Beet juice utilization: Expeditious green synthesis of nobel metal nanoparticles (Ag, Au, Pt, and Pd) using microwaves

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Abstract: Metal nanoparticles of Ag, Au, Pt, and Pd were prepared in aqueous solutions via a rapid microwave-assisted green method using beet juice, an abundant sugar-rich agricultural produce, served as both a reducing and a capping reagent. The Ag nanoparticles with capping prepared by beet juice exhibit higher catalytic activity and durability than that prepared by $NaBH_4$ for the transformation of 4-nitrophenol to 4-aminophenol.

1. Introduction

Noble metal nanoparticles always attract significant interest due to their unique optical, electronic, mechanical, magnetic, and chemical properties, which result in numerous applications in different technological areas.[1-6] Although various methods have been employed for the synthesis of metal nanoparticles, most of them proceed via the use of highly reactive reducing agents, such as sodium borohydride ($NaBH_4$) and hydrazine, which are not environmental-friendly. The use of toxic chemicals in these synthetic procedures limits their practical applications taking into account the environmental security.

Green technology is a set of principles or rather a chemical philosophy that encourages the design of products and processes that reduce or eliminate the use and generation of hazardous substances.[7] Following these principles, the use of organisms in this area, including microbes, fungi, and plants, is rapidly increasing due to several advantages namely being thermally and chemically stable, inexpensive, biocompatible, and most importantly, environmentally friendly.[8-12] The ability of plants in the production of metal nanoparticles has opened a new and exciting approach toward the development of these natural nano-factories. Plants which can capture almost 75% of the light energy from sun and convert it into chemical energy have more advantages as sustainable and renewable resources than microbes and enzymes that need expensive methodologies for producing.[8,13,14] Furthermore, the chemicals in the plants, such as antioxidants and sugars, play significant roles in the fabrication of nanoparticles. Consequently, plants with reducing compounds are the preferred choice for noble metal synthesis, because metal ions could be reduced to corresponding metals in the absence of any other chemical. [11, 13-16]

In the synthesis of noble metal nanoparticles by the reduction of the corresponding metal ion salt solutions, the reducing agent is an important factor. As a result, plants with various reducing agents are favourable candidates for

the fabrication of noble metal nanoparticles. Beet is an abundant agricultural produce in the *Chenopodiaceae* family, whose purple root is very important in the production of table sugar and mangelwurzel. Because of the sugar-rich content, it has great reductive capability, which can be utilized in the synthesis of nanomaterials, but it has not been investigated in detail. [17, 18]

In the present investigation, beet juice was used for the synthesis of nano metals such as Ag, Au, Pt, and Pd under microwave (MW) irradiation conditions, in an environmentally benign solvent, water. Further, a comparative investigation was conducted under different conditions. The prepared Ag nanoparticles show excellent catalytic efficiency to transform 4-nitrophenol to 4-aminophenol with high reusability, which is much higher than that prepared by $NaBH_4$.

2. Experimental

2.1 Preparation of beet juice

50 g beet root (product of Mexico) and 100 mL water was placed in a blender and blended for 10 min (3 x10 min for each time). Then the blended mixture of juice and pulp was filtered through a filter paper to obtain beet juice.

2.2 Synthesis of metal nanoparticles

A typical procedure, 0.3 mmol silver nitrate ($AgNO_3$) and 6 mL beet juice were mixed in a 10 mL thick walled glass tube sealed with a cap at room temperature to form a clear solution. The reaction mixture was irradiated in a CEM Discover focused MW synthesis system maintaining a temperature of 100 ^{o}C (monitored by a built-in infrared sensor) for 20 min with a maximum pressure of 280 psi. The resulting precipitated Ag nanoparticles were then washed several times with water to remove excess beet juice. Similar experiments were carried out by varying the beet juice content, temperature, and reaction time. A control experiment under conventional heating condition was also conducted in a stainless steel autoclave with a Teflon liner, and heated in oven at 100 ^{o}C for 60 min, the same temperature reached in the MW system. Comparative experiments were performed using 2 mmol of glucose or $NaBH_4$ as a reducing reagent.

2.3 Characterization

The crystal structures of prepared samples were detected by an X-ray diffractometer (Xpert, Pro, Holland). The morphology was examined by transmission electron microscopy (TEM) (JEOL, JEM-2100, Japan) and field emission scanned electron microscopy (FESEM) (JEOL, JSM-7600F, Japan). The as-prepared Ag nanoparticles and dried beet were detected by fourier transform infrared spectroscopy (FTIR) (Perkin elmer, spectrum 2000, USA) and thermogravimetric analyzer –gas chromatography –mass spectroscopy (TGA-GC-MS) (Perkin elmer, pyris 1 TGA, USA – Perkin elmer, Clarus 600, USA – Perkin elmer, Clarus 600T, USA)

2.4 Evaluation of catalytic activity of as-prepared Ag nanoparticles

Catalytic reduction experiments of 4-nitrophenol were performed to evaluate the catalytic efficiency and reusability of prepared Ag nanoparticles. In a typical experiment, a mixture of 19.5 mL water, 0.5 mL of 10 mM 4-nitrophenol, and 0.125 mol $NaBH_4$ was first prepared in a 40 mL vial at room temperature, and then 0.075 mol Ag nanoparticles was added with magnetic stirring. After reaction, the reaction mixture was filtered by a Millipore syringe driven filter to get clear solution for UV/Vis spectroscopy (Agilent Hewlett-Packard, 8453, USA) analysis. For comparison, the control experiment was also carried out under similar conditions without Ag nanoparticles.

