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EFFECT OF TEMPERATURE AND NaCl CONCENTRATION ON SYNTHESIS OF SILVER NANOPARTICLES PREPARED IN AQUEOUS MEDIUM

Nurul Akma Reduan, Suriati Ghazali and Saidatul Shima Jamari
Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, Pahang, Malaysia
E-Mail: suriati@ump.edu.my

ABSTRACT

Unique optical and physical behaviour of nanoparticles compared to corresponding bulk materials has gain considerably interest and the research in synthesizing and application of nanoparticles has expanded rapidly over a last decade. This present study reported on the well-dispersity synthesis of nano-size material via chemical reduction of silver nitrate ($AgNO_3$) by sodium borohydride ($NaBH_4$) in an aqueous medium. In this study, there are two parameters that were manipulated which are temperatures; varied from 25 °C until 90 °C and concentration of sodium chloride (NaCl) that was varied from 0.0mM to 30.0 mM respectively. The UV-Vis analysis of silver nanoparticles shows maximum peak were determined at the range of 404nm- 410 nm which is the characteristic of Ag particles. Meanwhile, the morphology of as-synthesized silver nanoparticles (AgNPs) that investigated by using Field Emission Scanning Electron Microscopy (FESEM) reveals a spherical particles size with the size range of 20 nm-160 nm. Analysis of AgNPs diameter by using Image J reveal that the smallest nano-size AgNPs is at 3.0 mM NaCl and at temperature 45°C which is ~50 nm.

Keywords: silver nanoparticles, temperature, sodium chloride, silver nitrate, concentration.

INTRODUCTION

The huge potential of silver nanoparticles had been a domain subject in nanotechnology which attract researcher to further investigate the physico-chemical properties of silver nanoparticles (AgNPs) (Majumder *et al.* 2014). The physico-chemical properties of silver nanoparticles are widely useful in optical, electrical, biomedical, catalysis and magnetic due to the high surface area to volume ratio of the AgNPs colloids compared with the conventional or bulky form (Majumder *et al.* 2014), (El-Kheshen and El-Rab, 2012). In general, smaller size of AgNPs leads to the increasing in functionality and selectivity. These unique properties of the AgNPs were strongly depending on size and shape which are the most challenging part during the synthesizing process. In the synthesis process, the size of the AgNPs is much related to the controlling the nucleation and the growth of the AgNPs at the atomic level (Tao *et al.* 2008). Moreover, concentration of substance such as reducing, protective and stabilizer agent, reaction time and environmental condition allows control over the nucleation and growth process, providing effective means to tune the size, and often also the shape of AgNPs (Khan *et al.* 2012), (Rivero *et al.* 2013).

In order to obtain the nano-size range, the chemists, engineers and physicists were develop three pathways synthesizing which is a chemical, physical and biological method and also varying the parameter involved on this production (Zielińska *et al.* 2009), (Iravani *et al.* 2014). Among these methods, chemical reduction is most widely used in synthesizing nanoparticles due to the simple and applicable in lab scale production.

Thus, this study was carried out in order to get spherical shape, uniform in size and mono-disperse AgNPs via chemical reduction method by using sodium borohydrate (NaBH4) as reducing agent in an aqueous medium. In spite of aggressive on synthesizing of AgNPs, however the challenge in synthetically controlling the size, shape and reproducibility of monodisperse AgNPs has achieved limited success and needs to be explored considering a high demand of AgNPs in various field of applications (Akinwunmi *et al.* 2014). As an example, the application of nanoparticle as a catalyst in a reaction process is dependent on the size particles itself which affected the catalyst activity (Takami *et al.* 1996). According to Zhang *et al.* (2011), chloride ions can acts as a stabilizer against aggregation of particles which could sufficiently retard the particle growth. Thus, the present work has been aimed to obtain mono-dispersed and shape controlling by manipulated temperature and NaCl concentration. This parameter that had been varies during the synthesis reaction as it was found as crucial parameters in the tailoring size and morphology of AgNPs.

MATERIALS AND METHODS

Materials

Silver nitrates (AgNO3), sodium borohydride (NaBH4), cetyltrimethylammonium bromide (CTAB), sodium chloride (NaCl) were purchase from Sigma Aldrich. All the chemicals are 99.9% pure and used without further purification.

