

Green synthesis of silver and palladium nanoparticles at room temperature using coffee and tea extract

Mallikarjuna N. Nadagouda† and Rajender S. Varma*

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An extremely simple green approach that generates bulk quantities of nanocrystals of noble metals such as silver (Ag) and palladium (Pd) using coffee and tea extract at room temperature is described. The single-pot method uses no surfactant, capping agent, and/or template. The obtained nanoparticles are in the size range of 20–60 nm and crystallized in face centered cubic symmetry. The method is general and may be extended to other noble metals such as gold (Au) and platinum (Pt).

Introduction

Noble metal nanoparticles have found widespread use in several technological applications,^{1–5} and various wet chemical synthesis methods have been reported.^{6–14} There is a great interest in synthesizing metal and semiconductor nanoparticles due to their extraordinary properties which differ from when they are in bulk. Recently, there is a renewed interest in using green chemistry principles to synthesize metal nanoparticles.^{8,15–25} For example, silver and gold nanoparticles produced from vegetable oil can be used in antibacterial paints.²⁶ Green chemistry is the design, development and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment.²⁵ Strategies to address mounting environmental concerns with current approaches include the use of environmentally benign solvents, biodegradable polymers and non toxic chemicals. In the synthesis of metal nanoparticles by reduction of the corresponding metal ion salt solutions, there are three areas of opportunity to engage in green chemistry: (i) choice of solvent, (ii) the reducing agent employed, and (iii) the capping agent (or dispersing agent) used. In this area, there has also been increasing interest in identifying environmentally friendly materials that are multifunctional. For example, the caffeine/polyphenols used in this study functions both as a reducing and capping agent for Ag and Pd nanospheres. In addition to its high water solubility, low toxicity, and biodegradability, caffeine is the most widely used behaviourally active drug in the world. In North America, 80–90% of adults report regular use of caffeine. However, there are no reports on preparation of noble metals using caffeine, which also play a crucial role in many medical applications. Hence, this paper reports, for the first time, preparation of noble metals like Ag and Pd using tea/coffee

extract. Caffeine/polyphenols can form complexes with metal ions in solution and reduce them to the corresponding metals. This approach therefore addresses several key requirements from a green chemistry perspective.

Experimental

To prepare the coffee extract, 400 mg of coffee powder (Tata Bru coffee powder 99%) was dissolved in 50 mL of water. Then 2 ml of 0.1 N AgNO₃ (AgNO₃, Aldrich, 99%) was mixed with 10 ml of coffee extract and shaken to ensure thorough mixing. The reaction mixture was allowed to settle at room temperature. For the tea extract, 1 g of tea powder (Red label from Tata, India Ltd. 99%) was boiled in 50 ml of water and filtered through a 25 µm Teflon filter. A similar procedure was repeated for Pd nanoparticles (using 0.1 N PdCl₂, Aldrich, 99%). To evaluate the source (tea and coffee extract) effect on morphology of the Ag and Pd nanoparticles prepared, several experiments were performed employing the above described procedure using the sources as shown in Table 1.

For transmission electron microscopy (TEM), 0.1 mL of the product was dispersed in 5 mL water. TEM grids were prepared by placing a drop of the particle solution on a carbon-coated copper grid and drying at room temperature. The samples for UV-visible measurements were the reaction mixtures that were dispersed in distilled water. TEM was performed with a JEOL-1200 EX II microscope operated at 120 kV. XRD patterns were obtained from Scintag X-ray diffractometer at 2 theta range 2–60° using CuKα radiation. Open-circuit voltage potentials were obtained using 1 M NaCl with reference to a saturated calomel electrode (SCE).

