Green Synthesis of Gold, Platinum and Palladium Nanoparticles by Lignin and Hemicellulose

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Research Article

ABSTRACT

Herein, we report an environmentally benign method for the preparation of Pt, Au and Pd NPs in water. Water insoluble alkali lignin (AL) and hemicellulose was used soly as the reducing and protecting agents. Both of the AL and hemicellulose show excellent reduce ability in the metal precursor reduce process. The solid AL could support the obtained metal NPs. The metal particles reduced by hemicellulose are aggregated and the extent of aggregation increased along with the time.

INTRODUCTION

Nowadays, noble metal nanoparticles (NPs) are at a leading edge of the rapidly developing field of nanomaterials [1-3]. Preparation of noble metal NPs, such as platinum, gold and palladium, have been studied intensively based on their wide usefulness in magnetic, electronic, catalytic and mechanic technologies [4,5] Various methods have been developed for their preparation, including citrate reduction, sodium borohydride reduction, polyol process and physical radiolytic synthesis etc [6-9]. However, in those cases, harmful or petroleum-derived chemical reduce agents or dispersant were used to prepare stable metal NPs. Under the growing concern over the depleting of fossil fuels and the excessive emission of greenhouse gases, "green processes" in terms of eco-friendly reducing and stabilizing agents, "green" solvent and rout are attracting increasing attention to the production of metal NPs. Biomass with abundant availability and renewable nature plays an important role in the preparation of metal NPs [10]. Biomass such as vitamin B1, vitamin B2 and Honey et al. has been reported widely for the formation of noble metal NPs [11-15].

Lignin is the second-most-abundant biopolymer on the Earth, second only to cellulose. Furthermore, lignin is the only biomass constituent that is based on aromatic units which have strong anti-oxidant property. It has been studied in the reduction of metal cations to metal NPs based on its reducibility of phenolic hydroxyl groups [16]. Coccia et al. illustrated a one-pot synthesis method for lignin-stabilized platinum and palladium NPs using water soluble lignin and fulvic acid [15]. For most plant resource, lignin exist in solid state mixing with cellulose and hemicellulose. The phenol hydroxyl groups on the surface of solid lignin possess reducibility. The three-dimensional network of the solid phase could be used as support of the metal NPs. Preparation of noble metal NPs with solid lignin remains an important goal with significant industrial consequences.

Hemicelluloses are heterogeneously branched polymer of pentoses and hexoses, mainly xylose, arabinose, mannose, galactose, and glucose. It has been reported that water-soluble primary alcohols, secondary alcohols and diethers are available as reductants for preparation of metal colloidal dispersions [17]. Hemicellulose is a heterogeneous biopolymer composed of several

different types of monosaccharides which have secondary alcohol and ethers in structure. Therefore, hemicellulose could be considered as a reducing agent to prepare metal NPs. Peng et.al. have reported the preparation of Ag NPs with hemicelluloses and glucose [18]. Synthesizing other noble metal NPs such as Pt, Pd and Au NPs using hemicellulose reagents remains an important task which will allow us to utilize our renewable resources to a greater extent.

In this study, preparation of Pt, Pd and Au NPs with solid lignin and hemicelluloses in water at ambient pressure has been investigated. The reduce ability as well as the stabilize ability of solid lignin and hemicellulose in the formation of noble metal NPs were evaluated. This is the first time that Au, Pt and Pa NPs were successfully formed using solid lignin and water soluble hemicelluloses. This research would provide useful information for the utility of natural biomass which contains lignin or hemicelluloses.

EXPERIMENTAL

Lignin (Sigma-Aldrich 370959) powder was crushed by ball milling method (Fritsch Pulverisette 7) in water. Hemicellulose powder (Xylanase, BR) was used as received. The structures of these compounds are shown in **Figure s1.** The specific surface area of the solid lignin was determined by nitrogen adsorption (BET analysis).

A desired amount of the metal precursor, H_2PtCl_6, $HAuCl_4$ or $PdCl_2$, was added to 10 ml of aq. suspension (0.5 wt% for lignin and 1.0 wt% for hemicellulose) contained in a glass bottle equipped with a reflux condenser. The mixture was stirred for 2 h at 100°C under atmospheric pressure.

The resultant metal NPs were examined by transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and UV-vis absorption spectrum.

