Original Article

Silver and palladium nanoparticles produced using a plant extract as reducing agent, stabilized with an ionic liquid: sizing by X-ray powder diffraction and dynamic light scattering

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ABSTRACT

Powder X-ray diffraction and dynamic light scattering (DLS) sizing of silver (Ag) and palladium (Pd) nanoparticles produced within aqueous plant extract and the effect of introducing of an ionic liquid are reported in this paper. The simple and novel synthesis of silver and palladium nanoparticles using the reducing power of Persea americana (Pa) bark extract is reported and the effect of adding 1-ethyl-3-methylimidazolium tosylate [EMIm][Tos] is described. Detailed powder X-ray interpretation allowed determination of the crystalline grain sizes of 16 ± 4 nm for Ag-Pa, 13 ± 2 nm for Ag-Pa[EMIm][Tos], 16 ± 3 nm for Pd-Pa and 9 ± 1 nm for Pd-Pa[EMIm][Tos] according to the Scherrer peak analysis. A size contraction occurs when moving from plant extract alone to plant extract/ionic liquid. These grain sizes are 9 nm for Ag-Pa and for 9 nm Ag-Pa[EMIm][Tos], 15 nm for Pd-Pa and 7 nm for Pd-Pa[EMIm][Tos] when the Williamson–Hall plot intercept is used. Modal hydrodynamic sizes were determined by DLS as 57 nm for Ag-Pa, 72 nm for Ag-Pa[EMIm][Tos], 390 nm for Pd-Pa and 98 nm for Pd-Pa[EMIm][Tos] providing indications on how the particles behave in solution. Intrinsic stresses of 0.177 GPa for Ag-Pa, 0.219 GPa for Ag-Pa[EMIm][Tos], 0.382 GPa for Pd–Pa and 0.190 GPa for Pd–Pa[EMIm][Tos] and dislocation densities of (6 ± 3) × 10−3 nm−2 for Ag–Pa, (9 ± 3) × 10−3 nm−2 for Ag–Pa[EMIm][Tos], (5 ± 2) × 10−3 nm−2 for Pd–Pa and (16 ± 4) × 10−3 nm−2 for Pd–Pa[EMIm][Tos] have been obtained.

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1. Introduction

This decade has witnessed a huge growth in the use of plant extracts in the synthesis of nanoparticles. This is a breakthrough in science since it is regarded as a green methodology contributing to a global attempt to save the planet from further damage by man-made pollutants. Although the planet is endowed with an abundance of plants, the scientific exploration of the most effective plant for the fabrication of nanoparticles has just begun [1].

When the size or dimension of a material is continuously reduced from a large or macroscopic size, such as centimetre to a very small size, the properties remain the same at first, and then small changes begin to occur, until finally when the size drops below 100 nm, dramatic changes in properties can occur [2]. One of the most direct effects of reducing the size of materials to the nanometer range is appearance of quantization effects due to the confinement of the movement of electrons, which leads to discrete energy levels that depend on the size of the structure. Similarly, there exist artificial and natural structures with properties different from the corresponding bulk materials. Control over dimensions as well as composition of structures makes it possible to tailor material properties to specific applications that are influenced by the quantum confinement effect (QCE) [3]. Quantum confinement (QC) in semiconductors results from the geometric confinement of electrons, holes or excitons (electron-hole bound pair). The normal size of an exciton in a large bulk crystal is expressed as an exciton Bohr radius (BER). When an electron–hole pair is squeezed below the dimensions of the BER, QC effects become prominent in the structure and the effective band gap increases. The smaller the nanostructure the larger the effective band gap and the greater the energy of the optical emission, which changes the optical and the electronic properties when the sample size is sufficiently smaller than 10 nm [4]. The most obvious applications are in tailoring the band gap for specific applications, such as the tuning of the absorption or emission energy in electronic, electrooptical, optoelectronic, or purely optical devices [5]. Moreover, nanomaterials with reduced particle size have higher active surface area, which makes the materials more chemically and biologically active. Bound electron–hole pairs, or excitons, should also be treated as quantum–mechanical systems with wavefunctions that resemble those of simple H-atom system. The photogenerated electron–hole interactions are weak in bulk semiconductors, and the binding energies are sufficiently small that the electron–hole pairs are not bound at room temperature [6]. The excitons formed in the nanoparticles can lead to generation of various reactive oxygen species with suitable precursors that interact with various parts of the bacteria and enhance the antibacterial nature of the nanoparticle [7]. The capability to control the spatial evolution of metal nanoparticles (MNPs) within a confined space provides great benefits for the development of sensing and diagnostic system/techniques [8,9].