Table 1 Various brands of tea/coffee used to generate nanoparticles

Item	Brand Names
1	Sanka coffee
2	Bigelow tea
3	Luzianne tea
4	Starbucks coffee
5	Folgers coffee
6	Lipton tea

Sustainable Technology Division, US Environmental Protection Agency, National Risk Management Research Laboratory, 26 West Martin Luther King Drive, MS 443, Cincinnati, OH, 45268, USA.
E-mail: varma.rajender@epa.gov; Fax: +1 (513) 569-7677;
Tel: +1 (513) 487-2701

† Present Address: Pegasus Technical Services, 46 E Hollister Street, Cincinnati, Ohio 45219, USA

Results and discussion

TEM results show that Ag and Pd nanoparticles of varying sizes were formed using coffee and tea extract (Fig. 1a–d). At low magnification, a number of highly polydisperse Ag nanoparticles of varying sizes were observed (Fig. 1a,b). It is evident from the TEM image that Ag nanoparticles were well-separated from each other with an apparently uniform inter-particle separation. This indicates that the Ag nanoparticles were capped by organic molecules, namely polyphenols and caffeine. Pd nanoparticles seemed to be smaller than Ag nanoparticles and the inter-particle distance was uniformly separated and well aligned (Fig. 1c,d).

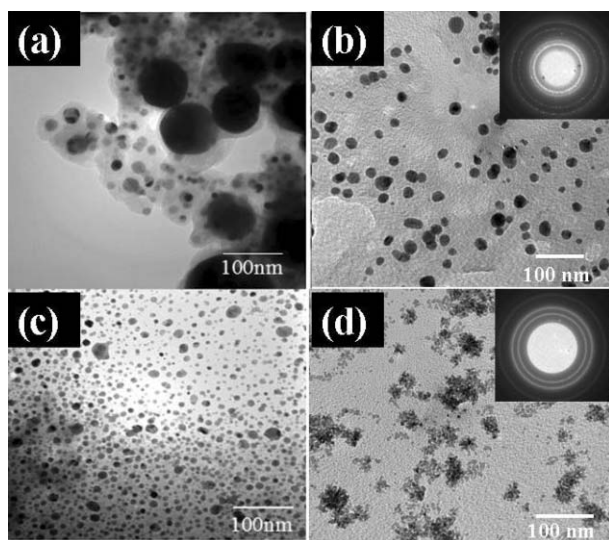


Fig. 1 TEM images of Ag and Pd nanoparticles in aqueous solutions of coffee and tea extract cast on a Cu grid coated with carbon, (a–b) Ag nanoparticles from coffee and tea extract, respectively, and (c–d) Pd nanoparticles from coffee and tea extract, respectively. The inset shows corresponding selected area diffraction patterns.

It is interesting to note that polyphenols acted as a reducing agent as well as a capping agent for the ensuing nanoparticles in the range of 20–60 nm. The control experiments carried out with pure catechin yielded tennis ball-like structures for Au (see Fig. 2). However, pure caffeine yielded wire-like structures for Au (see Fig. 3). The reaction with AgNO_3 was very slow with less yield, and Pd forms a complex without any definite structure. This strategy was extended to different coffee and tea sources (Table 1), and corresponding TEM images are shown in Fig. 4 and 5. The Ag and Pd nanoparticles were found to be mostly spherical with sizes ranging from as low as 5 nm to 100 nm depending upon the source of coffee or tea extract used (see Fig. 4 and 5).

The control experiments carried out with pure catechin yielded spherical structures for Ag and Pd (see Fig. 6).

The formation mechanism of Ag and Pd was studied using UV spectroscopy, which has proved to be a very useful technique for the analysis of nanoparticle formation over time. In order to determine completion of the reaction, 0.1 N AgNO_3 was reacted with tea extract and spectra were recorded every 20 minutes. Initially, no characteristic plasma resonance peak was observed at 1 minute. After 20 minutes of reaction, the plasma resonance

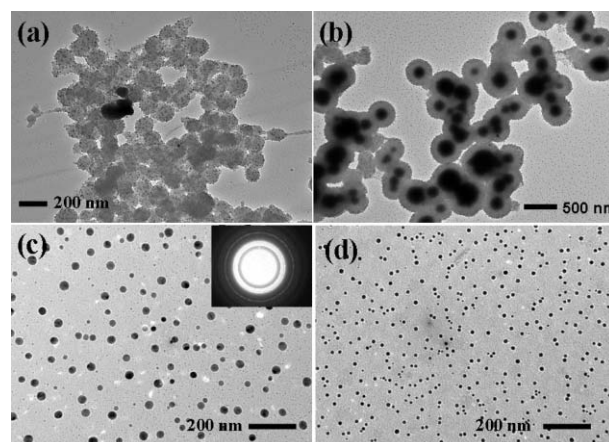


Fig. 2 TEM images of gold nanoparticles (2 mL 0.01 N) reduced with (a) 2 mL (b) 4 mL (c) 6 mL and (d) 8 mL of catechin (0.1 N) aqueous solution. The inset shows corresponding selected area diffraction pattern.