Methods

In the preparation of AgNPs, silver nitrate (AgNO3) was used as a precursor while sodium borohydride (NaBH4) and cetyltrimethylammonium bromide (CTAB) were used as a reducing agent and surfactant, respectively. In this study, the effects of the

NaCl concentration and reaction temperature on the properties of AgNPs were observed. As a detail, 80 ml of AgNO3 was first heated to various temperatures (25 °C, 45 °C, 60 °C, 75 °C, and 90 °C) and was then added (with vigorously stirring, 1000 rpm) into 20 ml of a NaBH4, CTAB, and NaCl solution (0.0mM, 3.0mM to 30.0mM), that was pre-heated to 60 °C. The mixture then was stirred for 20 minutes. After that, the heating was stopped and the solution was cooled at room temperature with continuous stirring. The as-synthesized AgNPs colloids were then washed before characterized by X-Ray Diffraction (XRD), FESEM, and UV-Vis.

CHARACTERIZATION OF SAMPLE

X-Ray diffraction (XRD)

One drop of washed AgNPs was then let to dry on the glass slide (1cm x 1cm). Next, sample was analyzed under XRD at scan range 30 °C to 80 °C with Cu/30 kV/15 Ma for detecting AgNPs pattern.

UV-Vis

2 ml of unwashed AgNPs was mixed with 2 ml of deionized water was poured into the UV-Vis cuvette. After that, the UV-Vis Hitachi 1800 had been setup at wavelength of 300-800 nm.

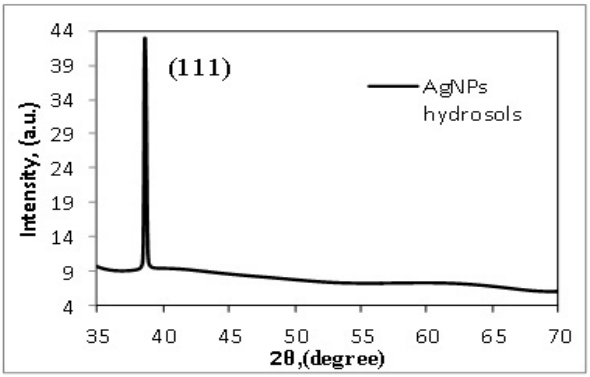
Field emission scanning electron microscopy (FESEM)

One drop washed as-synthesized AgNPs placed and dried on the copper stud. The morphology analysis was done at 20 k and 30 k magnifications.

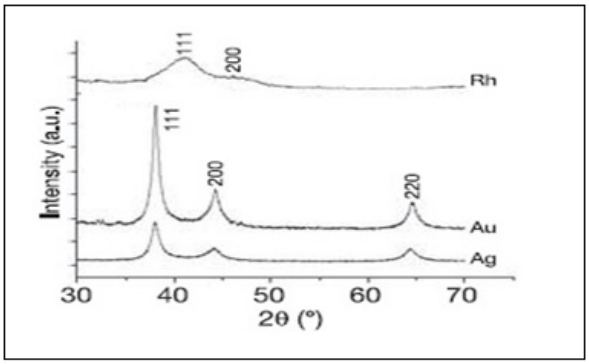
RESULTS AND DISCUSSIONS

Effect of NaCl concentration

Figure-1 show the representative of XRD pattern of as-synthesized AgNPs obtained in this study. From Figure-1, it can be seen that the XRD patterns show a diffraction peak at 2θ = 38.60° which is corresponding to (111) miller indices of face centered cubic structure of silver nanoparticles. The existence of this peak confirmed the presence of silver nanoparticles. In addition, according to the Wang *et al.* (2005), the XRD diffraction angle and the standard diffraction angle of Ag particles (JCPDS 4-783) as depicted in Figure-2 indicates the as-synthesized AgNPs have face centred cubic (FCC) which is corresponds to the (111) planes index.



(a)



(b)

Figure-1. (a) XRD patterns of as-synthesized AgNPs XRD diffraction angle and (b) the standard diffraction angle of Ag specimen from JCPDS 4-783 file.

In this study, the reduction of silver nitrate by $NaBH_4$ is shown in Equation 1:

$$AgNO_3 + NaBH_4 \rightarrow Ag + H_2 + B_2H_6 + NaNO_3 \quad (1)$$

The formations of silver nanoparticles during the synthesis process for different concentrations of NaCl were further confirmed by UV-Vis in Figure-2. According to Mie theory (Kreibig and Vollmer, 1995), the resonance conditions could described the size and shape of the nanoparticles obtained in which the single SPR bands exhibit spherical nanoparticles while multiple SPR bands is results from various nanoparticles shapes. As depicted in Figure-2, the addition of NaCl resulted on blue shift as the wavelength at maximum peak was shifted from 407 nm to 404 nm with the increasing NaCl concentration from 0.0 mM to 3.0 mM. However, the addition of NaCl from 3.0 mM to 30.0 mM somehow resulted on the red shift as the wavelength at the maximum peak was changed from 404 nm to 410 nm. This red shift might be due to the excess Cl^- ions presence during reaction that makes the nuclei of spherical particles growth rapidly into larger size. Despite of the larger size of the AgNPs at 30.0 mM, this concentration of Cl^- however shows the highest absorption peak which implies that the highest yield of the AgNPs. As the SPR absorption peak indicates the yield of products