The durability of the Ag nanoparticles catalytic activity was evaluated using repeated experiments of 4-nitrophenol reduction. In this experiment, the 4-nitrophenol concentration of the reacted solution was measured after 2 min of addition. In the beginning of each experimental cycle, 0.5 mL 10 mM 4-nitrophenol and 0.125 mol $NaBH_4$ were added into the reactor to compensate.

3. Discussion

TEM images of Ag particles obtained under different conditions are shown in Fig. 1. When the use of beet juice was 6 mL, the obtained Ag nanoparticles are found to be mostly spherical with size ranging from 20 to 40 nm (Fig. 1a). With decreasing amounts of beet juice, the obtained Ag nanoparticles become bigger; in addition, the shape and size of the nanoparticles lose uniformity. The sizes of as-prepared Ag nanoparticles range from 10 to 100 nm with 3 mL beet juice, while 10 to 150 nm with 1 mL beet juice. Moreover, chemicals in beet juice served as capping agent on the surface of Ag nanoparticle when the beet juice amounts used were 6 mL and 3 mL, according to the TEM images (Fig. 1a and 1b). However, no obvious capping can be observed when 1 mL beet juice was (Fig. 1c) used. These results imply that beet juice acts as a reducing agent as well as a capping agent for the formation of Ag nanoparticles; the usage of beet juice can also affect their shape and size. In comparison, no Ag nanoparticle is produced without beet juice, which indicates the crucial reductive role of beet juice on the formation of Ag nanoparticles. Temperature also plays a significant role on the assembly of these core-shell structures. Ag nanoparticles prepared at 80 ^{o}C (Fig. 2a) and 60 ^{o}C (Fig. 2b) are not as uniform as that obtained at 100 ^{o}C (Fig. 1a). However, the formation of Ag nanoparticles is not so sensitive to reaction time. The structures of obtained nanoparticles at 10, 20, and 60 min are similar (Fig. 3), which are spherical with size of 20-40 nm. Therefore, the Ag crystals do not grow once they are formed under MW irradiation conditions in presence of the beet juice. To compare with beet juice, Ag particles were also prepared using glucose as a reducing agent; the ensuing Ag particles are bigger (500 nm) than those obtained by using beet juice (Fig. S1(SI)) .

It is interesting to note that a lot of microspheres are formed in the products except when using the aforementioned organic molecule capping on the surface of Ag nanoparticles (Fig. 4). When the use of beet juice was 6 mL (reaction temperature: 100 ^{o}C), the diameters of most microspheres are all about 0.5-0.6 μm in spite of the different MW irradiation times (10, 20 and 60 min). The consumption of beet juice is significant for the formation of the microspheres. With 1 mL of beet juice, no microsphere was detected in the product. When the use of beet juice was 3 mL, the diameters of microspheres, 0.35-0.45 μm, are smaller than that of 6 mL,. The reaction temperature also

can affect the construction of microspheres that can be produced at 60 ^{o}C but the size is very big (12 μm of diameter), and is not as compact as that of 100 ^{o}C, according to the TEM image (Fig. 4e). The microspheres were also detected by SEM (Fig. 4f), and their surfaces are smooth.

In order to clarify the composition of the microspheres and capping in the as-prepared Ag sample, energy dispersive X-ray spectroscopy (EDX) was used to distinguish the elements in different areas (Fig. 5). TEM grid with carbon film was avoided to determine the carbon element in the samples; TEM grid with pure silicone monoxide file was used. In the area Edx1 and Edx3, which respectively correspond to formed microsphere and capping, only the elements carbon and copper were found. As is commonly known, copper peaks can be attributed to the copper grid. In addition, the hydrogen element cannot be detected because of the limits of EDX detector. Thus, it can be speculated that the microsphere may be capped with simple carbon or organics. According to the aforementioned results, the microsphere and capping should come from the chemical constituents in beet juice, which does not have simple elemental carbon according to the U. S. Department of Agriculture (USDA) nutrient database. It is almost impossible for organics to dehydrogenate to get carbon in the reducing aqueous solution, so the composition of the microsphere and the capping agent should be organics. Additionally, no organic microsphere was observed when simply beet juice without $AgNO_3$ was irradiated (Fig. S2, SI), implying the important role of $AgNO_3$ on the formation of the organic microsphere. The reason may be that $AgNO_3$ can absorb MW to reach high temperature, conducing to the aggregation of organics in beet juice around $AgNO_3$. The organic microsphere also was not produced without MW irradiation (Fig. S3, SI). All of the results mentioned above suggest that the organic microsphere cannot be obtained in the absence of beet juice and MW irradiation. As shown in Fig. 5c and 5f, the Edx2 and Edx4 areas all have silver, copper, and carbon, and Edx2 also has traces of chlorine elements. Because copper and carbon should be assigned to copper grid and capping, respectively, the Edx2 and Edx 4 areas should be silver nanoparticles. According to the high angle annular dark field (HAADF) images (Fig. 5b and 5e), Ag nanoparticles are enclosed by capping. However, it is worth noticing that Ag nanoparticles seldom deposit on the surface of formed microsphere. Consequently, the organic molecule of microsphere may be different from that of capping. Fig. 5g is a high resolution transmission electron microscopy (HRTEM) image of Ag nanoparticle. The lattice fringes show a fringe spacing of 0.204 nm, corresponding to the (200) plane of Ag. Fast Fourier transforms (FFT) can be obtained according to the HRTEM image (Fig. 5h), implying that the as-prepared Ag nanoparticle is single crystal.