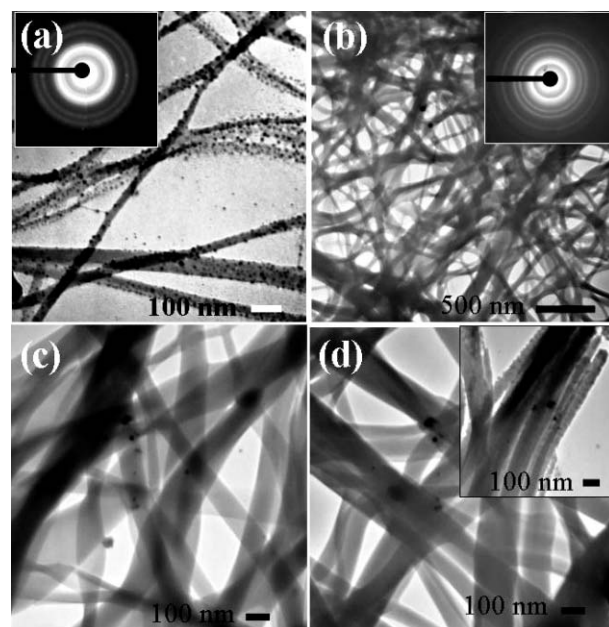


Fig. 3 TEM images of gold nanowires (2 mL of 0.01 N) reduced with (a) with 25 mg (b) 100 mg (c) 200 mg and (d) 300 mg of pure caffeine. The inset in (a–b) shows corresponding selected area diffraction pattern and in (d) shows different magnification image.

peak at ~ 460 nm started appearing and became more prominent at 60 minutes. The reaction was completed after 120 minutes, as there was no increase in intensity of the plasma resonance peak (see Fig. 7a–f). A strong absorption peak was observed at ~ 340 nm corresponding to the absorption of polyphenol compounds present in the tea.

UV spectra of Ag and Pd nanoparticles prepared from coffee and tea extracts are shown in Fig. 8. The broad plasma resonance peak at 460 nm corresponds to Ag nanoparticles prepared from coffee and tea extract (see Fig. 8a,b). The continuous absorption in the UV region was observed for Pd nanoparticles prepared from coffee and tea extract as expected (see Fig. 8c,d). The observation of strong but broad surface plasmon peaks is well

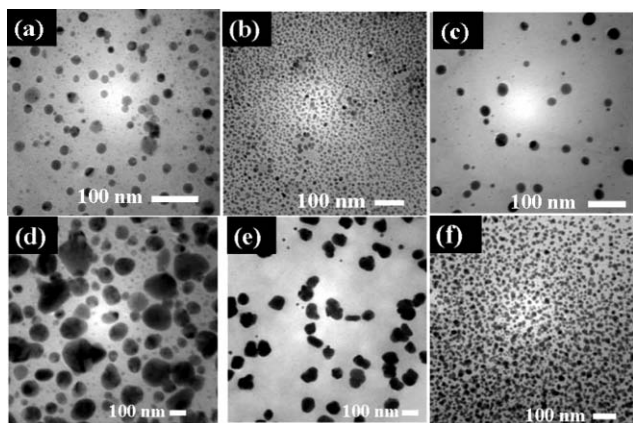


Fig. 4 TEM image of silver nanoparticles synthesized using (a) Bigelow tea, (b) Folgers coffee, (c) Lipton tea, (d) Luzianne tea, (e) Sanka coffee and (f) Starbucks coffee extract at room temperature in one step without using any hazardous reducing chemicals or non-degradable capping agents.