during the reaction process, it can be stated that the higher absorption peak, the higher in yield of productions (Link and El-Sayed, 2000). This observation is in accordance to the previous work by Bae *et al.* (2002) that the addition of Cl^- ions greatly enhanced the efficiency of reduction process and tailoring the smaller size of the AgNPs. Therefore, in this study, the highest absorption value corresponding to sample that prepared at 30.0 mm NaCl implies that at this concentration of NaCl, the highest yield of as-synthesized AgNPs were produced during the synthesis reaction. This experiment shows that, the reaction rate of synthesizing silver nanoparticles can be increased with the increasing of NaCl concentration.

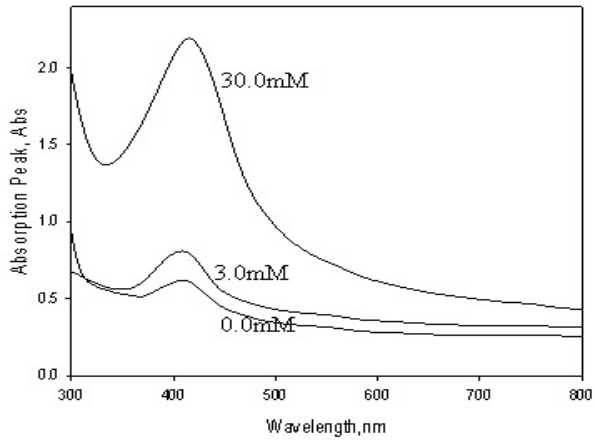


Figure-2. UV-Vis spectra at different NaCl concentration.

Figure-3 shows the morphology and particles distribution of the as-synthesized AgNPs examined by using FESEM. The as-synthesized AgNPs without the presence of NaCl (Figure-3 (a)) was slightly agglomerated with each other compared to that prepared at 3.0 mM (Figure-3(b)). From this observation, it can be suggested that the presence of the Cl^- in the solution was able to reduce the agglomeration of the particles. The similar observation obtained by the previous work by (Mulfinger *et al.* 2007) which is claimed that the presence of low concentration NaCl or potassium iodide (KI) could shield the particles produced from clump together forming aggregates with each other particles. However, at 30.0 mM of NaCl (Figure-3(c)), most of the as-synthesized AgNPs tends to agglomerate with each other compared to the other samples. It was believed that the growth kinetic of AgNPs was affected at high concentration of chloride ions and hence formed an aggregate of AgNPs as the efficiency of CTAB is reduce and cannot be fully attached to the AgNPs.

The particles distributions of the as-synthesized AgNPs then were determined by using Image J software. The 100 particles were randomly measured on its diameter and then were summarized in Figure-4. Based on Figure-4(a), (b) and (c), the histogram shows that the particles diameter measurement is consistent and having similar trend with analysis UV-vis. The average diameter length of as-synthesized AgNPs at 0.0 mM, 3.0 mM and 30.0 mM of NaCl concentration are 63 nm, 49 nm and 91 nm, respectively. Compare to the sample prepared at 0.0 mM of NaCl, the introduction of Cl^- at 3.0 mM results in the smaller particle size whilst at 30.0 mM results in larger diameter size of the AgNPs.