RESULTS and DISCUSSIONS

Lignin is a heterogeneous aromatic polymer containing various biologically stable carbon-to-carbon and ether linkages interspersing with hemicelluloses surrounding cellulose microfibrils. Because of the unstable chemical structure and complex connection with cellulose and hemicellulose, it is difficult to extract lignin from plant while keep its body structure. The specific structures of lignin vary with the extraction method. In this paper, water insoluble alkali lignin (AL) was employed; its molecular structure is shown in **Figure s1.** The main functional group of AL is phenolic hydroxyl group, tertiary hydroxyl group, mercapto group and ether. Since the AL does not dissolve in water, the functional groups that capable of contacting the metal ions are on the surface of AL totally. Increasing the specific surface area of AL would greatly improve the utilization of the functional groups. In addition, higher specific surface area of AL can also provide more loading location for metal particles. This effect is based on the strong interaction between metal particles and phenolic hydroxyl and mercapto group on the AL. We used the ball milling method to crush lignin and the specific surface area of AL is increased from 1.9 to 10.9 m^2/g (based on BET test). TEM and FTIR were taken to the AL before and after ball milling which are shown in **Figures 1 and 2** respectively. From **Figure 1** we can see that the AL is woody powder with three-dimension irregular network. After milling the diameter of the powder would be decrease to nanometer-scale which is coincidence with its specific surface area changes. **Figure 2** shows the FTIR of lignin before and after ball-milling, there is no significant signal change in the region of 3000 cm^{-1} and 1271 cm^{-1} which could attribute to phenol peak and -C-O stretching peak, respectively. The AL after milling with the specific surface area of 10.9 m^2/g was used to reduce metal ions in this paper.
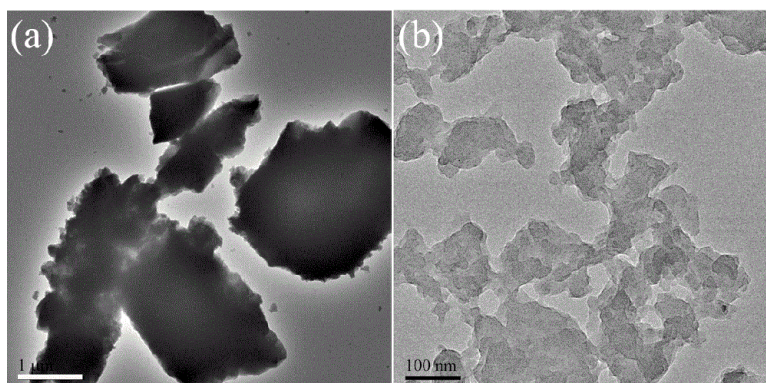

Figure 1. TEM of solid lignin (a) before and (b) after ball-milling. For (a) and (b) the scale bar are 1 μm and 100 nm respectively.