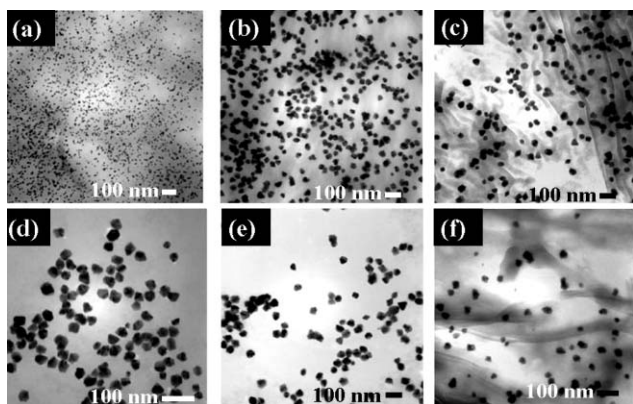


Fig. 5 TEM image of palladium nanoparticles synthesized using (a) Sanka coffee, (b) Bigelow tea, (c) Luzianne tea, (d) Starbucks coffee, (e) Folgers coffee and (f) Lipton tea extract at room temperature in one step without using any hazardous reducing chemicals or non-degradable capping agents.

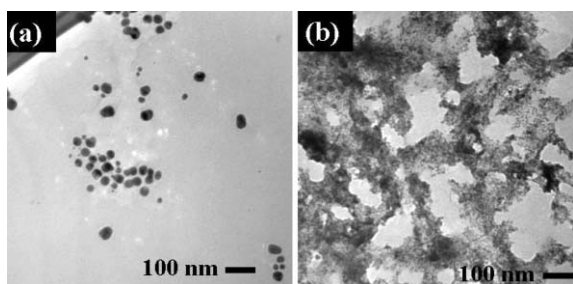


Fig. 6 TEM images of Ag and Pd nanoparticles respectively prepared in aqueous solution using catechin.

known in the case of various metal nanoparticles over a wide range of 200–1200 nm.

The reduction potential of caffeine is ~ 0.3 V vs. SCE (see Fig. 9) which is sufficient to reduce metals *viz.* Pd (reduction potential 0.915 V vs. SCE) and Ag (reduction potential 0.80 V vs. SCE), as well as Au^{+3} to Au^0 (reduction potential is 1.50 V vs. SCE) and Pt (reduction potential 1.20 V vs. SCE). The formation of Ag and Pd nanoparticles with caffeine/polyphenols takes

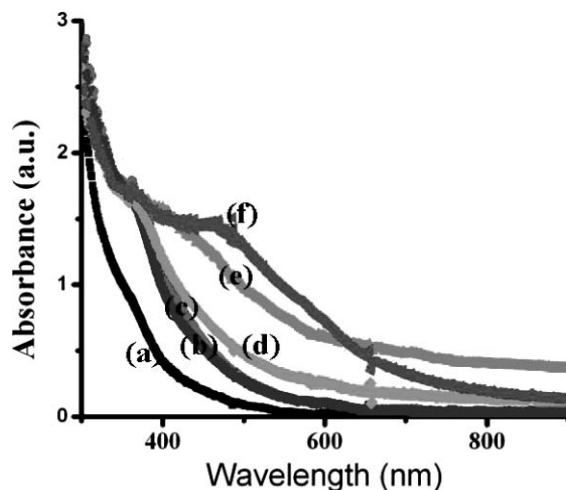


Fig. 7 Reaction profile of tea extract with AgNO_3 over the time; (a) pure tea extract, after (b) 1 min (c) 20 min (d) 40 min (e) 60 min and (f) 2 h.

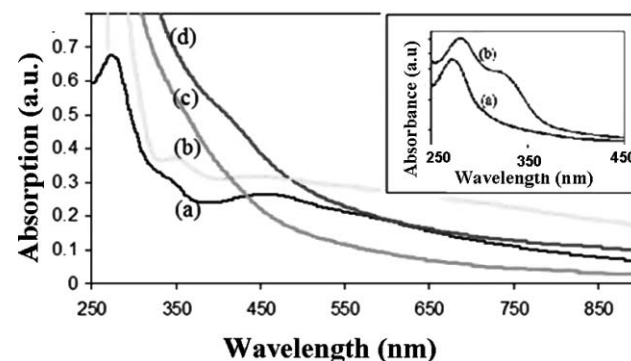


Fig. 8 UV-Vis spectra of Ag and Pd nanoparticles in aqueous solution of coffee and tea leaves extract. (a) Ag nanoparticles from coffee extract, (b) Ag nanoparticles from tea extract, (c) Pd nanoparticles from coffee extract and (d) Pd nanoparticles from tea extract. The inset shows UV-Vis of (a) coffee and (b) tea extract.