Common analytical techniques associated with nanoparticles sizing are dynamic light scattering (DLS), transmission electron microscopy (TEM), atomic force microscopy (AFM), thermomagnetic measurement or powder X-ray diffraction (PXRD). X-ray powder diffraction was pioneered by Debye and Scherrer in 1916 and is now a well-established technique that has been used successfully for nearly 100 years [10]. X-ray diffraction (XRD) is now a routine technique that has been applied successfully to a huge variety of (crystalline) materials – from simple solids to complex proteins [11]. The wavelength of X-rays is on the atomic scale, so XRD is a primary tool for probing the structure of nanomaterials and is ideal for in situ studies.

DLS, also known as photon correlation spectroscopy, is one of the most popular methods used to determine the size of MNPs. During the DLS measurement, the MNP suspension is exposed to a light beam (electromagnetic wave), and as the incident light impinges on the MNP, the direction and intensity of the light beam are altered due to a process known as scattering [12]. DLS has several advantages for sizing nanoparticles and has been widely used to determine their hydrodynamic size. The measuring time for DLS is short, and it is almost all automated, so the entire process is not labour intensive and can be routinely performed and is non-destructive for the sample [13].

Some reviews note a parallel and synergistic development of nanoparticles and ionic liquids (ILs) for materials chemistry [14–19]. The surface stabilization of MNPs (both electrostatic and steric) is thought to occur through the formation of an ion layer around the MNPs. The type of this ion layer, hence the mode of stabilization of MNPs in ILs, is still a matter of some discussion [15–20]. The use of ILs and plant extract in the synthesis of nanoparticles is an interesting way to produce materials with advanced properties such as shape, size and stability making them suitable for biological and medical applications.

Persea americana (family Lauraceae), a tree plant known as ‘avocado’, is cultivated in tropical and subtropical climates around the world. The plant is used in traditional medicine for the treatment of various ailments, such as menorrhagia, hypertension, stomachache, bronchitis, diarrhoea, and diabetes [14,21]. The dry bark phytochemical research has come up with various compounds like the secondary metabolites saponins, tannins, flavonoids and terpenoids [15,22]. A C 20 alkyl–alkene acetonil methyl ester designated persealide with moderate cytotoxicity against three solid tumour cell lines (human lung carcinoma (A-549), human breast carcinoma (MCF-7), and human colon adenocarcinoma (HT-29)) has been isolated from the bark by Janiak et al. [16] and Ye et al. [23]. The plant extract can be also considered as an eco-friendly bioreductor for the simple reduction process of silver ions. Persea americana is a cost-effective alternative to other biological reductants such as bacteria or fungi. Due to the plant availability and accessibility, the scale-up translation from laboratory to industry is possible.

