

# Synthesis of Silver and Gold Nanoparticles Using Antioxidants from Blackberry, Blueberry, Pomegranate, and Turmeric Extracts

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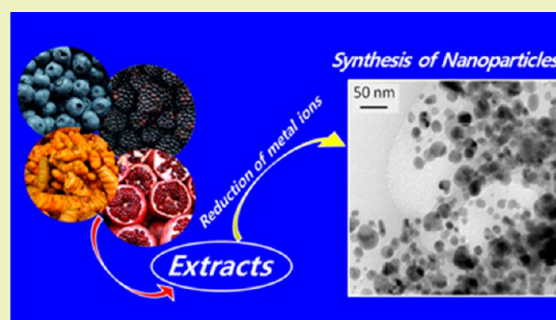
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## S Supporting Information

**ABSTRACT:** Greener synthesis of Ag and Au nanoparticles is described using antioxidants from blackberry, blueberry, pomegranate, and turmeric extracts. The synthesized particles were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), particle size analysis, UV–vis spectroscopy, and thermogravimetric analysis. The XRD patterns indicated the formation of Ag and Au nanoparticles, and the results are in line with UV plasma resonance peaks.



**KEYWORDS:** Green synthesis, Noble metals, Antioxidants, Fruits, Spices

## INTRODUCTION

Gold and silver nanoparticles (Au/Ag NPs) are commonly used in the fields of electronics, optics, and medicine.<sup>1–3</sup> Conventional synthesis techniques for these nanoparticles are currently under scrutiny due to the requirement of toxic chemicals in their production and the generation of hazardous by-products.<sup>4–8</sup> For example, sodium borohydride (NaBH<sub>4</sub>) and hydrazine are often used as efficient reducing agents for the synthesis of AgNPs followed by addition of a capping agent, such as polyvinylpyrrolidone (PVP). Yet, NaBH<sub>4</sub> can be the source of caustic salts and flammable gases. Consequently, a multitude of greener and more environmentally friendly synthesis techniques are being investigated.<sup>9–18</sup>

Green synthesis techniques for assembly of Au/AgNPs include the use of plant extracts, biodegradable polymers, bacteria, enzymes, and fungi in place of dangerous chemicals and an alternate form of heating, microwave irradiation.<sup>19–24</sup> Fruit extracts that are novel, greener, and cost-effective can be used as capping as well as reducing agents in the synthesis of AuNPs and AgNPs. *Tanacetum vulgare*,<sup>19</sup> *Carica papaya*,<sup>25</sup> and *Citrus sinensis*<sup>26</sup> are some examples of fruits that have been used to synthesize AuNPs and AgNPs. In view of these successes, we have explored the use of common antioxidants present in everyday edible products to synthesize AuNPs and AgNPs by deploying blueberry, blackberry, turmeric, and pomegranate extracts.

Nadagouda et al. have investigated the use of different tea varieties (popular store-bought brands including Lipton) and

coffee extracts for the synthesis of metal NPs.<sup>27</sup> It was determined that this method did not require the use of any surfactants, capping agents, or templates for the generation of stable nanoparticles. Thus, the synthesis of AgNPs and AuNPs generated using tea extracts were compared herein with fruit extracts. Similar to tea polyphenols, turmeric extracts (containing 2% curcumin dry weight of turmeric ground roots; Scheme S1, Supporting Information) are considered in view of the invaluable constituents, curcuminoids. The synthesized nanoparticles were characterized using XRD, TEM, HR-TEM, and UV–vis spectroscopy. The XRD patterns indicated that the formation of the nanoparticles and the results are in line with UV plasma resonance peaks. Thus, it was demonstrated that the nanoparticles could be successfully synthesized using green synthesis techniques, which may find application even for the delivery of beneficial cancer chemo-preventive antioxidant entities.