The FTIR and TGA-GC-MS were used to analyze the organics in beet before and after MW irradiation. The FTIR spectra were measured within the range from 4,000 to 500 cm^{-1}. Before reaction, the broad peak located at 3335 cm^{-1} may be attributed to O-H stretching modes of vibration in hydroxyl functional group in alcohol and N-H stretching vibrations in amides and amines. The presence of peak of 2910 cm^{-1} indicates the C-H stretching vibrations in the hydrocarbon chains. The frequency observed at 1739 cm^{-1} is due to the carbonyl functional group of ketones, aldehydes, and carboxylic acid, while that of 1609 cm^{-1} is assigned to amide band. The frequencies at 1245-1232 cm^{-1} are attributed to the CH_2 and CH_3 symmetric bending. In addition, the peaks at 1027 and 657 cm^{-1} should be due to C-O stretching vibrations and out-of-plane rocking of N-H or aromatic C-H, respectively. [17, 18] It is worth

noting that after MW irradiation, the frequencies of samples are totally different. All of the aforementioned peaks are lost, and two new peaks appear. The peak of 2328 cm^{-1} is assigned to CO_2, and that of 2103 cm^{-1} should be attributed to the stretching of –C=C=C- or –N=C=O-. As a result, the condensation reaction should occur in a metal salt–beet juice solution under MW irradiation, which promotes the formation of an organic microsphere. The weight loss data and total ion chromatogram detected by TGA-GC-MS are shown in Fig.7.TGA experiments were performed at a heating rate of 10 ^{o}C/min. Both TGA and GC-MS results are obviously different between the as-prepared Ag sample and dried beet without MW irradiation. The apparent organic decomposition of the Ag sample and dried beet occurs between 200-445 ^{o}C with mass loss of 14.7%, and 200-400 ^{o}C with mass loss of 62.4%, respectively. Accordingly, the obtained chromatogram peaks of Ag sample and dried beet are also different. The highest peak of Ag sample locates at 13.09 min (mass 41, 57, 70, 83, 98, 112) which may be organics with ethyl fragments, while that peak was not detected in the dried beet. There are more peaks obtained in the dried beet; the two highest peaks locate at 12.52 (mass 52, 66, 99) and 14.23 min (mass 53, 81, 109, 124), which possibly assign to phenol and methoxy phenol, respectively. The TGA-GC-MS experiments were repeated 3 times for each sample, and similar results were obtained. These facts further prove the changes of the chemicals in beet before and after MW irradiation.

The XRD patterns of the as-prepared samples prove the phase of Ag nanoparticles (Fig. 8a and 8b). The peaks at 37.9, 44.1, 64.7, and 77.5 can be assigned to (111), (200), (220), and (311) planes of the cubic Ag. However, AgCl peaks were also detected in addition to the Ag peaks, because of the Cl element present in beet juice. In the elemental analysis, chlorine does exist in beet juice (Fig. 5c). XRD patterns obtained at different reaction times are shown in Fig. 8a. The AgCl peaks are higher when the irradiation time was shorter. Hence, AgCl can be reduced to form Ag by beet juice under MW irradiation conditions. The effect of temperature was also investigated. When the reaction temperature was 60 ^{o}C, the peaks of Ag are weak. With the increase of reaction time, the peaks of Ag increase while those of AgCl decrease. Consequently, the peaks of Ag nanoparticles obtained at 100 ^{o}C are the highest among 60, 80, and 100 ^{o}C, thus, indicating that high temperature is helpful for the formation of Ag nanoparticles. Comparative experiments were carried out under conventional heating conditions, as shown in Fig. S4 (SI). Even after 60 min, the peaks of Ag obtained by conventional heating are still very weak, and no peaks can be found in the pure beet juice. The beet juice method is general and can be extended to other noble metals such as Au, Pt, and Pd; XRD analysis clearly confirms their metallic state, as Fig. 8c shows. The peaks at 2θ = 38.3, 44.6, 64.7, and 77.5 for Au nanoparticles are easily indexed respectively, to the diffraction of the (111), (200), (220), (311) planes (PDF#01-1174); the Pt peaks at 2θ = 39.7, 46.3, 67.3 correspond to (111), (200), and (220) (PDF#01-1190); the peaks at 40.4, 46.8, and 68.4 can be assigned to (111), (200), and (220) planes of the Pd crystal (PDF#01-1201). Fig. 9 displays the TEM image of typical Au, Pt, and Pd samples. The sizes of all of these samples are below 100 nm; the average diameters of Au, Pt, and Pd nanoparticles are 70, 3, 5 nm, respectively, and all of them are capped with organics. In addition, organic microspheres are formed in these samples as well, as shown in Fig. 9d, 9e, and 9f. Similar to the Ag samples, the obtained Au and Pd nanoparticles cannot deposit on the surface of the formed organic

microspheres. However, Pt nanoparticles can cover the surface of microspheres. These results mean that Pt nanoparticles have better interaction with the microsphere than other metals.

