies and satisfy the principles of *Green Chemistry*.[16] Ascorbic acid (AA), commonly known as vitamin C, is among the most extensively used reducing agents for this purpose because it is biodegradable, environmentally benign, naturally available, and has low toxicity.[17,18] Cinchonidine (CD) is one of the main components of the bark extracted from the plants belonging to the Cinchona species, and is well-known as a catalyst for asymmetric organocatalysis, a ligand for transition metal complexes, and a surface modifier for asymmetric heterogeneous reactions.[19-21] Like other cinchona alkaloids, CD is a relatively small molecule (M=294g/mol) comprising an aromatic quinoline and an aliphatic quinuclidine moieties that are connected by two C–C bonds to form different stereometric conformations.[22,23] CD is a promising material from the view of *Green Chemistry* because this organic chemical is naturally occurring, eco-friendly, biodegradable, and nontoxic. To date, there have been only a few reports of colloidal metal syntheses using derivatives of CD as stabilizers with modest catalytic performances.[24,25] Furthermore, there have been no reported studies for the applications of CD as a capping agent in the synthesis of supported metal catalysts.

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In the present paper, we come forward some significant advances in the synthesis of supported Pd catalysts. First, we introduce a facile one-pot approach to the fabrication of an activated carbon-supported palladium (Pd/AC) hybrid with ultrafine and homogeneously dispersed Pd NPs. This synthesis is genuinely green since it utilizes CD as an efficient capping agent for the first time and AA as a mild reductant in an aqueous medium at room temperature. Next, we demonstrate that the removal of residual CD after catalyst preparation can easily be achieved with a simple rinsing step, in contrast to the inherent problems of using conventional capping agents; thus, making the present approach to catalytic applications more profitable. Owing to the ultrafine, well-dispersed, and purified Pd NPs, the prepared Pd/AC catalyst exhibits excellent catalytic performances in the borohydride reductions of 4-nitrophenol and methylene blue (MB) under mild aqueous conditions.

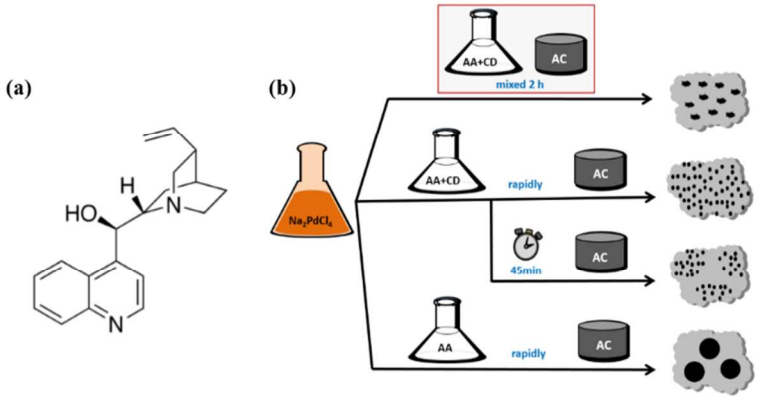

Fig. 1 (a) The cinchonidine (CD)molecule and (b) a schematic diagram of the method for the preparation of the Pd/AC hybrids.

2. Experimental section

2.1 Chemicals

All reagents were of analytical grade and used as received without further purification. AC (Darco, powder, −100 mesh), AA (99%), CD (96%), Na_2PdCl_4 (99.99%), $NaBH_4$ (powder, ≥98%), 4-nitrophenol (powder, spectrophotometric grade), and MB (powder, dye content ≥82%) were purchased from Sigma-Aldrich. Double distilled water was used in catalyst preparation, in reduction reactions, and in all of the rinse processes.

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2.2 Preparation of Pd/AC samples

The AC suspension was prepared by ultrasonicating 100 mg AC in 15 mL H_2O for 30 minutes followed by 1 hour of stirring. The Na_2PdCl_4 solution was prepared by ultrasonicating 14 mg Na_2PdCl_4 in 5 mL H_2O for 10 minutes. All the synthetic processes were carried out under vigorous stirring (1000 rpm).

The Pd/AC(wash) hybrid was synthesized as follows. A mixture containing 30 mg AA and 20 mg CD in 15 mL H_2O was thoroughly ultrasonicated for 20 minutes to complete the dissolution of AA and CD. The Na_2PdCl_4 solution was then added, and the resulting mixture was rapidly added to the AC suspension. The suspension was stirred for 3 hours and then filtered, washed (see the section 'Rinsing process'), and dried in the ambient atmosphere at 110ºC overnight.