## EXPERIMENTAL SECTION

To obtain blueberry, blackberry, and pomegranate extracts, 85 g of the particular fruit was measured and added to 100 mL of distilled water. After grinding, the solution was filtered through a paper filter. Green tea extract was obtained by boiling 300 mL of water for 15 min with

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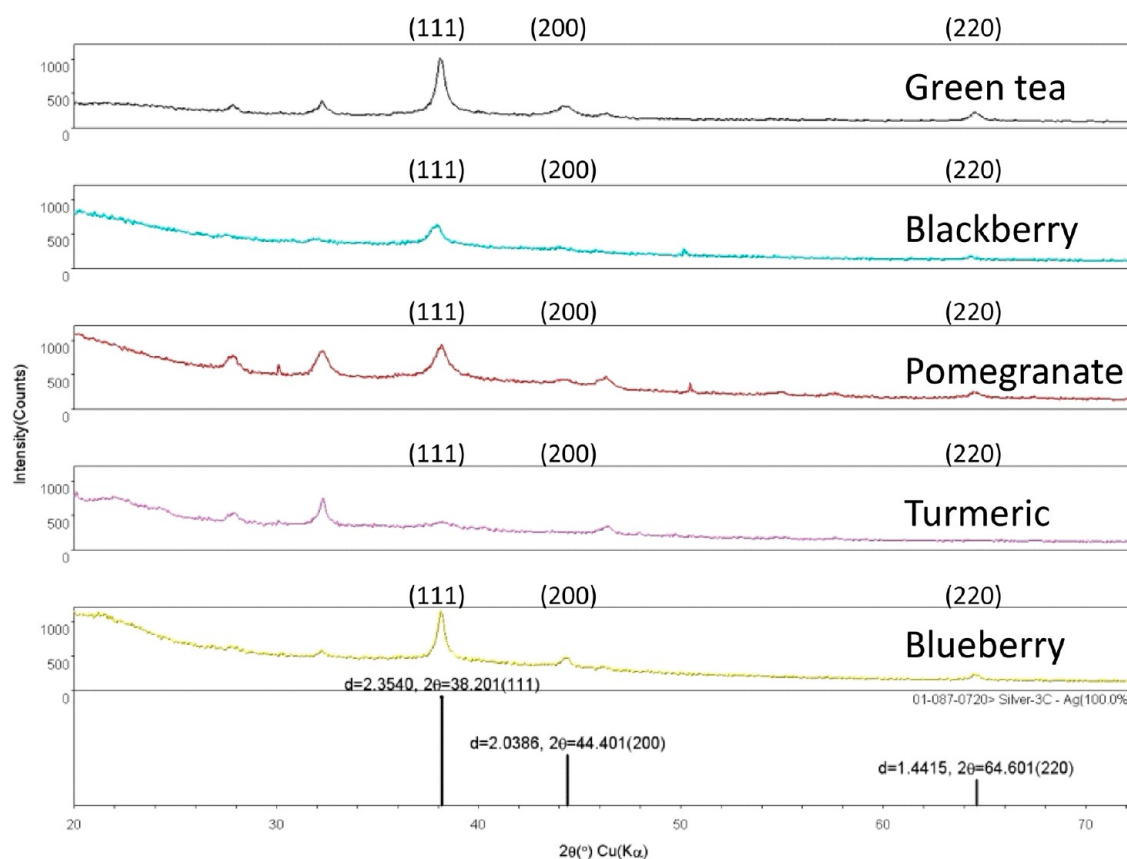


Figure 1. XRD patterns of silver nanoparticles produced from green tea, blackberry, pomegranate, turmeric, and blueberry extracts.