The reduction of 4-nitrophenol to 4-aminophenol was used as a model to investigate the potential catalytic properties of as-prepared Ag nanoparticles. Before reaction, only the peak at 400 nm is observed, which can be assigned to 4-nitrophenol (Fig. 10). After the addition of Ag nanoparticles, the peak of 4-nitrophenol disappear, and a new peak appears at 290 nm, which is ascribed to the product, 4-aminophenol.[19, 20] The catalytic reduction efficiency of as-prepared Ag nanoparticles could quickly reach to 100% within 2 min. The yellow color of 4-nitrophenol solution faded and became colorless. The catalytic durability of Ag nanoparticles was found to be very encouraging; 4-nitrophenol could be completely reduced within 2 min after every addition even after five runs, thus, implying the excellent stable catalytic performance of Ag nanoparticles. After 5 runs, the Ag nanoparticles were recovered for XRD analysis and as the Fig. S5 (SI) shows, all of the XRD diffraction peaks correspond to Ag peaks and no impurity was produced in the reaction, further confirming the stability of the Ag nanoparticles. In contrast, the solutions in the absence of a catalyst did not show any change in the intensity of absorption peak of 4-nitrophenol even after 30 min (Fig. 10c). In addition, the catalytic activity of Ag nanoparticles prepared by $NaBH_4$ was investigated to compare with that prepared by beet juice. Under the same condition, the reaction rate on the Ag sample prepared by $NaBH_4$ is much lower than that prepared by beet juice. The complete conversion of 4-nitrophenol needs 20 min on the former catalyst, while 2 min on the latter, as Fig. 10d displays. Moreover, the catalytic activity decreased after every run of reaction; the complete conversion of 4-nitrophenol needs 40 min in the third run. These facts mean the Ag catalyst prepared by beet juice is more efficient and displays more durable catalytic activity than that prepared by $NaBH_4$. The good dispersion of Ag nanoparticles in the reaction mixture should be one of reasons. Additionally, the formed organic capping may be helpful to enhance the contact between reactant and catalyst, as well as protect the Ag nanoparticles from inactivation.

4. Conclusion

In summary, a rapid microwave-assisted green method has been developed for the facile synthesis of metal nanoparticles. The method uses no additional surfactants or reducing agents and is green in nature. Beet juice acted as both a reducing and a capping agent. The sizes of obtained Ag, Au, Pt, and Pd nanoparticles are all below 100 nm, and capped with organics. The Ag nanoparticles prepared by beet juice exhibit higher catalytic activity and durability than that prepared by $NaBH_4$ for the reduction of 4-nitrophenol to 4-aminophenol, possibly because of the organic capping and better dispersion.

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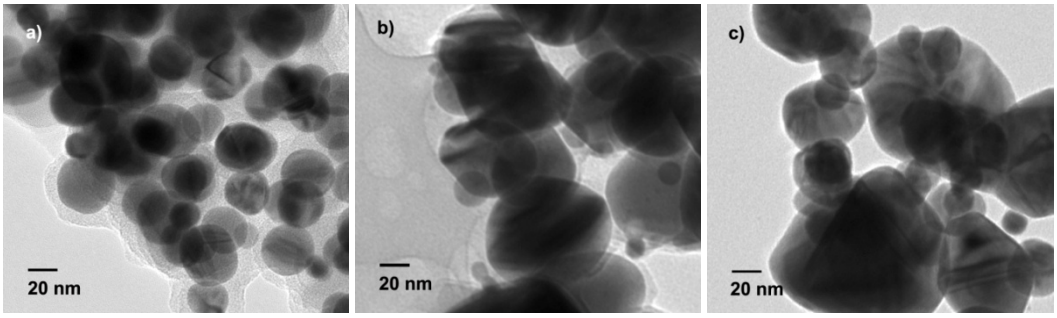

Fig. 1. TEM images of Ag nanoparticles obtained by using different beet juice content. a) 6 mL; b) 3 mL; c) 1 mL.

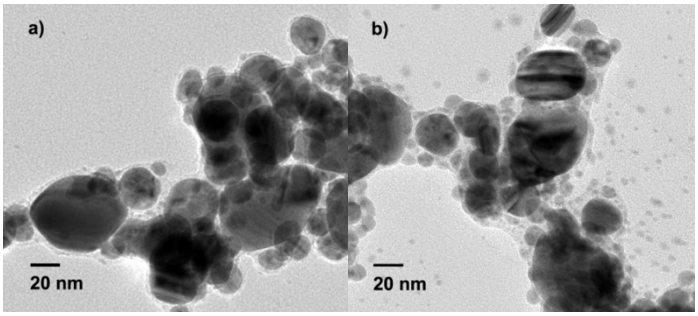

Fig. 2. TEM images of Ag nanoparticles obtained at different temperature. a) 80 ^{o}C; b) 60 ^{o}C.