The Pd/AC-noCD sample was synthesized with a procedure identical to that used to synthesize the Pd/AC(wash) hybrid, but in the absence of CD. Typically, 30 mg AA was dissolved in 15 mL H_2O followed by the addition of the Na_2PdCl_4 solution. This mixture was quickly added to the AC suspension and the reaction was continued for 3 hours.

The Pd/AC-1 sample was synthesized by using a procedure identical to that for preparing the Pd/AC(wash) hybrid, with the exception that after adding the Na_2PdCl_4 solution to the aqueous mixture containing 30 mg AA and 20 mg CD, the solution was stirred for 45 minutes to form a Pd colloid. The resulting mixture was then added to the AC suspension followed by 3 hours of stirring.

The Pd/AC-2 sample was synthesized with a procedure identical to that used to synthesize the Pd/AC(wash) hybrid, but with an altered reaction sequence. Typically, the aqueous mixture containing 30 mg AA and 20 mg CD was added to the AC suspension and the mixture was stirred for 2 hours. The Na_2PdCl_4 solution was subsequently added to this suspension followed by 3 hours of stirring.

2.3 Rinsing process

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The Pd/AC(wash) sample was washed twice with acetone (50 mL each time) followed by twice with water (50 mL each time). In a typical rinsing, the wet solid Pd/AC collected from the previous filtration was dispersed in 50 mL acetone (or water) followed by 15 minutes of stirring (1000 rpm). The suspension was then filtered with a Whatman filter paper.

The Pd/AC(no wash) sample was collected directly after the synthesis by filtration without washing.

2.4 Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded by using a D2-phaser (Bruker) equipped with Cu radiation (30 kV, 10 mA) and a LYNXEYE detector that scanned 2θ values between 10° and 90°. Transmission electron microscopy (TEM) images were obtained with a Tecnai F30 microscope operated at 300 kV to analyze the morphologies of the Pd-based catalysts. The catalysts were dispersed in acetone by using an ultrasonicator (SD-250H, Mujigae) for 3 minutes and then dropped onto a carbon film containing holes supported by a 200 mesh grid of copper. The system was then dried overnight. High-resolution X-ray photoelectron spectroscopy (XPS) was performed on a Thermo VG Scientific Sigma Probe spectrometer with an Al Ka radiator, and the vacuum in the analysis chamber was maintained at 10^{-10} mbar. Thermal gravimetric analysis (TGA) was carried out by using a Q 50 (TA Instruments, U.S.) apparatus in air (flow rate 40 $mLmin^{-1}$). The samples were placed onto a platinum pan and inserted into the furnace. The temperature was increased from room temperature to 850°C at a rate of 20°$Cmin^{-1}$. The weight change was calculated based on the initial weight of the sample. The elemental composition of C, N, and H in the samples were analyzed by combustion method using an ELTRACS-800 analyzer (Germany). Ultraviolet-visible spectroscopy (UV-vis) was carried out on a JASCO V-530 spectrophotometer (Japan) equipped with 10 mm quartz cells at room temperature. The Pd loadings before and after 5 recycling runs were determined by using a Thermal Scientific iCAP 6300 inductively coupled plasma optical emission spectroscopy (ICP-OES) instrument.

2.5 Catalytic testing

2.5.1 Reduction of 4-nitrophenol

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The reduction of 4-nitrophenol was carried out in a quartz cell at room temperature and was *in situ* monitored by using UV-vis spectroscopy (JASCO V-530) scanning in the range 250–500 nm. In a typical reaction, 1 mL of an aqueous solution of 4-nitrophenol (0.1 mM) was added to 1 mL of an aqueous solution of $NaBH_4$ (10 mM), which results in a change in color from light yellow to yellow green. After adding 0.1 mL of 0.05 $mg.mL^{-1}$Pd/AC(wash) catalyst to the mixture, the cell was immediately placed into the UV-vis spectroscopy chamber for the measurements. A similar procedure was applied to the samples Pd/AC-noCD and Pd/AC(no wash).

2.5.2 Reduction of MB

The reduction of MB was performed in a quartz cell at room temperature and was *in situ* monitored with UV-vis spectroscopy (JASCO V-530) scanning in the range 550–725 nm. Typically, 1 mL of an aqueous MB solution (10 $mg.L^{-1}$) was added to 1 mL of an aqueous solution of $NaBH_4$ (10 mM). After adding 0.1 mL of 0.05 $mg.mL^{-1}$Pd/AC(wash) catalyst to the mixture, the cell was rapidly placed into the UV-vis spectroscopy chamber for the measurements. A similar procedure was applied to reduction processes with AC or without catalyst for comparison.