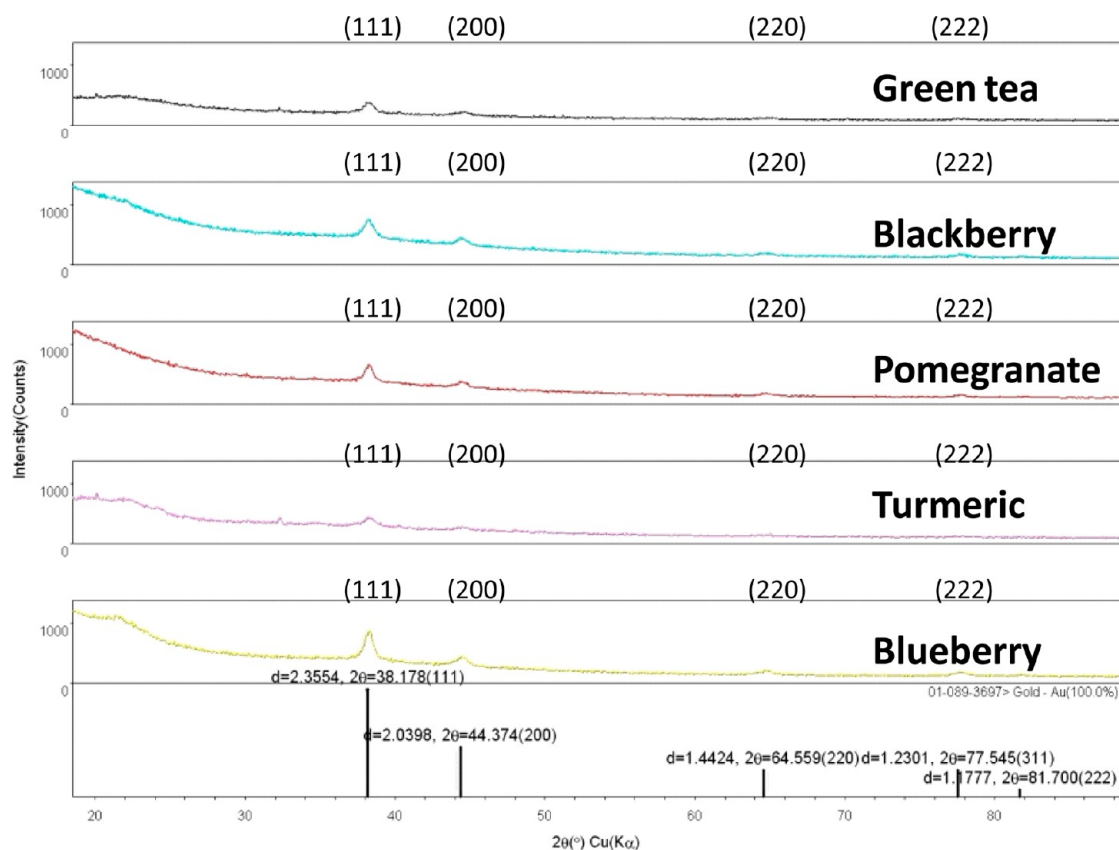
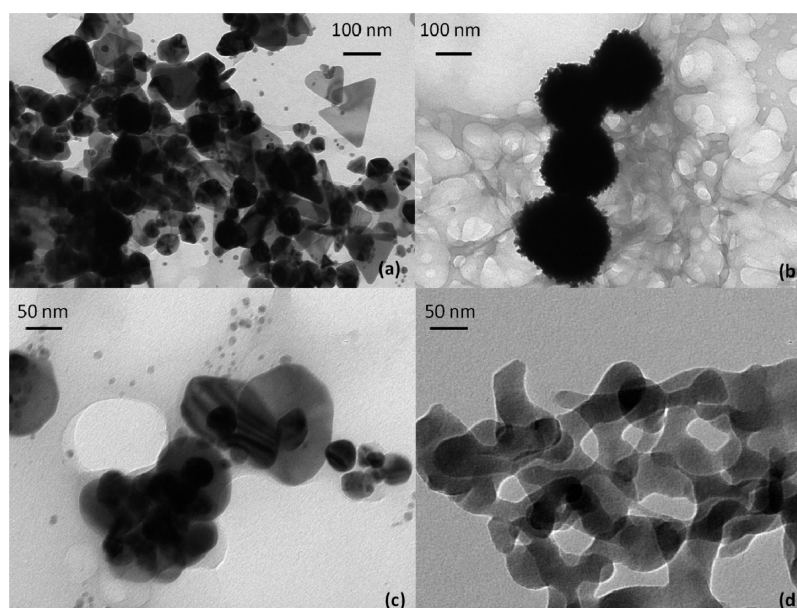
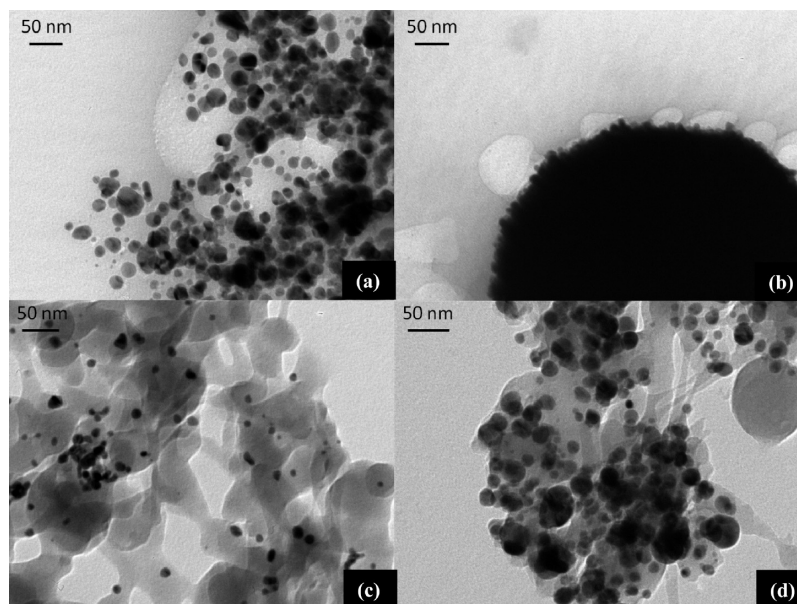