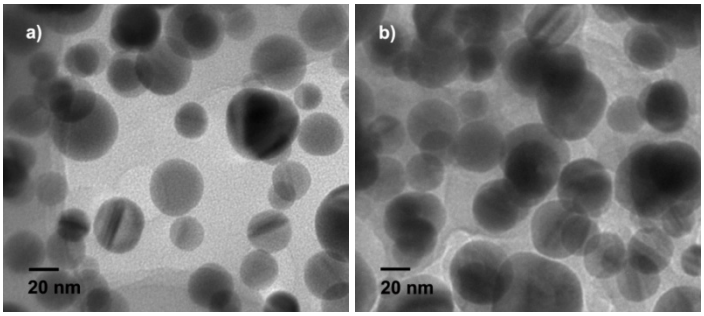

Fig. 3. TEM images of Ag nanoparticles obtained at different time. a) 10 min b) 60 min

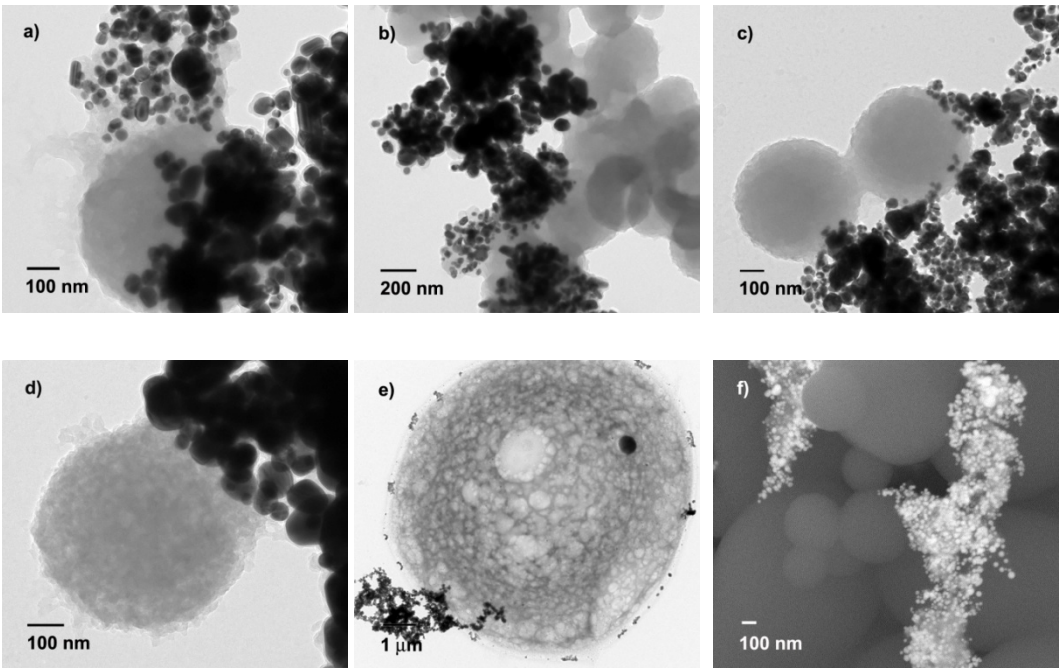

Fig. 4. The formation of organic microsphere under different condition. TEM image of a) 6 mL of beet juice, 20 min, 100 ^{o}C; b) 3 mL of beet juice, 20 min, 100 ^{o}C; c) 6 mL of beet juice, 10 min, 100 ^{o}C; d) 6 mL of beet juice, 60 min, 100 ^{o}C; e) 6 mL of beet juice, 20 min, 60 ^{o}C; SEM image of e) 6 mL of beet juice, 20 min, 100 ^{o}C.