We present in this work the grain size evaluation for silver and palladium nanoparticles formed with Persea americana (Pa) bark extract and the ionic liquid 1-ethyl-3-methylimidazolium tosylate ([EMIm][Tos]). This particle size is evaluated using PXRD patterns by the Scherrer equation, Williamson–Hall plots (microstrain) and the results compared with those obtained from DLS study.
2. Experimental

2.1. Plant material and synthesis

Barks of *Persea Americana* were procured from the University of Douala, Cameroon. Plant identification was confirmed at the National Herbarium of Cameroon under voucher number specimen 57756 HNC. *Persea Americana* (Avocado) is a tree classified as a member of the flowering plant family Lauraceae and generally refers to the tree's fruit, which is botanically a large berry containing a single seed [24]. The dried bark organic material was powdered in a mixer and sieved using a 20-mesh sieve to get a uniform size range. Aquous plant extracts were prepared by boiling 10 g of organic material in 200 mL of de-ionized water for 5 min at 80 °C. The extract was filtered through a Whatman No. 1 filter paper to remove particulate matter, and obtain clear solutions that were stored at 4 °C for further use. These were usable for one week due to the gradual loss of plant extract viability upon prolonged storage [25]. Silver nitrate (AgNO₃) was obtained from Sigma-Aldrich Chemicals Germany, and potassium tetrachloroplatinate(II) (K₂PtCl₄) from Acros Organics Germany. 1 Ethyl-3-methylimidazolium tosylate (99%) was purchased from PoliLiTec Germany. De-ionized water was used throughout the reactions. All glassware was washed with dilute nitric acid (HNO₃) and de-ionized water, and then dried in a hot air oven. Solutions of AgNO₃ of 10⁻³ mol/L and PtCl₂ of 3 x 10⁻³ mol/L were prepared in de-ionized water. As a standard procedure, 10 mL of organic material extract was added to 50 mL of 10⁻³ mol/L aqueous silver or palladium salt solution, hand shaken for 10 s, and incubated at room temperature in the dark to minimize the photoactivation of silver nitrate. The reactions were made under static conditions. In the case of plant extract and ionic liquid mediation, the organic material extraction was made using a 2% aqueous solution of [EMIm][Tos]. After 24 h of incubation the nanoparticles produced were centrifuged for 1 h at 6000 rpm, dried in an oven and stored for further analyses.

2.2. Powder X-ray diffraction

Powder X-ray diffraction measurements were carried out at ambient temperature using a BRUKER D2 Phaser diffractometer (Cu Kα [Å] 1.54182, 30 kV) by preparing a film of the silver-organic nanopowder on a flat, low-background silicon sample holder. The peaks and phase were identified using the profile matching routine of the MATCH Version 3 programme [26] and Rietveld refinement was carried out using the FullProf 2000 software package [27].

X-ray diffractograms of nanomaterials provide a wealth of information – about phase composition, crystallite size, lattice strain, and crystallographic orientation. The lattice planes in a crystal are separated by a distance d. Bragg’s law relates the wavelength (λ) of the reflected X-ray, the spacing between the atomic planes (d) and the angle of diffraction (θ) as follows:

\[ 2d \sin \theta = n\lambda \]  

The angle between the incident and diffracted beams is equal to 2θ. This angle can be obtained readily in experimental situations and the results of X-ray diffraction are therefore given in terms of 2θ. The average crystallite grain size of the synthesized NPs is determined using the Scherrer equation [28]:

\[ D_v = \left( \frac{K\lambda}{p\cos \theta} \right) \cos \theta \]  

where \( D_v \) is the average crystalline size; \( K \) is a dimensionless shape factor, with a value close to unity (0.9); \( \lambda \) is the wavelength of Cu-Kα; \( \beta \) is the full width at half-maximum (FWHM) of the diffraction peaks, and \( \theta \) is the Bragg angle.

In materials science, a dislocation is a crystallographic defect, or irregularity, within a crystal structure. The intrinsic stress \( (\sigma_s) \) developed in nanoparticles due to the deviation of measured lattice constant of silver nanoparticles over the bulk is calculated using the relation below [29].

\[ \sigma_s = \frac{Y(a - a_0)}{2a_0\gamma} \]  

Here, \( Y \) is the Young’s modulus (83 GPa for Ag and 121 GPa for Pd), \( a \) is the lattice constant (in nanometers) measured from XRD data, \( a_0 \) is the bulk lattice constant (0.4079 nm for Ag and 0.3893 for Pd) and \( \gamma \) is the Poisson’s ratio (0.37 for Ag and 0.39 for Pd).