2.5.3 Recyclable test of the Pd/AC(wash) catalyst

The stability of the Pd/AC(wash) catalyst was investigated by carrying out the same reduction reactions with the magnification of 20 times. For each test, the reaction was performed 10 minutes. After that, the catalyst was recovered by a short centrifugation, washed with water and EtOH before it was reused for the next catalytic cycle. The procedure was repeated totally 10 times.

3. Results and discussion

3.1 Characterization of the synthesized Pd/AC(wash) hybrid

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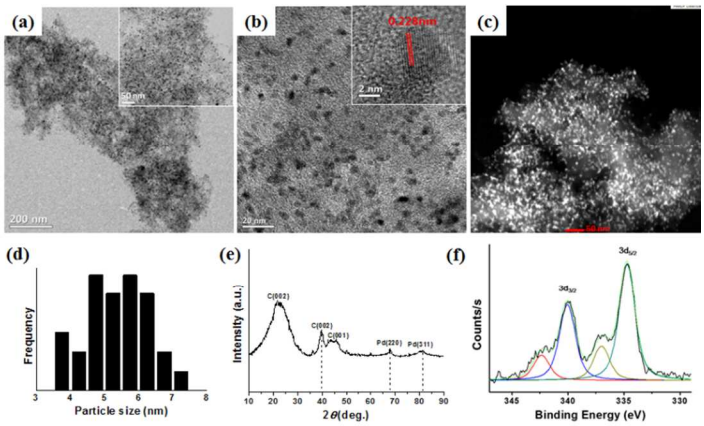

Fig. 2 Characterization results for the Pd/AC(wash) hybrid. (a),(b) bright-field TEM images at various magnifications,(c) dark-field TEM image, (d) Pd particle size distribution, (e) XRD pattern, and (e) XPS data for the Pd 3d peaks.

The Pd/AC(wash) hybrid was synthesized by performing a facile one-step addition of an aqueous solution containing a mixture of AA, CD, and Na_2PdCl_4 to an activated carbon (AC) suspension, followed by the rinsing process (see Section 2.3). Transmission electron microscopy (TEM) was carried out to examine the morphology of the synthesized Pd/AC(wash) hybrid. The representative bright-field TEM images at various magnifications in Figs. 2(a) and (b) and the typical dark-field TEM image in Fig. 2(c) show that the resulting Pd NPs are ultrafine and homogeneously dispersed on the AC surface. The HR-TEM image in the inset of Fig. 2(b) of a randomly selected Pd nanoparticle exhibits a lattice fringe distance of 0.228 nm, which corresponds to the mean value of a typical (111) plane of an *fcc* Pd surface.[26] Moreover, the TEM images reveal that the Pd particles mainly have sphere-like shapes. The particle size histogram in Fig. 2(d) shows that the size distribution of the Pd NPs is uniform with sizes predominantly in the range 4 to 7 nm. We also performed XRD analysis in the range 10°–90° to examine the crystalline structure of the Pd/AC(wash) sample. The XRD pattern shown in Fig. 2(e) contains diffraction peaks at 2θ values of 40.1º, 68.2º, and 82º, which were assigned to the (111), (220), and (311) planes of polycrystalline Pd NPs, respectively (JCPDS #46-1043). In addition, broad peaks at 26º and 45º attributed to the typical (002) and (100) planes of the hexagonal graphite structure of the AC support are also evident. The electronic state of the Pd species in the synthesized Pd/AC(wash) hybrid was determined with the XPS technique. The Pd 3d XPS spectrum shown in Fig. 2(f) contains doublet peaks with binding energies at 334.7 eV

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and 340.1 eV, which correspond to the species Pd^0 $3d_{5/2}$ and Pd^0 $3d_{3/2}$, respectively.[27] A small portion of Pd^{2+} species ($3d_{5/2}$: 337 eV and $3d_{3/2}$: 342.3 eV) can be observed, which is probably due to the fraction PdO or the interaction of Pd with oxygen from the carbon support. The XPS data indicate that most of the Pd precursor has been reduced to metallic Pd^0. The obtained results clearly indicate the successful synthesis of a Pd/AC(wash) hybrid with highly dispersed and ultrafine Pd NPs.