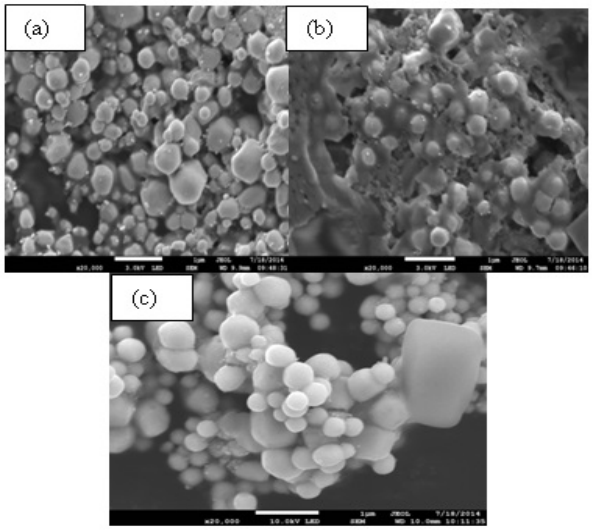
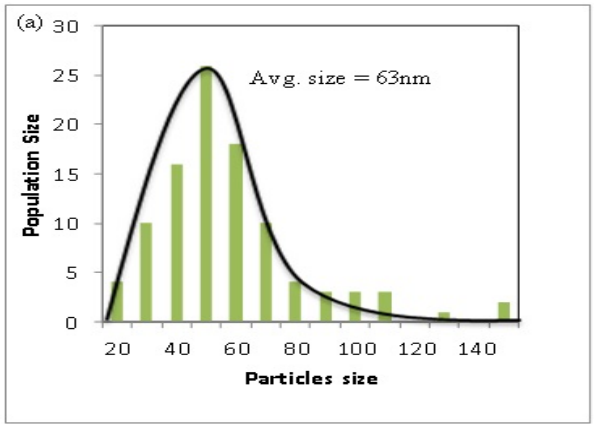
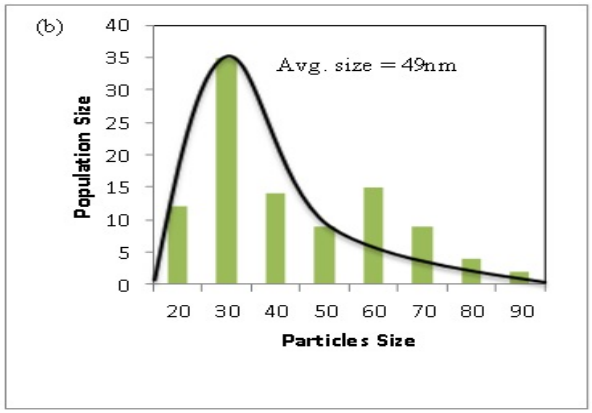


Figure-3. FESEM image of different NaCl concentration at (a) 0.0 mM (b) 3.0 mM and (c) 30.0 mM.





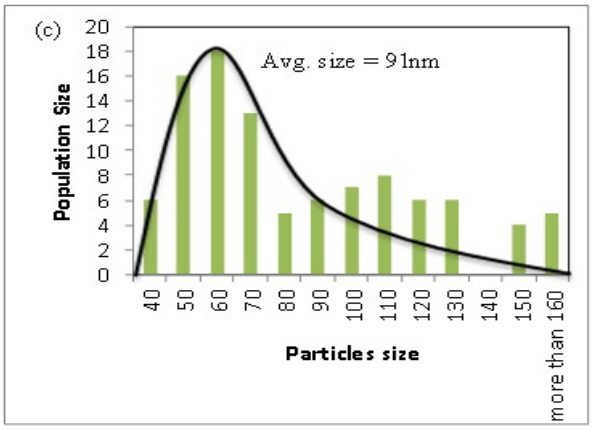


Figure-4. Particles distribution of as-synthesized AgNPs at different NaCl concentration (a) 0.0 mm (b) 3.0 mm and (c) 30.0 mm.

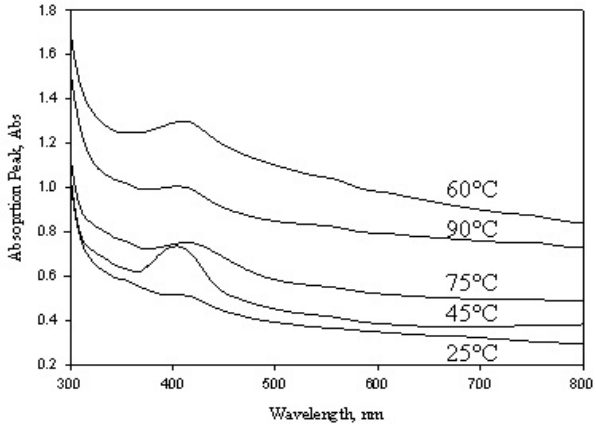


Figure-5. UV-Vis absorption of AgNPs at various temperatures.