The presence of dislocations strongly influences many of the properties of materials [28]. The dislocation density \( (\delta) \) in the sample has been determined using expression [30].

\[ \delta = \frac{15\beta \cos \theta}{4aD} \]  

where \( \delta \) is dislocation density, \( \beta \) is the broadening of diffraction line measured at half of its maximum intensity (in radian), \( \theta \) is the Bragg angle (in degrees), \( a \) is the lattice constant (in nm) and \( D \) is particle size (in nm).

The Scherrer equation gives an estimate of particle size. Despite the well-known accuracy of this method, it neglects the importance of the microstrain, \( \varepsilon \), and its effects in the powder diffraction [31]. These are introduced by the Williamson–Hall (WH) plot:

\[ \beta \cos \theta = C + 4\varepsilon \sin \theta \]  

where \( \beta \) is FWHM in radian, \( t \) is the grain size in nm, \( \varepsilon \) is the strain, \( t \) is X-ray wavelength in nanometers, and \( C \) is a correction factor taken as 0.94 [32].

2.3. Dynamic light scattering

Particle sizes and size distributions were evaluated using a Zetasizer (Malvern Nano S Zetasizer) operating with a He–Ne laser at a wavelength of 633 nm. Each analysis was performed in triplicate and the mean value is reported. In each run, 10–15 measurements were made. Size analysis by DLS utilizes the Brownian motion that particles, emulsions, and molecules in suspension undergo as a result of bombardment by solvent molecules. If the particles are illuminated with a laser,
the intensity of the scattered light fluctuates at a rate that is dependent upon the size of the particles. Smaller particles are “hit” more frequently by the solvent molecules and move more rapidly. Analysis of these intensity fluctuations yields the velocity of the Brownian motion and hence the particle size using the Stokes–Einstein relationship [33,34].

\[
D = \frac{k_B T}{6\pi \eta r}
\]  

(6)

where \(D\) is the diffusion constant (m² s⁻¹), \(k_B\) is the Boltzmann’s constant (J K⁻¹), \(T\) is the absolute temperature (K), \(\eta\) is the viscosity of the solvent (kg m⁻¹ s⁻¹) and \(r\) is the particle radius (m).

2.4. UV–visible spectroscopy

The reaction was monitored by ultraviolet–visible spectroscopy of 1 mL of the reaction suspension using an UV–visible Spectrometer UV-VIS SPECORD S600 from Analytik Jena operating at 0.5 nm resolution with optical length of 10 mm.

3. Results and discussion

3.1. Powder X-ray diffraction study

Despite many advantages, there are drawbacks in the biosynthesis of nanoparticles with plant extracts. It is difficult to control the particle size and morphology, and the diverse and often unknown functionalities of the components in plant extracts hinder an understanding of the formation mechanisms as compared to established chemical approaches [35]. Previous syntheses of nanoparticles using plant extracts and ILs are limited to gold nanoparticles [36–39]. Synthesis using extracts of palm leaves showed a particle size reduction when ILs were present. The ILs investigated in these studies were 1-ethyl-3-methylimidazolium chloride and 1-ethyl-3-methylimidazolium acetate along with the effects of ageing or microwave heating [Fig. 1] [36–39]. In the current work, silver and palladium nanoparticles are synthesized by ageing using Persea americana (Pa) bark extract and 1-ethyl-3-methylimidazolium tosylate [EMIm][Tos] (Fig. 2) in order to compare the size reduction and strain effect due to the use of an ionic liquid component.