Figure 2. XRD patterns of gold nanoparticles produced from green tea, blackberry, pomegranate, turmeric, and blueberry extracts.



**Figure 3.** TEM images of (a) Ag blueberry, (b) Au blueberry, (c) Ag blackberry, and (d) Au blackberry.



**Figure 4.** TEM images of (a) Ag pomegranate, (b) Au pomegranate, (c) Ag turmeric, and (d) Au turmeric.

**Table 1. Ingredients of Plant Extracts Rich in Antioxidants**

extracts	main ingredients
blackberry	polyphenols, cyanidin 3-glucoside, cyanidin 3-rutinoside, ellagitannins, and procyanidins
blueberry	polyphenols, catechin, quercetin, peonidin, malvidin, and cyanidin glycosides
pomegranate	anthocyanins, polyphenols, ellagic acid, pelargonidin 3-glucoside, cyanidin 3-glucoside, and cyanidin 3,5-diglucoside
turmeric	polyphenols, fisetin, quercetin, myricetin, and curcumin

five green tea bags (10 gms). Turmeric extract was acquired by boiling 100 mL of water for 12 min with 1 tsp (6.8 gms) of turmeric powder. The obtained extracts of green tea and turmeric were then filtered using a paper filter before being used for the synthesis of nanoparticles.

In order to investigate the effect of extracts on the synthesis of AgNPs and AuNPs, the extracts were mixed with silver nitrate ( $\text{AgNO}_3$ ) and auric chloride ( $\text{HAuCl}_4$ ), respectively. Each extract

(9 mL) was added to 0.1 mL of  $\text{AgNO}_3$  or 0.01 mL of  $\text{HAuCl}_4$ . The solutions were left overnight at room temperature under vigorous stirring for completion of the synthesis.

XRD was used to identify crystalline phases of Ag and Au NPs. PANalytical Xpert Pro  $\theta$ - $2\theta$  diffractometer using a  $\text{Cu K}\alpha$  radiation at 45 kV and 40 mA was used. Scans were typically over the range from  $5^\circ$  to  $90^\circ$  ( $2\theta$ ). A pattern analysis was performed using Jade+ software, v.7 or later (MDI, Inc., Livermore, CA), which generally followed the ASTM D934-80 procedure. Reference patterns were from the 2004 PDF-2 release from the ICDD (International Center for Diffraction Data, Newtown Square, PA).