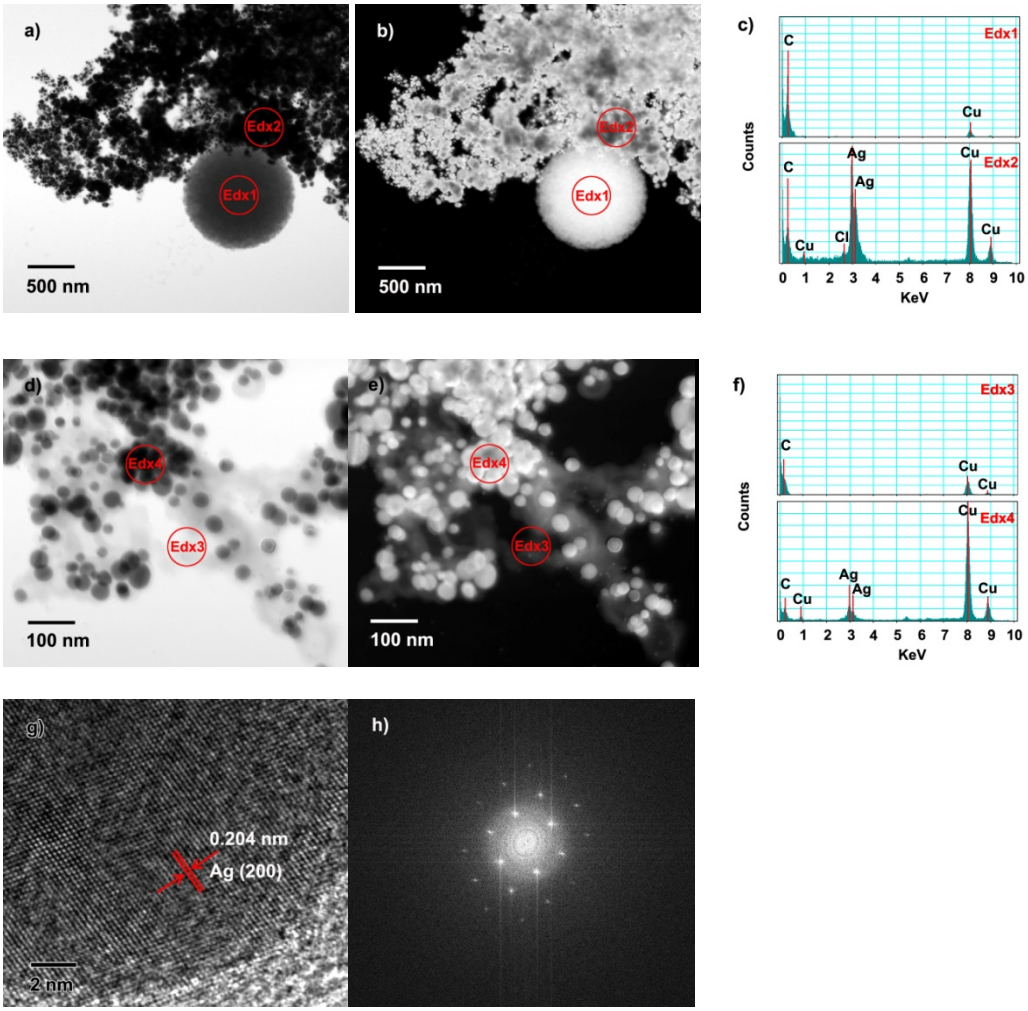

Fig. 5. Images of the typical Ag nanoparticles prepared with beet juice. a) TEM image; b) HAADF images; c) EDX spectra of area Edx 1 and Edx 2; d) TEM image; e) HAADF images; f) EDX spectra of area Edx 3 and Edx 4; g) HRTEM image; h) FFT image obtained according to HRTEM.

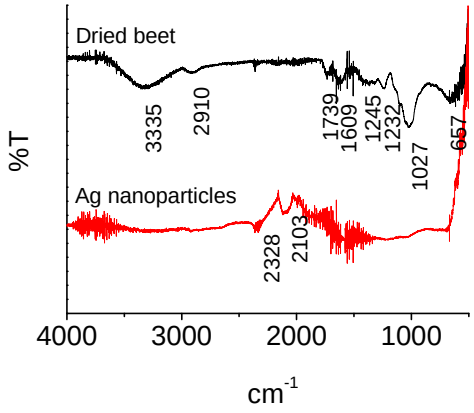

Fig. 6. FTIR spectra of dried beet and as-prepared Ag nanoparticles.

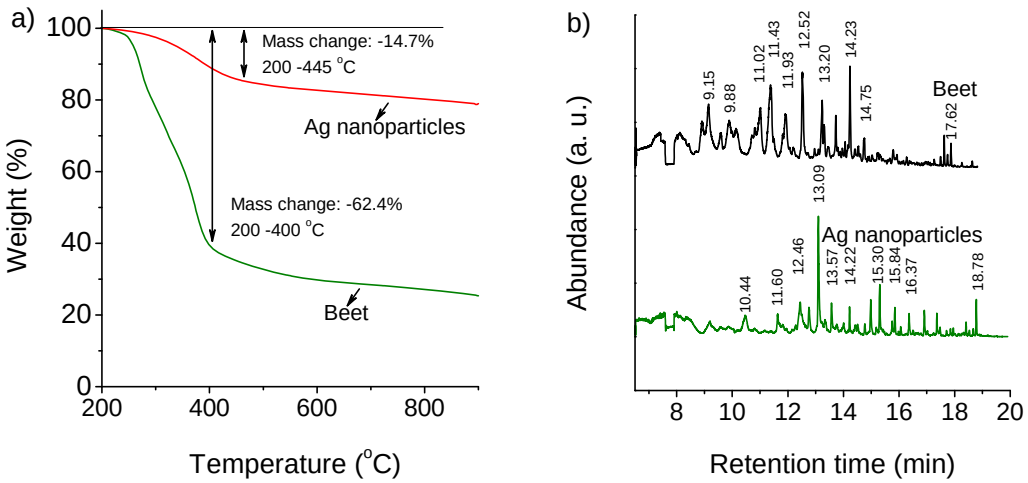

Fig. 7. TGA-GC-MS image of as-prepared Ag nanoparticles and dried beet. a) Weight loss data from TGA; b) total ion chromatogram detected by GC-MS.