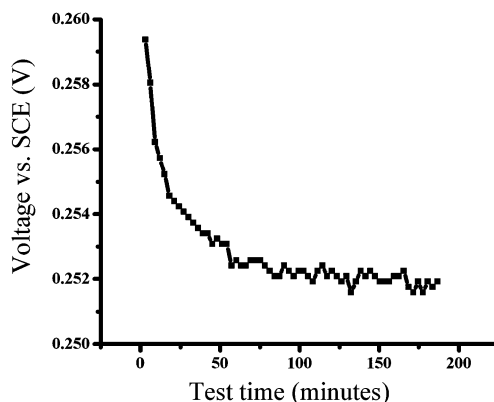


Fig. 9 Open-circuit potential for (V_{oc}) coffee extract in 1 M NaCl.

place *via* the following steps: (1) complexation with Ag and Pd metal salts, (2) simultaneous reduction of Ag and Pd metal, and (3) capping with oxidized polyphenols/caffeine.

Fig. 10a–d shows the XRD patterns of Ag and Pd nanoparticles obtained from coffee and tea extracts, respectively, from

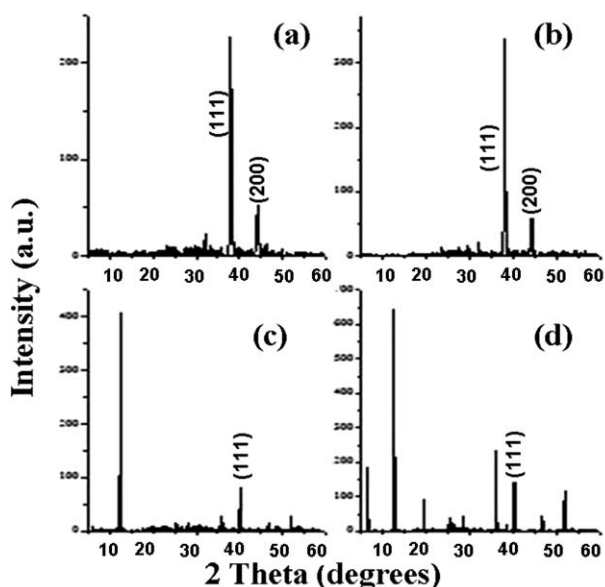


Fig. 10 Representative XRD patterns of nanoparticles in aqueous solution of coffee and tea extract casted on glass plate (a–b) Ag nanoparticles from coffee and tea extract, respectively, and (c–d) Pd nanoparticles from coffee and tea extract, respectively.

an aqueous solution drop-coated film on glass plate. From the XRD patterns, prominent Bragg reflections at 2θ values of 38.3 and 42.6 were observed, which correspond to the (111) and (200) Bragg reflections of face centered cubic (fcc) Ag nanoparticles (Fig. 10a,b).² However, in the case of Pd nanoparticles, layered structures of caffeine²⁷ remained, with a well developed progression of intense reflections, which are successive orders of diffraction with a large d spacing (see Fig. 10c,d). It is clear that diffraction patterns can be interpreted in terms of a crystal structure in which Pd and caffeine molecules occurred in regularly stacked layers with a very large interlayer lattice dimension, and that the interlayer two dimensional lattice possessed relatively small distances. The presence of narrow interlayer reflections indicates that there is crystallographic registry of layers.

Conclusions

In summary, for the first time, we have synthesized Ag and Pd nanoparticles using coffee and tea extracts. Specifically, we describe an environmentally friendly one-step method to synthesize noble nanoparticles, such as Ag and Pd, by reduction of corresponding metal solutions using tea and coffee extract without usage of any special capping agents at room temperature. This green approach may find various medicinal as well as technological applications. The method is general and may be extended to other noble metals such as Au and Pt.

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