Once the extracts or extracts and IL were added to the metal precursor a sudden colour change to yellow-brown was noted. The main advantage of the ionic liquid [EMIm][Tos] with the bulky tosylate anion is to produce less hygroscopic material when compared to methylimidazolium salts with smaller anions such as chloride. PXRD confirmed the formation of face-centred cubic (Fm-3m) nanoparticulates of both pure silver and palladium (100%) which is in good agreement with previous reports [40]. The nanostructured powder exhibited only a set of diffraction lines ascribed to the silver structure, which was identified from the ICDD card number 65-2871 and of the palladium nanostructure identified from the ICDD number 46-1043. The two main properties extracted from peak width analysis are the crystallite size and lattice strain [41]. The lattice parameters of 4.0854 Å for Ag–Pa, 4.087 Å for Ag–Pa[EMIm][Tos], 3.9026 Å for Pd–Pa and 3.8977 Å Pd–Pa[EMIm][Tos] were obtained using the Rietveld refinement package Fullprof following initial identification using the MATCH3 routine and agree with those obtained for silver and palladium materials [42,43]. According to the peak analysis using the Scherrer equation for four peaks, the sizes are 16 ± 4 nm for Ag–Pa, 13 ± 2 nm for Ag–Pa[EMIm][Tos], 16 ± 3 nm for Pd–Pa and 9 ± 1 nm for Pd–Pa[EMIm][Tos]. The slope of the straight-line of the Williamson–Hall plot gives the lattice strain (\(\sigma\)) and the average crystallite size (\(t\)) is extracted from the intercept. These grain sizes are therefore 9 nm for Ag–Pa, 9 nm for Ag–Pa[EMIm][Tos], 15 nm for Pd–Pa and 7 nm for Pd–Pa[EMIm][Tos] when the Williamson–Hall plot intercept is used (Fig. 3).

The outcomes of refinement are plotted in Figs. 1–4 of the Supporting Information. The observed peaks, the calculated ones, and their difference in profiles of the sample are presented in the figures. Abdulwahab [44] pointed out that the accuracy of the Scherrer equation in particle size determination is greater than that of the Williamson–Hall equation. This is because the first equation uses the slope to calculate the average crystallite size while...
the later equation uses the line intercept. Deviations from perfect crystallinity extend infinitely in all directions. This leads to broadening of the diffraction peaks. The crystallite size and lattice strain are the two main properties that could be extracted from the peak width analysis. Due to the formation of polycrystalline aggregates [45], the crystallite size, which is not the same as particle size, varies as 1/cosθ and strain varies as tanθ from the peak width. The strain within the samples, calculated using Williamson–Hall analysis is close to zero. The Williamson–Hall analysis is an integral breadth method. Size-induced and strain-induced broadenings are known by considering the peak width as a function of 2θ [46]. However, the Williamson–Hall method has many assumptions: Its absolute values should not be taken too seriously but it can be a useful method if used in a relative sense; for example, a study of many powder patterns of the same chemical compound, but synthesized under different conditions, might reveal trends in the crystallite size/strain, which in turn can be related to the properties of the product [47]. Lattice strain is a measure of the distribution of lattice constants arising from crystal imperfections, such as lattice dislocations. Other sources of strain include the grain boundary triple junction, contact or sinter stresses, stacking faults and coherency stresses [48]. The strain, which can be uniform or nonuniform, impacts the peak broadening. The strain obtained are −0.0025 for Ag–Pa, −0.0009 for Ag–Pa[EMIm][Tos], 0.0005 for Pd–Pa and −0.0007 for Pd–Pa[EMIm][Tos] (cf. Table 1).

The negative strain values for silver and palladium nanoparticles may be due to lattice shrinkage, a case described for ZnO nanoparticles [41]. For comparison matter Si powder is almost free of microstrain (0.01%) [49]. Nanoparticle size estimation by the Scherrer equation is slightly higher than the Williamson–Hall plot estimation method. This difference can be explained by the induction of broadening by microstrain in the diffraction peak. In the Scherrer equation, the full width of the diffraction peak is considered in the calculation [50]. Burton and coworkers found that large crystal sizes can be underestimated by orders of magnitude when the effects of stress are not (or cannot be) included in the analysis [51]. Second Scherrer calculations are made when only the contribution of the size βD is considered by removing value βε to separate the line width contributions due to microstrain and due to particle size to the overall full line width. Hence β = βD + βε when instrument broadening is neglected with βε = 4πtanθ. The obtained values are listed in Table 2 and are closer to the values obtained by the Williamson–Hall plot.