3.2 Effects of varying the reaction conditions

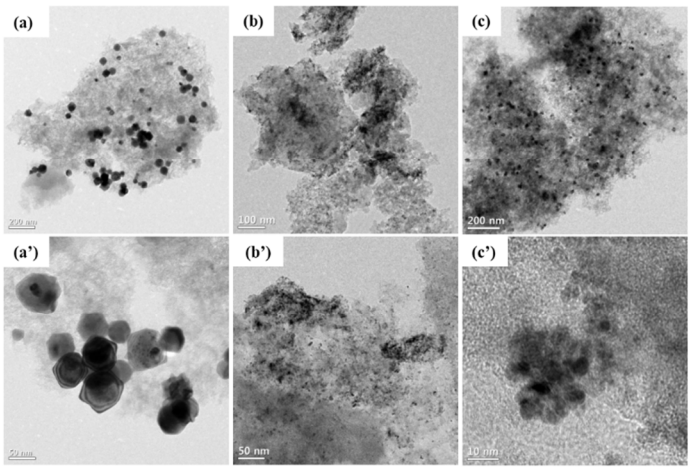

Fig. 3 TEM images at various magnifications: (a), (a') Pd/AC-noCD sample, (b), (b') Pd/AC-1 sample, and (c), (c') Pd/AC-2 sample.

To clarify the role of CD, we prepared a new sample by using a procedure identical to that used to synthesize the Pd/AC(wash) hybrid, only without the presence of CD. Interestingly, after adding the AA solution to the Na_2PdCl_4 solution, the mixture immediately turned black, which indicates the formation of Pd NPs. The mixture was then rapidly added to the AC suspension (denoted Pd/AC-noCD). The representative TEM images of the Pd/AC-noCD sample in Fig. 3(a) and (a') reveal very large Pd particles with sizes larger than 50 nm, which suggests that CD is the key factor to the synthesis of Pd/AC hybrids with ultrafine Pd NPs. We further investigated the influence of the reaction conditions on the synthesis of the Pd/AC(wash) hybrid by preparing the samples Pd/AC-1 and Pd/AC-2 with methods described in detail in the Experimental section. Briefly, a mixture of CD, AA, and Na_2PdCl_4 was allowed to react for 45 minutes to form colloidal Pd NPs, and was subsequently added to the AC suspension to prepare the Pd/AC-1

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sample. The Pd/AC-2 sample was prepared by adding the Na_2PdCl_4 solution to a mixture containing AC, AA, and CD. Typical TEM images of the Pd/AC-1 sample are shown in Fig. 3(b) and (b'), and reveal that the Pd NPs are not homogeneously deposited on the AC support, which is most likely due to the agglomeration of Pd NPs when they are formed in the colloid (Fig. S1). The TEM images of the Pd/AC-2 sample in Fig. 3(c) and (c') display large Pd particles with sizes above 20 nm and irregular shapes. These TEM data demonstrate that a precise preparation is critical to achieving Pd/AC hybrids with ultrafine and well-dispersed Pd NPs.

Based on the data obtained from the influence of various synthetic conditions, we can propose the formation of Pd NPs as follow. In the sample Pd/AC(wash), the mixture of AA, CD, and Na_2PdCl_4 was rapidly added to the AC suspension; hence, Pd NPs growing in this sample have a similar strategy like that growing in the Pd colloid (Fig. S1). Pd nuclei are formed in the solution and they grow to form Pd NPs while CD molecules play role as capping agents. In the presence of AC, these Pd nuclei anchor on the AC surface and gradually grow to form Pd NPs. Because the Pd nuclei are homogeneously formed in the solution, the growth of Pd NPs on AC surface is well-dispersed with uniform size. On the other hand, the Pd/AC-2 sample was prepared by adding Na_2PdCl_4 to the mixture of AA, CD, and AC. In this case, the AC surface is already well-covered by layers of CD molecules; therefore, the Pd nuclei formed on the sample Pd/AC-2 actually anchor on the CD-covered AC surface. When these nuclei grow larger, they have a tendency to aggregate to reduce the surface energy. Since the adsorption of CD on AC surface is sufficiently weak,[28] these Pd nuclei can migrate and aggregate during their growth; consequently, form Pd particles with irregular shape and big size.