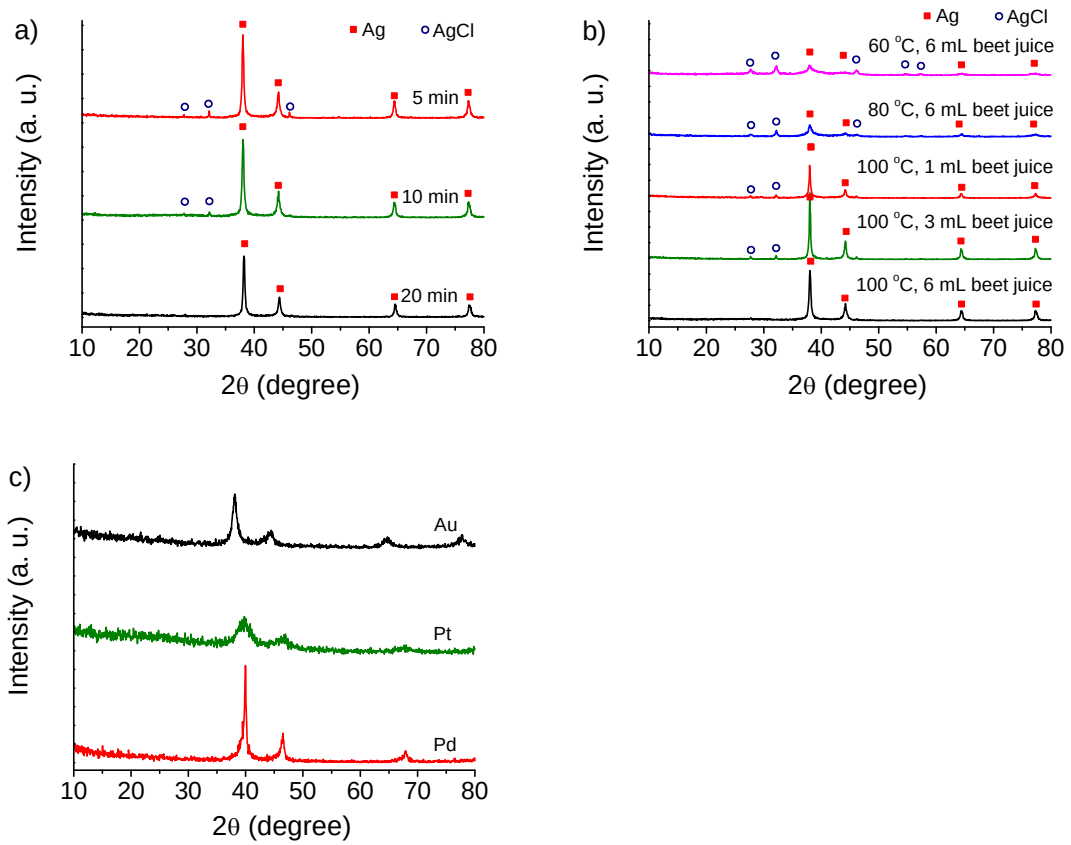

Fig. 8. XRD patterns of as-prepared samples. a) Ag samples obtained at different times; b) Ag samples obtained by using different temperature and beet juice amount; c) Au, Pt, and Pd samples.