**Table 1 – Size-strain by Williamson–Hall plot and lattice parameters.**

<table>
<thead>
<tr>
<th>MNPs</th>
<th>Size/nm</th>
<th>Strain</th>
<th>Lattice parameters/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag–Pa</td>
<td>9</td>
<td>−0.0025</td>
<td>4.0854</td>
</tr>
<tr>
<td>Ag–Pa[EMIm][Tos]</td>
<td>9</td>
<td>−0.0009</td>
<td>4.087</td>
</tr>
<tr>
<td>Pd–Pa</td>
<td>15</td>
<td>0.0005</td>
<td>3.9026</td>
</tr>
<tr>
<td>Pd–Pa[EMIm][Tos]</td>
<td>7</td>
<td>−0.0007</td>
<td>3.8977</td>
</tr>
</tbody>
</table>
### Table 2 – MNPs parameters (part1).

<table>
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<th>MNPs</th>
<th>Parameters</th>
<th>2θ(°)</th>
<th>FWHM(/°)</th>
<th>Lattice spacing/nm</th>
<th>Lattice constant/Å</th>
<th>Size/Å</th>
<th>αs/ nm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag–Pa</td>
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<td>38.16</td>
<td>0.7</td>
<td>2.35</td>
<td>4.0703</td>
<td>13</td>
<td>7.46 × 10⁻³</td>
</tr>
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<td></td>
<td></td>
<td>44.3</td>
<td>0.7</td>
<td>2.04</td>
<td>4.08</td>
<td>14</td>
<td>7.15 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>64.55</td>
<td>0.4</td>
<td>1.44</td>
<td>4.0729</td>
<td>22</td>
<td>2.65 × 10⁻³</td>
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<td></td>
<td></td>
<td>77.45</td>
<td>0.7</td>
<td>1.23</td>
<td>4.0794</td>
<td>16</td>
<td>5.07 × 10⁻³</td>
</tr>
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<td>AgPa[EMIm][Tos]</td>
<td></td>
<td>38.15</td>
<td>0.7</td>
<td>2.35</td>
<td>4.0703</td>
<td>13</td>
<td>7.46 × 10⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>44.31</td>
<td>0.9</td>
<td>2.04</td>
<td>4.08</td>
<td>10</td>
<td>12.71 × 10⁻³</td>
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<td></td>
<td>64.51</td>
<td>0.7</td>
<td>1.44</td>
<td>4.0729</td>
<td>15</td>
<td>5.97 × 10⁻³</td>
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<td>4.0794</td>
<td>12</td>
<td>9.01 × 10⁻³</td>
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<tr>
<td>Pd–Pa</td>
<td></td>
<td>40.03</td>
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<td>2.25</td>
<td>3.8971</td>
<td>20</td>
<td>3.42 × 10⁻³</td>
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<td></td>
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<td>46.53</td>
<td>0.7</td>
<td>1.95</td>
<td>3.9</td>
<td>14</td>
<td>7.36 × 10⁻³</td>
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<td>67.94</td>
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<td>1.37</td>
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<td>6.04 × 10⁻³</td>
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<td>81.85</td>
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<td>1.17</td>
<td>3.8804</td>
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<td>PdPa[EMIm][Tos]</td>
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<td>40.1</td>
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<td>13.75 × 10⁻³</td>
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<td></td>
<td>46.61</td>
<td>1.1</td>
<td>1.94</td>
<td>3.88</td>
<td>8</td>
<td>20.55 × 10⁻³</td>
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<td></td>
<td>68.05</td>
<td>1.1</td>
<td>1.37</td>
<td>3.8749</td>
<td>9</td>
<td>16.74 × 10⁻³</td>
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<td>3.8804</td>
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### Table 3 – MNPs parameters part2 (Size 1 strain included, Size 2 strain excluded).