3.3 Removal of the CD capping agent

Although capping agents ensure the homogeneous dispersion of NPs on supports, their presence restricts the free access of reactants to active sites on the particle surfaces, which leads to reduced catalytic activity. Thus, the depletion of the capping agent to attain an ultrapure surface of particles after the synthesis has generally been a crucial part of the process for preparing catalysts with the desired performance. Most capping agents reported in the literature are high molecular weight organic compounds that bind strongly to the surface of particles, resulting in severe purification difficulties.[29] In the present approach, the capping agent CD and

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byproducts of the synthesis were found to be easily removed with a simple rinsing process. Briefly, the synthesized Pd/AC hybrid was washed twice with acetone followed by twice with water; this sample is denoted Pd/AC(wash) to distinguish it from the Pd/AC sample collected without washing, Pd/AC(no wash). TEM study of these samples shows similar to each other (Fig. S2), suggesting that the distribution and morphology of Pd NPs are not affected by the washing process. The complete removal of CD was demonstrated by performing TGA, EDS, elementary analysis, and XPS methods.

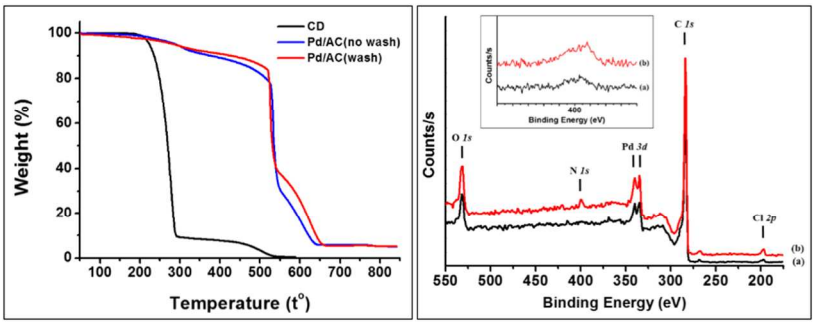

Fig. 4 Left panel: TGA data for CD (black), and for the Pd/AC hybrids before washing (blue) and after washing (red). Right panel: XPS spectra for (a) Pd/AC(wash) and (b) Pd/AC(no wash). The inset shows high-resolution scans of the N 1sregion.

TGA was conducted for the two samples in the range 50ºC to 850ºC to study their thermal behaviors and to compare their weight losses. TGA was also carried out for CD as a reference. As shown in the panel on the left of Fig. 4, approximately 90% of the mass of CD decomposes in the range 200–300ºC, and it completely decays above 550ºC. The Pd/AC(wash) and Pd/AC(no wash) samples exhibit similar thermal behaviors. An initial weight loss of 5% at 300ºC followed by a ~15% mass loss at 550ºC were observed, which are due to the removal of oxygen-functional groups present on AC and residual CD. Subsequently, the TGA curves of these samples rapidly drop to 5% wt in the range 550–650ºC, which is assigned to the decomposition of their graphitic carbon components.[30] Above 650ºC, the two samples retain only a mass of approximately 5% wt. It is worth to point out that the Pd/AC(no wash) sample undergoes slightly more weight loss in the range 350–550ºC than the Pd/AC(wash) sample. Since the two samples are identical with only the exception of the washing step, this minor difference in weight loss must be due to remaining CD. The results obtained with TGA indicate that the washing step effectively removes the residual CD; however, this weight loss comparison can only relatively evaluate the removal

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of CD and it does not directly assess the depletion of CD. We further analyzed the elimination of CD quantitatively by tracking the presence of nitrogen in each sample, since a CD molecule contains two N atoms. EDS, elementary analysis, and XPS, which are very sensitive and helpful techniques generally used to detect the presence of capping agents after their removal,[31-33] were carried out to determine the amounts of N in the two samples.

The quantity of N in the sample Pd/AC(wash) was determined by recording an EDS spectrum of the area marked as a small red spot in the corresponding dark-field image (Fig.S3). The peaks near 0.28 and 2.90 keV are due to the K-shell emission of C and the L-shell emission of Pd, respectively.[34] There is no peak at 0.38 keV corresponding to the K-shell emission of N, which indicates that almost all of the capping agent CD has been removed. Moreover, the data obtained from the elementary analysis (Table S1) reveals that the Pd/AC(wash) sample contains a very small amount of N element (0.45%) compared to that in the Pd/AC (no wash) sample (2.48%). The panel on the right of Fig. 4 shows the XPS survey spectra of the Pd/AC hybrid before and after the rinsing process. Both the Pd/AC(wash) and the Pd/AC(no wash) samples contain only the elements O, N, Pd, C, and Cl, which is in agreement with the chemical compositions of the starting materials used in the synthesis. Note that the N 1s and Cl 2p peaks are clearly detected in the spectrum of the sample Pd/AC(no wash), but are not present in the spectrum of the sample Pd/AC(wash), indicating the effective removal of CD and byproducts by the washing process. The high-resolution scans of the N 1s region for the sample Pd/AC(wash) in the inset of the panel on the right of Fig. 4 contain a very low intensity peak, which confirms that the residual CD is almost completely depleted by the rinse. It has been reported that CD interacts weakly with the Pd surface through the π-bonding system (the quinoline moiety nearly parallel to the Pd surface) or through the σ-bonding system (the N lone pair predominates and induces a tilting of the ring with respect to Pd).[28] Thus, the straightforward removal of CD by washing is most likely due to these weak interactions. The results obtained from the EDS, elemental analysis, and XPS demonstrate that a simple washing process can almost completely eliminate residual CD.