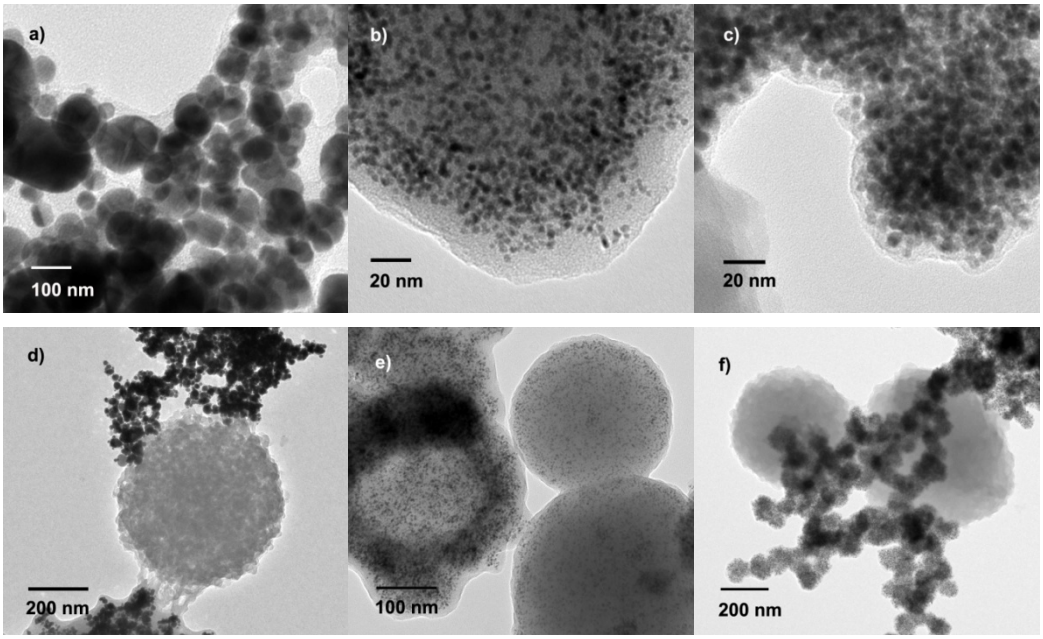

Fig. 9. TEM images of typical Au, Pt, and Pd samples. a) Au with capping; b) Pt with capping; c) Pd with capping; d) Au with organic microspheres; e) Pt with organic microspheres; f) Pd with organic microspheres.

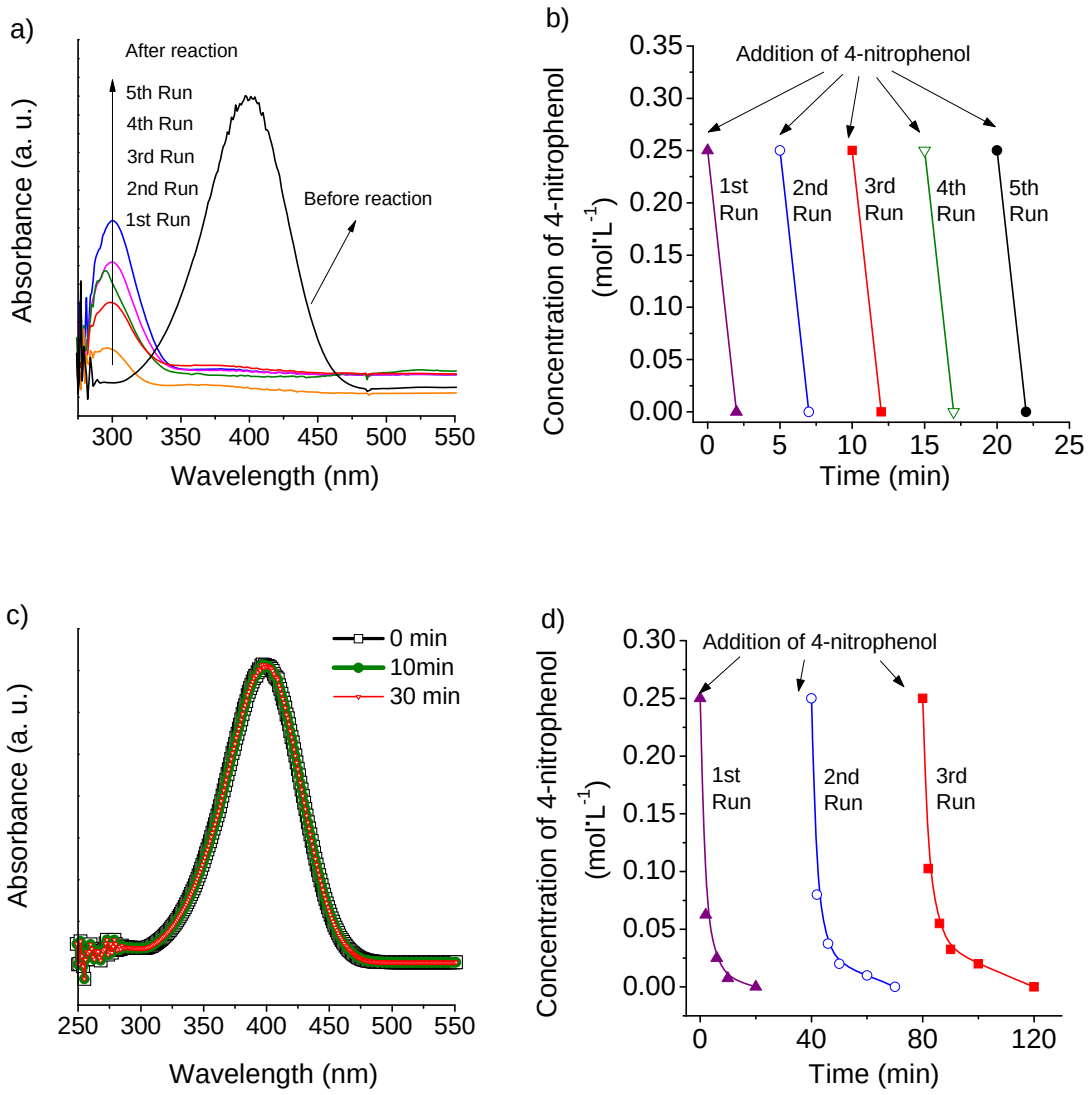

Fig. 10. Catalytic reduction of 4-nitrophenol. a) UV-vis spectra of solutions of reaction mixture in the presence of Ag nanoparticles prepared by beet juice; b) catalytic activity and recyclability of Ag nanoparticles prepared by beet juice; c) UV-vis spectra of solutions without catalyst; d) catalytic activity and recyclability of Ag nanoparticles prepared by $NaBH_4$.

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