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<th>Parameters</th>
<th>2θ(°)</th>
<th>FWHM(/°)</th>
<th>βε = 4α tan(θ)/ °</th>
<th>βD/ Å</th>
<th>Size 1/nm³</th>
<th>Size 2/nm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag–Pa</td>
<td></td>
<td>38.16</td>
<td>0.7</td>
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<td>0.6605</td>
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<td>13</td>
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<td></td>
<td></td>
<td>44.3</td>
<td>0.7</td>
<td>-0.0040</td>
<td>0.6611</td>
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<td>14</td>
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<td>-0.0063</td>
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<td>22</td>
</tr>
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<td></td>
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<td>-0.0080</td>
<td>0.6651</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>AgPa[EMIm][Tos]</td>
<td></td>
<td>38.15</td>
<td>0.7</td>
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<td></td>
<td></td>
<td>44.31</td>
<td>0.9</td>
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<td>0.8775</td>
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<td>10</td>
</tr>
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<td></td>
<td>64.51</td>
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<td>0.6593</td>
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<td>-0.0024</td>
<td>1.0975</td>
<td>10</td>
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</tr>
</tbody>
</table>

a Obtained by the Scherrer equation (size 1).
b Obtained by the Scherrer equation with βD = β – βε (size 2).
Experiments for 

ECAP actions nanoparticles. 

subject 3.2. line (5) can called Pd–Pa[EMIm][T os]. 

It has been shown for different pure face-centred cubic (fcc) metals processed by Equal Channel Angular Pressing (ECAP) that the dislocation density increases while grain size decreases with increasing strain and ultimately these parameters reach saturation values [53].

3.2. Dynamic light scattering and ultraviolet–visible study

Experiments were made in an attempt to correlate the PXRD size with DLS-based sizes. Many studies have proposed that surface active molecules or stabilizers in the reaction mixture create electrostatic interactions providing more stable nanoparticles. Hence, it was suggested that the presence of ILs can produce electrostatic and electrosteric forces to improve the stability of AuNPs, demonstrated by higher zeta value from aqueous extract [39]. Macromolecules or surfactants act similarly to ionic liquid by disrupting the electrostatic interactions between nanoparticles. ILs are known to cover the nanoparticle surface to produce electrostatic repulsion forces [15–19,54]. The comparatively large tosylate anions (when compared to small negative halide ions) are adsorbed on the surface of silver and palladium while imidazolium cations orientated outward create a bulky surface layer for steric repulsion. Tosylate anions are in competition with plant secondary metabolites acting as capping agents. In DLS, light from a coherent source is directed at a particle suspension where it is scattered [55,56]. Due to the random Brownian motion of the particles, the scattering fluctuates with time due to the constantly changing distances of the scatterers. Hence the size of ionic liquid and plant extract mediated nanoparticles, determined by DLS, may appear smaller than plant mediated nanoparticle without ionic liquid when palladium is considered. Plant-mediated nanoparticles are in most studies fast aggregating, DLS in this work is recorded after four hours of ageing. DLS has previously been used to determine the size distribution profile of nanoparticles in suspension [57]. The tendency to aggregate is slowed down when Persea Americana bark plant extracts, [EMIm][Tos] ionic liquid, and palladium is used, while a similar aggregation time is observed for silver nanoparticles. Fig. 4 shows the variation of the size distributions.