3.4 Catalytic performance

Reduction of 4-nitrophenol

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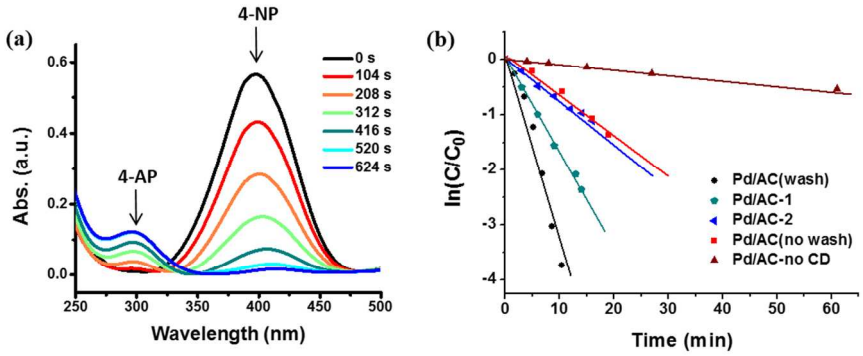

Fig. 5 (a) UV-vis spectra of the reduction of 4-nitrophenol in aqueous solution using the catalyst Pd/AC(wash), (b) the relationships between $\ln(C/C_0)$ and reaction time for the synthesized catalysts.

Like other aromatic nitro-compounds, 4-nitrophenol is a hazardous and carcinogenic chemical used as a main component of pesticides, plasticizers, and herbicides,[35] whereas 4-aminophenolis an important intermediate for industrial manufacturing processes, including the production of analgesic drugs and anticorrosion lubricants.[36] The development of efficient approaches for the reduction of nitro to amino groups based on novel catalysts has attracted great attention in synthetic organic chemistry.[37] In the field of catalysis, the borohydride reduction of 4-nitrophenol to 4-aminophenol has generally been used as a benchmark system for the assessment of the catalytic abilities of metal-based materials.[38,39] In the present study, this reaction was carried out in an aqueous medium at room temperature to evaluate the catalytic activity of the prepared Pd/AC(wash) hybrid; the kinetics of the reaction were monitored with UV-vis spectroscopy in the range 250–500 nm.

The UV-vis spectra of the reduction of 4-nitrophenol in aqueous solution using the catalyst Pd/AC(wash) are shown in Fig. 5(a). As the reaction time increases, the intensity of the absorption peak at 400 nm, which is due to 4-nitrophenolate ions in alkaline conditions, decreases gradually and a new absorption peak appears at 300 nm, which is due to 4-aminophenol. The peak at 400 nm disappeared after 9 minutes, which indicates complete conversion. It is worth to note that there is no induction time for this reaction as it proceeded immediately after the addition of the Pd/AC(wash) catalyst, unlike the results from other reported studies.[40,41] This advantage is due to the depletion of the CD capping agent, which enables the easy and rapid access of reactants to the purified Pd surfaces. Control experiments