The particle size and zeta potential were determined with a zetasizer (3000HSA, Malvern). A HR-TEM (JEM-2010F, JEOL) with a field emission-transmission gun at 200 kV was used to analyze the morphology and crystallinity of synthesized nanoparticles. For HR-TEM analysis, the particles were dispersed in isopropyl alcohol (99.8%, Pharmco) using an ultrasonicator (2510R-DH, Branson) for more than 15 min and drop-casted on a Formvar carbon-coated copper grid (FCF400-Cu, EMS).



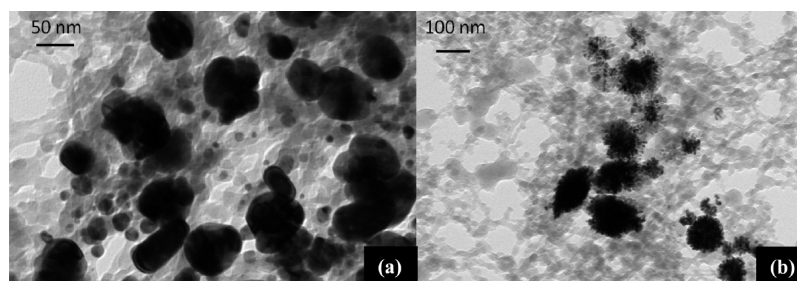


Figure 5. TEM image of (a) Ag using green tea, and (b) Au using green tea.

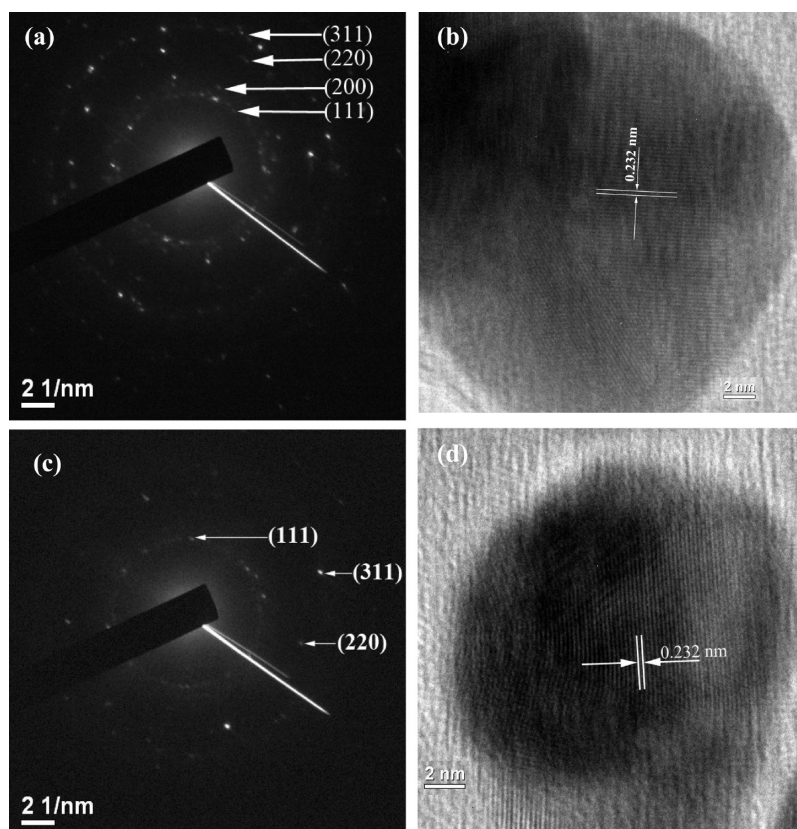


Figure 6. (a) Selected area electron diffraction pattern. (b) HR-TEM image of Ag nanoparticle synthesized using blackberry. (c) Selected area electron diffraction pattern. (d) HR-TEM image of Au nanoparticle synthesized using pomegranate.