Related to the agglomeration of particles using plant extract and ILs, the particles measured by using DLS in solution tend to appear larger compared to the method of powder X-ray diffraction. The latter method determines the crystallite size (crystalline domain size) in the dried particle form while DLS gives the hydrodynamic size consisting of particles and any molecules attached at the surface like metabolites and solvent molecules (~nanoparticle and stabilizers complex). DLS raw data generally did not meet the quality criteria of the instrument, potentially due to the presence of large and

![Fig. 4 - DLS size distribution (nm) of Ag–Pa, Ag–Pa[EMIm][Tos], Pd–Pa and Pd–Pa[EMIm][Tos] nanofluids.](image-url)
sedimenting particles. The polydispersity makes cumulative analysis difficult. Indeed, the DLS data generally showed more than one peak. Domingos and coworkers found that some particle aggregation was nearly always observed when titanium and zinc oxides are considered, and thus diameters were expected to vary in the order TEM < AFM < Fluorescence Correlation Spectroscopy ≈ Flow Field Flow Fractionation < DLS [58]. Fig. 4 is the result of a significant overlap in electron and hole wave functions that can be considered as a very weak perturbation in bulk material.

Noble metals in general, exhibit unique optical properties, due to the surface plasmon resonance (SPR) [59]. For nanocrystals, the enhanced overlap of the electron and the hole wavefunctions in the spatially confined structure increases the excitonic binding energy. Thereby, making observation of the excitonic peak possible, even at room temperature. The UV absorption spectrum can also provide a qualitative indication of the size distribution. For example, a sharp excitonic peak in the absorption spectra in the case of small nanocrystals (see Fig. 5) is indeed indicative of the narrow size distribution of the nanocrystals in the sample [60].

The absorption spectra of the synthesized silver nanoparticles used for DLS experiment was recorded against water in order to study the stability of the nanoparticles, principally the aggregation. Fig. 5 presents UV–Vis spectra of the reaction media after 4 h of reaction used in DLS experiments. A SPR absorbance band has been obtained at 421 nm for Pd–Pa[EMIm][Tos]. In contrast, a high kinetic rate of formation is generally a source of particle instability, as observed for palladium nanoparticles with plant extract (Pd–Pa) with a plasmon resonance at 400 nm. These particles are much more able to aggregate. This observation is confirmed by the DLS distribution curves showing very high mean particle sizes in solution. The plasmon resonance values obtained for palladium are consistent with the literature [61]. UV–Vis spectra of the silver nanoparticles (Ag–Pa and Ag–Pa[EMIm][Tos]) have the form of a plateau with a plasmon resonance between 400 and 450 nm. No disclosure of silver plasmon resonance bands (to isolate them from extract secondary metabolites bands), by redissolution in water followed by centrifugation, has been performed in the present work [62]. Based on UV–Vis, these nanoparticles may have comparable sizes and the observation is confirmed by DLS experiment. Both plant extract and extract with ionic liquid are able to reduce the silver cations. Capping by plant extract and ionic liquid gives much more stable silver and palladium nanoparticles and retards aggregation. The emergence of new quantum size effects in objects on the nanoscale is a key feature that differentiates nanoscale objects from the bulk. The results of the experiments describe here illustrate the idea that the optical spectra are very sensitive to shape, size, and nature of the nanostructure. The presence of defects on the surface of nanoparticles would provide an active morphology for electron and charge transport thereby yielding improved characteristics for applications [63,64].

4. Conclusion

A one-pot reduction of silver or palladium ions occurs with avocado plant extract alone. Addition of an ionic liquid to this system also yields stable silver and palladium nanoparticles. A size contraction is observed when avocado plant extract and 1-ethyl-3-methylimidazolium tosylate is used. Parameters like strain, intrinsic stresses, 4-spacing and dislocation densities have been evaluated. The crystallinity of the nanoparticles is confirmed by powder X-ray diffraction. When DLS technique is used, larger sizes particles are obtained in the liquid dispersion. Ultraviolet-visible characterization with plasmon resonance completed the analysis and proved that the synthesis of nanoparticles using plant extract and ILs can tailor material properties generated by QC effects to specific applications.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

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Appendix A. Supplementary data

REFERENCES