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were also carried out with the Pd/AC-noCD, Pd/AC(no wash), Pd/AC-1, and Pd/AC-2 samples as catalysts (Fig. S4). In all experiments, similar adsorption behaviors are observed in the UV-vis spectra, but the reactions required much more time. Since we utilized a concentration of $NaBH_4$ in significant excess with respect to the concentration of 4-nitrophenol, the reaction is considered to follow pseudo-first-order kinetics with respect to 4-nitrophenol (or rather, the 4-nitrophenolate ion). Fig. 5(b) shows the relatively linear dependence of $\ln(C/C_0)$ on the reaction time, as expected fora first-order reaction. The kinetic rate constant k of the reaction when we used the catalyst Pd/AC(wash) was calculated to be 0.32 min^{-1}, which is significantly higher than that obtained with the catalysts Pd/AC(no wash) (0.07 min^{-1}), Pd/AC-noCD (0.01 min^{-1}), Pd/AC-1 (0.17 min^{-1}), and Pd/AC-2 (0.08 min^{-1}). These results demonstrate that the very high reactivity of the Pd/AC(wash) catalyst is solely due to the ultrafine, well-dispersed, and purified Pd NPs present on the AC support, and further confirm the efficient removal of CD by the washing process. Moreover, this rate constant is also comparable with the excellent k values obtained in other corresponding studies.[42-44]

Reduction of methylene blue (MB)

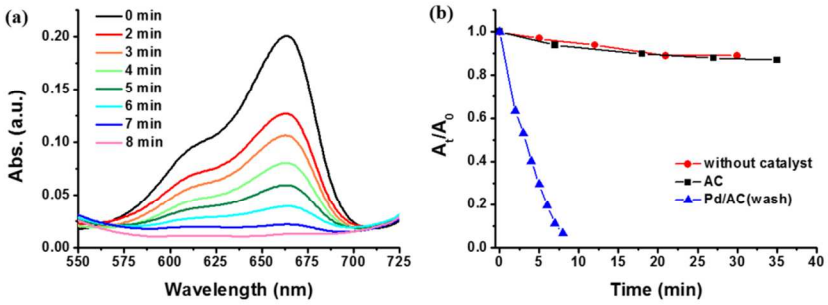

Fig. 6 (a) Absorption spectra of a MB solution in the presence of the catalyst Pd/AC(wash), (b) Plots of A_t/A_0 *vs* time for the borohydride reductions of MB solutions.

The excellent catalytic ability of the synthesized Pd/AC(wash) catalyst in the reduction of 4-nitrophenol inspired us to continue testing its catalytic activity in the degradation of MB dye, which is a toxic contaminant[45] released to wastewater during the industrial manufacture of textiles, paper, and paint. MB solutions are dark blue, and exhibit a strong absorption peak in

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visible light (550–750 nm) whereas the reduced MB solution is colorless, so UV-vis spectroscopy is commonly used to monitor this reduction process.

Fig. 6(a) shows the UV-vis spectra obtained during the MB degradation by $NaBH_4$ in the presence of the Pd/AC(wash) catalyst. The intensity of the absorption peak at 664 nm, which is assigned to the dark blue MB solution, continuously decreases as the degradation proceeds, and has completely disappeared within 8 minutes. Keeping in mind that AC is generally used as a good absorbent for dyes because of its amorphous structure and high surface area,[46] we also carried out the reduction of MB in the presence of AC alone (Fig. S5(a)) to elucidate the efficiency of the Pd/AC(wash) catalyst. The plot in Fig. 6(b) provides the relationship between the ratio A_t/A_0 (the ratio of the intensity of the absorption peak at 664 nm at reaction time t and the initial intensity) and the reaction time. As expected, the presence of AC decolorizes the MB solution but only to a small degree and the reaction proceeds very slowly, which indicates that only a small amount of MB is absorbed by AC; hence, the absorption capacity of AC is negligible in the presence of the Pd/AC(wash) catalyst. In addition, almost no change in the color of the MB solution was observed when we performed the reaction without catalyst (Fig. S5(b)), indicating that the Pd NPs are the active sites for the reduction of MB. The UV-vis data obtained from the MB reduction further confirm the high catalytic ability of the Pd/AC(wash) hybrid.

3.5 Catalyst recycling

The recyclability of catalysts is an important criterion to evaluate the practical applications of heterogeneous catalysts. As shown in Fig. 7, the Pd/AC(wash) catalyst exhibits highly stable and reusable properties. Although a slight decrease in conversion is observed in both reduction reactions, their conversions can achieve above 98.5% after 5 consecutive runs with only a small fraction of Pd leaching, as determined by the ICP analyses (Table S2). A further investigation of catalytic stability to 10 consecutive cycles shows that both reactions still have very high conversions which are over 97% (Fig. 7). The high stability of this catalyst makes it more economical and applicable for catalytic industry.