Thermogravimetric analysis (TGA, PerkinElmer) was carried out for the determination of the weight changes of the Au-containing samples during heat treatment from room temperature to 800 °C with a ramp rate of 10 °C and a gas flow rate of mL/min under nitrogen atmosphere. All Au-containing samples were centrifuged and then dried before the TGA analysis.

## RESULTS AND DISCUSSION

Turmeric extract mainly consists of phenolic compounds, predominantly curcuminoids (curcumin; Scheme S1, Supporting Information) and minor quantities of triterpenoids, alkaloid, and sterols. Water- and fat-soluble extracts of turmeric and its curcumin component exhibit strong antioxidant activity, comparable to vitamins C and E. These antioxidants are responsible for the reduction of Ag and Au cations for the NP synthesis; this concurs with our previous work with phenolic antioxidants that are responsible for the reduction of Ag and Au nanoparticles.<sup>27</sup>

Blueberries are rich in antioxidants,<sup>28</sup> substances that can help reduce the natural cell damage in our aging bodies that can

lead to cancer, heart disease, and other ailments. Similarly, blueberries and pomegranate are rich in antioxidants. The main constituents of all these fruit extracts are shown in Table 1.

The change in color of the reaction is the primary conformation of silver and gold nanoparticle formation. All the extracts changed color overnight after addition of silver and gold salts; blueberry was the slowest in displaying this colorimetric indication. XRD analysis was conducted to confirm the phases of the produced silver and gold nanoparticles.

Figures 1 and 2 show the XRD patterns of Ag and Au NPs, respectively, produced using blackberry, blueberry, pomegranate, and turmeric extracts. The peaks at  $2\theta$  values 38.2°, 44.4°, and 64.66° correspond to (111), (200), and (220) planes of Ag, respectively. Similarly, the peaks at  $2\theta$  values 38.17°, 44.37°, 64.55°, and 77.54° correspond to (111), (200), (220), and (222) planes of Au, respectively.

All the patterns were indexed to cubic Ag and Au NPs. The patterns were compared with JCPDS patterns shown in

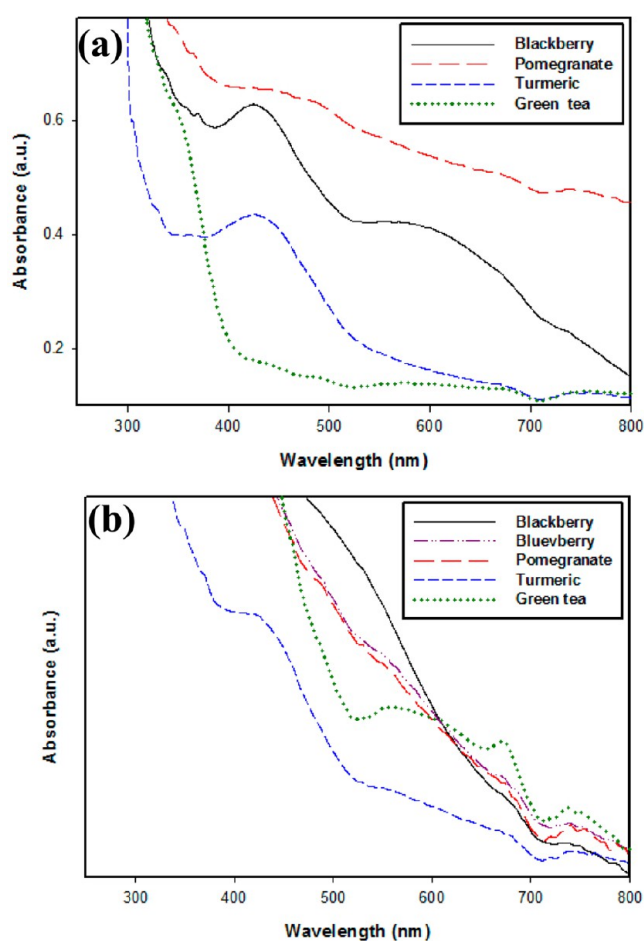
Figures 1 and 2. The XRD patterns are relatively broad and wide, indicating the formation of Ag and Au NPs.