The color of the AL suspension was brown. The suspension was used to biosynthesis Pt NPs directly. After reaction, the suspension turned to black. From the TEM we can see that Pt particles are formed and supported on the surface of the AL with slightly aggregation. HRTEM was used to characterize the Pt NPs reduced by AL. The image of the obtained Pt NPs shows the clear lattice with average lattice spacing of 0.23 nm **(Figure 3d)**, which matches the d-spacing of (111) plane of face-centred cubic (fcc) Pt and confirms formation of Pt NPs crystals.
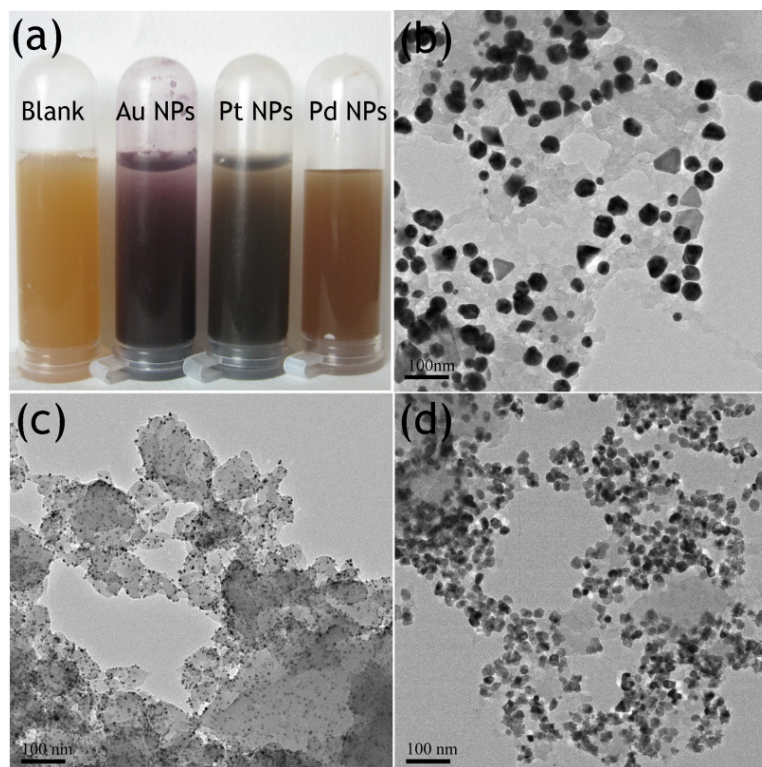
Figure 2. (a) photograph of bare lignin suspension and the Au, Pt NPs and Pd NPs suspension after reaction. (b-d): TEM of Au, Pt and Pd NPs obtained by reduction of 10 mM metal precursor for 1 h with 0.1% wt. lignin suspension. For (a-c) the scale bar is 100 nm.
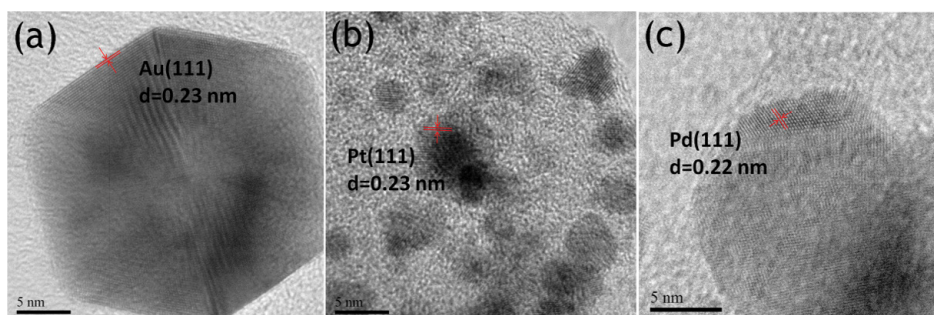

Figure 3. (a-c): HRTEM of Au, Pt and Pd NPs obtained by reduction of 10 mM metal precursor for 1 h with 0.1% wt. lignin suspension. For (a-c) the scale bar is 5 nm.

$HAuCl_4$ was used as precursor to synthesis Au NPs. The color of the suspension deepened as soon as the Au^{3+} was added. After a reaction time of 2 h, the color of the suspension turned to purple. From the TEM we can see that Au particles with triangle, pentagon, rodlike and circle shapes are formed **(Figure 2)**. All the particles are supported on the surface of the AL without apparent aggregation. HRTEM was used to characterize the Au NPs reduced by AL. We can see that the particles are polycrystalline with multiple grain zone **(Figure 3)**. The image of the obtained Au NPs shows the clear lattice with average lattice spacing of 0.23 nm **(Figure 3)**, which matches the d-spacing of (111) plane of face-centred cubic (fcc) Au and confirms formation of Au NPs crystals. Moreover, Pd NPs were also synthesized by AL at the same reaction conditions. From the TEM we can see that Pd particles are formed and supported on the surface of the AL. The HRTEM image shows the clear lattice of Pd NPs with average lattice spacing of 0.22 nm **(Figure 3)**, which matches the d-spacing of (111) plane of face-centred cubic (fcc) Pd and confirms formation of Pd NPs crystals. It has been reported that the morphologies of metal NPs are determined by reaction conditions such as reaction temperature, time, concentration and pH value of the system. Further work about the morphologies of metal NPs reduced by lignin under different reaction condition is required to clarify this phenomenon.