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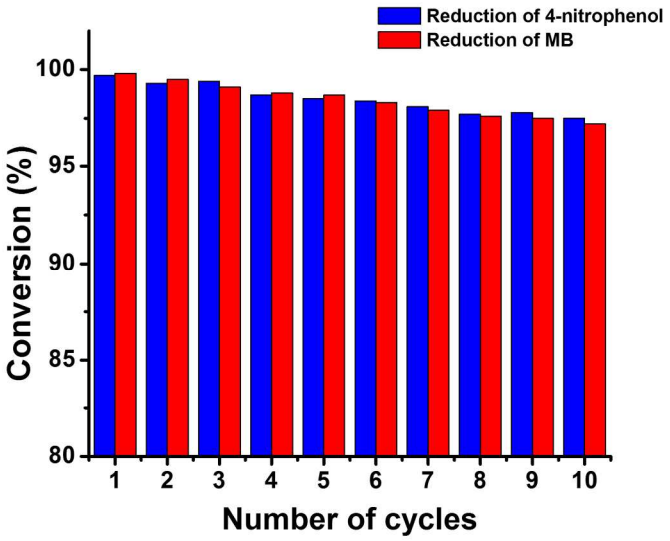

Fig. 7 The reusability of the Pd/AC(wash) catalyst for the reduction of 4-nitrophenol (blue) and MB (red).

4. Conclusion

A facile one-pot green synthesis of Pd/AC hybrids with uniform and well-dispersed Pd NPs was successfully achieved by using CD, a naturally available and environmentally friendly compound, as a capping agent for the first time. CD was found to be easily eliminated after the synthesis, which is a significant advantage over traditional capping agents. The synthesized hybrid was found to exhibit very high catalytic activities because of its ultrafine, homogeneously dispersed and purified Pd NPs. The application of this facile and green route for the synthesis of high-performance nanocatalysts using other catalytically active metals (Pt, Ag, *etc.*) supported on different carbon materials, such as graphene and carbon nanotubes, is ongoing. The present study furthers the quest for novel, naturally benign sources for the synthesis of heterogeneous catalysts, and the employment of CD can be extended to the green syntheses of other metal-based hybrids.

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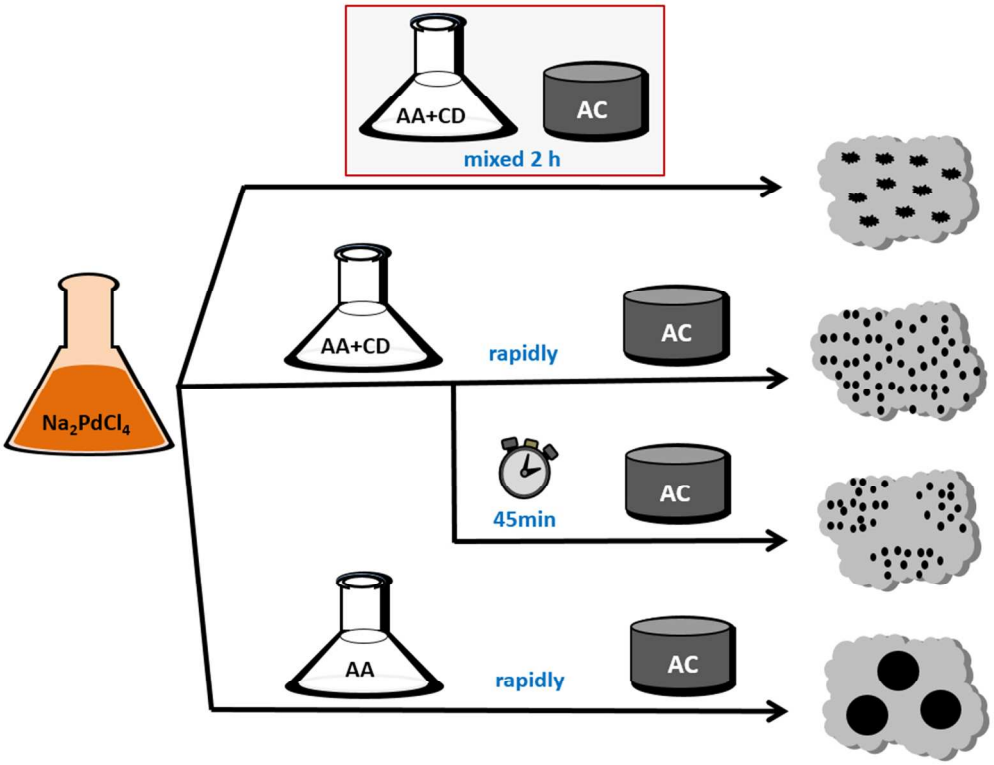

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