Figures 3, 4, and 5 illustrate TEM images of the various Ag and Au NPs synthesized using environmentally friendly blackberry, blueberry, pomegranate, and turmeric extracts. Figure 3a represents AgNPs synthesized with blueberry extracts, and particles were found to be from 50 to 150 nm of averaged size and comprise both types, spherically and triangularly shaped. Figure 3b represents spherical AuNPs synthesized with blueberry extracts. The size of these spherical particles was about 200 nm in diameter. Figure 3c illustrates AgNPs synthesized with blackberry extracts with particle size ranging from 25 to 150 nm. Figure 3d illustrates AuNPs synthesized with blackberry extracts; particles were oblong shaped with an average size of 100 nm. Figure 4a shows AgNPs synthesized with pomegranate extracts; spherical particles ranging from 5 to 50 nm in diameter were obtained. Figure 4b represents AuNPs synthesized with pomegranate extracts, and in this case, bigger spherical particles were formed, about 400 nm in diameter. Figure 4c shows AgNPs synthesized from turmeric extracts generating both large (100 nm) oblong spheres and small (5 to 10 nm) spherical particles. Figure 4d shows AuNPs synthesized with turmeric extracts, wherein spherical particles ranging from 5 to 60 nm in diameter were readily obtained. Figure 5a illustrate synthesized spherical AgNPs ranging from 10 to 50 nm in diameter using green tea extracts. In the case of AuNPs, larger spherical particles with a diameter of 100 nm were synthesized using the green tea (Figure 5b). The sizes and shapes of synthesized Ag and Au NPs were dependent on the extracts used for the synthesis method, which may be ascribed to differential antioxidant capacity (reduction potential) of the extracts used. It also depends upon the capping capability of the constituents present in the extracts.

Pomegranate extract, which is rich in anthocyanins, flavonoids, phenolic acids, and tannins,<sup>29</sup> produced more uniform silver and gold nanoparticle shapes and sizes as compared to turmeric, blueberry, blackberry and tea/coffee extracts. Anthocyanins are the major constituents present in pomegranate and probably are responsible for the particle size reduction and uniform shapes and sizes of the ensuing nanoparticles. Turmeric is not soluble in water and needs organic solvent to extract the key ingredients. However, its dispersed solution in contact with silver and gold salts played a major role in orchestrating the smaller sizes of nanoparticles as compared to blueberry, blackberry, and tea/coffee extracts. Gold nanoparticle formation was slower (required days) compared to silver nanoparticles.

Figure 6a and b show the selected area electron diffraction (SAED) analysis and HR-TEM image of AgNPs synthesized using blackberry extract. The SAED patterns of (111), (200), (220), and (311) were observed, which confirmed the synthesis of AgNPs by the green chemistry route.<sup>30,31</sup> The lattice spacing of 0.232 nm corresponding to the (111) plane of Ag is in good agreement with other studies on the synthesis of Ag nanoparticles.<sup>32–34</sup> Similar results were observed using pomegranate extract (Figure 6c and d). The formation of silver nanoparticles was also confirmed with energy dispersive X-ray analysis as shown in Figure S1 of the Supporting Information and with UV spectroscopy as shown in Figure 7.

UV spectra of Ag and Au nanoparticles prepared from blackberry, blueberry, pomegranate, green tea, and turmeric extracts are shown in Figure 7a and b. The symmetry of silver nanostructures governs the ways that they are polarized and the number of plasmonic peaks.<sup>35</sup> The extinction spectra of small



**Figure 7.** UV spectra of (a) silver and (b) Au nanoparticles produced using different plant and fruit extracts.

particles with spheres have just one peak, while cubic particles could be polarized both in dipole (in about 530 nm) and quadrupole modes. Therefore, they have two plasmonic peaks and polarization modes. The broad plasma resonance peak (Figure 7a) at 420–460 nm corresponds to Ag nanoparticles. Additional peaks around 550–650 nm correspond to dipole and quadrupole modes of silver due to different shapes and sizes. The plasmonic properties of gold nanoparticles are extremely sensitive to small variation in dimension.<sup>35</sup> The positions of surface plasma resonance peaks of gold nanospheres depend on the dielectric constant of the environment. Therefore, different solvents or adsorption of a capping agent onto the nanospheres may result in slight variation for the SPR peak position;<sup>35</sup> peaks around 560 nm and 650–800 nm (Figure 7b) correspond to plasma resonance peaks for gold nanostructures.<sup>36</sup>

The particle size distributions calculated from TEM images are shown in Figure S2 of the Supporting Information. The wide particle dispersivity was observed depending upon the source of the reducing agent used.