Xylanase, known as a kind of hemicellulose, had been chosen to illustrate the reduce ability of hemicellulose towards metal ions. Firstly colorless xylanase solutions of 1% wt. were prepared, and then metal precursors were added to the solution. Within an hour, the solutions became purple, yellow and brown corresponding to Au, Pt and Pd NPs solution respectively **(Figure 4)**. TEM images of the samples are shown in **Figure 4.** The images of the obtained Au, Pt and Pd NPs show that the majority of metal particles appear with irregular shape and the particles tend to aggregate. This result illustrates that the xylanase can be employed as efficient reduces agent to prepare metal NPs. However, water soluble hemicellulose could not prevent migration and secondary aggregation of metal NPs under the tested conditions. After keep for 5 days, the color of the aqueous solution changed significantly. The color of Pt and Pd NPs deepened and the violet color of Au NPs solution changed to blue **(Figure 4)**. UV-vis was

taken to exam the stabilization of xylanase based on the Au NPs aggregating process (left top of **Figure 4**). The Au NPs freshly prepared by xylanase show an absorption peak at 530 nm on the spectrum. For the sample that placed for 5 days, this absorption peak red shift to 536 nm. Meantime an absorption peak at 644 nm is shown indicating the further aggregation of Au NPs.
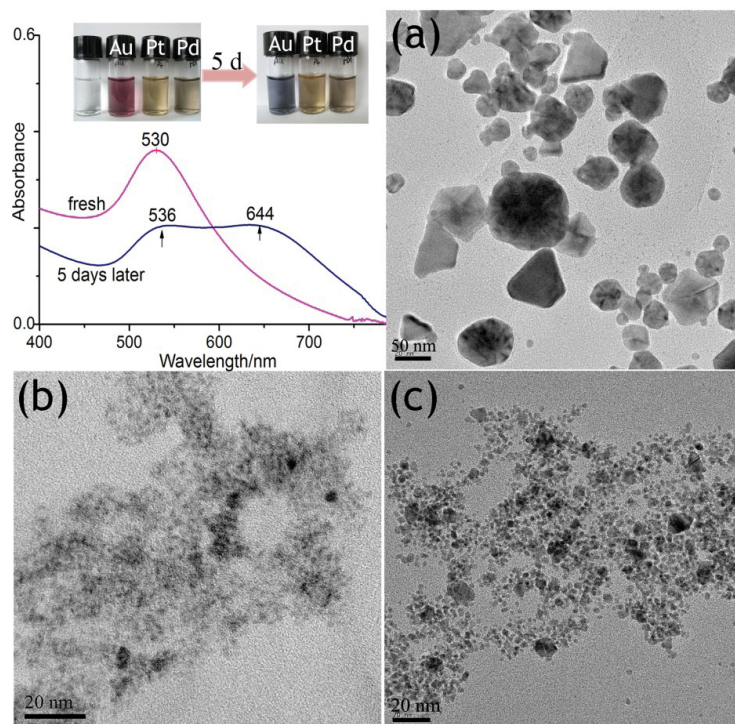

Figure 4. Top left: UV-vis absorption spectrum of Au NPs stabilizing by xylanase. insert: photograph of the Au, Pt and Pd NPs stabilizing by xylanase and after keeping for 5 days. (a-c) TEM of the Au, Pt and Pd NPs samples obtained immediately after reduce reaction. For (a) the scale bar is 50 nm. For (b) and (c) the scale bar is 20 nm.

It is well documented that the surface energy of nanoparticles is significantly higher as compared to that of the bulk. In the two-phase reduce process, it can be inferred that the particles incline to load on the surface of the solid phase to decrease surface energy. The phenolic hydroxyl and mercapto group on the surface of AL could reduce the metal ions and supply the supporting points to fix the nanoparticles through the electrostatic interaction. On the other hand, since water soluble hemicellulose are inclined to acid hydrolysis, our results illustrate that xylanase solution could reduce Pt, Au and Pd ions but could not prevent migration and secondary aggregation of metal NPs under the tested conditions.

CONCLUSION

We analysis the effect of solid lignin and hemicelluloses in the chemical reduce of kinds of metal NPs. Both of AL and hemicellulose show excellent reaction ability in the metal precursor reduce process. The presence of the solid phase enables the fabrication of metal NPs with the matrix. The metal particles reduced by hemicellulose are aggregated obviously and the extent of aggregation increased along with the time. This paper illustrated that AL and hemicellulose could be used as efficient reduce agents to prepare Pt, Au and Pd NPs, at the same time, the AL could be considered as useful stabilizing agent to disperse the obtained metal NPs.

ACKNOWLEDGEMENT

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