Thermal behavior of AuNP-containing samples was investigated with TGA, and three stages were observed in ensuing TGA curves (Figure 8). Absorbed water (around 8%) was evaporated at the first stage from 30 to 170 °C. At the second stage, from 170–420 °C, most organics were removed by combustion. At the third stage, weight changes for samples synthesized using pomegranate and turmeric extracts were minimized, but the weight of other samples synthesized using

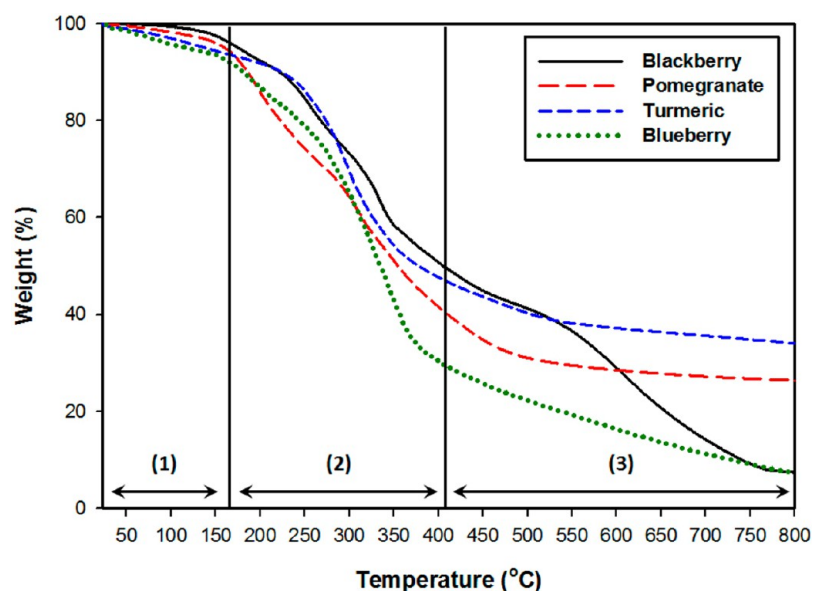


Figure 8. Thermogravimetric analysis of AuNP-containing samples.

blackberry and blueberry extracts still significantly decreased. This may relate to removal of larger tannin oligomers.

## CONCLUSION

Synthesis and characterization of Ag and Au nanoparticles using antioxidant constituents from the extracts of blackberry, blueberry, pomegranate, and turmeric are accomplished under ambient conditions. The synthesized particles were characterized using XRD for the phase confirmation, and it was found that the crystallized particles were of cubic symmetry. The TEM and HR-TEM were used to determine the shape and size of synthesized Ag and Au NPs. From the TEM images, the sizes of ensuing particles ranged from 20 to 500 nm, depending upon the extracts used. UV-vis spectroscopy was employed to confirm the plasma resonance peaks. Pomegranate extract produced more uniform silver and gold nanoparticle shapes and sizes as compared to turmeric, blueberry, blackberry, and tea/coffee extracts. These particles with antioxidant coatings can be potentially used for the delivery of useful oxidants and cancer chemo-preventive agents based on curcuminoids. Further, antioxidant-rich extracts can potentially be utilized from waste material generated during fruit/juice processing.

## ASSOCIATED CONTENT

### Supporting Information

Chemical structure of curcumin, energy dispersive X-ray analysis of Ag nanoparticles, and their size distribution using various extracts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

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The authors declare no competing financial interest.

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