Effect of reaction temperature

In synthesis process, the temperature used during the synthesis reaction is one of the crucial factors that influence the properties of the as-synthesized nanoparticles. According to Siva (Siva Kumar *et al.* 2011) the size of the nanoparticles is depending on the formation of nuclei during the reducing process. Fast or slow reaction rate during the synthesis process definitely could result in the different sizes and morphology of the nanoparticles. In order to investigate the effect of reaction temperature towards the morphology of the AgNPs, the synthesis temperature was varied from 25 °C, 45 °C, 60 °C, 75 °C, and 90 °C, respectively. Meanwhile, the concentration of the other raw material such as $AgNO_3$ NaCl, $NaBH_4$, and CTAB were kept constant. Figure-5 shows the UV-Vis spectrum recorded at different reaction temperatures. Figure-5 shows the SPR bands spectra were formed at 407 nm (25 °C), 404 nm (45 °C), 410 nm (75 °C) and 404 nm (90 °C). The curve-peak band around 404 nm- 410 nm is characteristic of AgNPs in solution. The position of the band shifted in two different shifts which is blue-shift and red-shift. Blue-shifted occurs at temperature from 25 °C to 45 °C and 75 °C to 90 °C respectively. Meanwhile, red-shifted occurs only at temperature 45 °C to 60 °C and for the temperature changes from 60 °C to 75 °C there is no changes on shift were observed. The blue-shift indicates the AgNPs particles size is decreased and red-shift is increasing in particles size. Besides that, as the temperature increased from 45 °C to 60 °C, the absorption peak shows an increase in intensity, which implies the increase in formation of Ag^+ in solution. Further increment in reaction temperature at above 60 °C somehow shows a decrease in intensity of absorption peak. Moreover, as the optical property which is including the size of AgNPs are related to the excitation of plasmon resonance (SPR) at specific wavelength, therefore it can be stated that localization of SPR bands at different wavelength reflects the different size of as-synthesize AgNPs obtained at different reaction temperature.

Figure-6 and Figure-7 show the FESEM images and the particles distribution of AgNPs at increasing reaction temperature, respectively. As illustrated on Figure 6, the as-synthesize AgNPs prepared at different reaction temperature shows a uniform in size and spherical shape. Figure-6 (a), (b), (c) and (d) with the reaction temperature of 45 °C, 60 °C, 75 °C, and 90 °C, respectively shows the average particles size that is 50 nm, 57 nm, 57 nm and 52 nm. The size of the as-synthesize AgNPs shows an increasing trend with the increasing reaction temperature (45 °C to 60 °C) while decreasing trend with further increase of reaction temperature (75 °C- 90 °C). According to Siva (Siva Kumar *et al.* 2011), the increasing in temperature condition will speed up the reaction rate causes the silver ions are reduce faster thus leaving less possibility for particles size at higher temperature. Even though reaction temperature at 90°C show more promising in obtaining a smaller particles size, however, the value of absorption peak somehow lower than sample at 60 °C. Therefore, it can be suggested that, at this particular system, 60 °C is the optimum reaction temperature to synthesize AgNPs.

CONCLUSIONS

As-synthesized AgNPs in aqueous medium composed several particles sizes which is from 20 nm up to more than 160 nm by stimulate on two significant factors which is temperature condition and different concentration of NaCl. The data obtained in the UV-Vis, XRD, FESEM and Image J analysis is parallel to each other on the effect of the particles size that had been investigated. It can be concluded that the concentration of chloride ions and the reaction condition could greatly influence the nucleation and growth of AgNPs, hence affect the particle distribution of AgNPs.

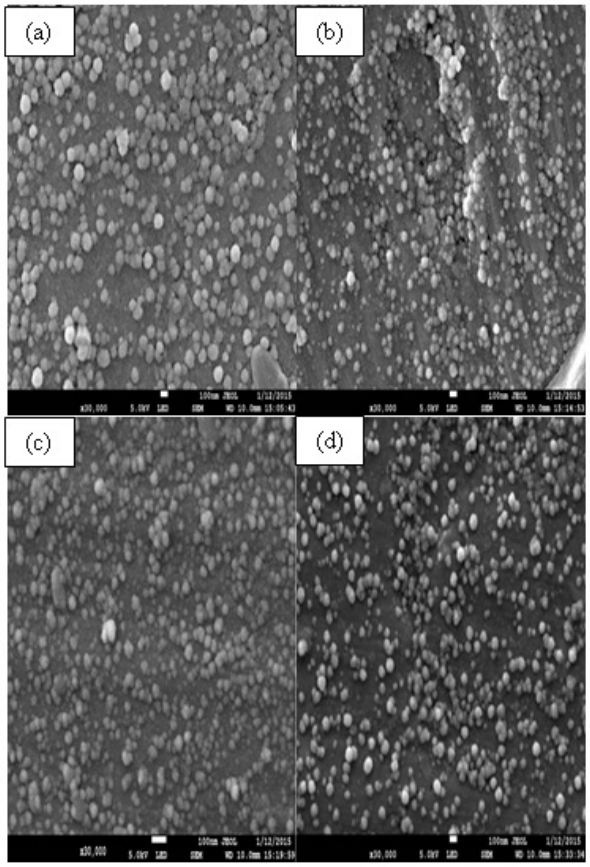
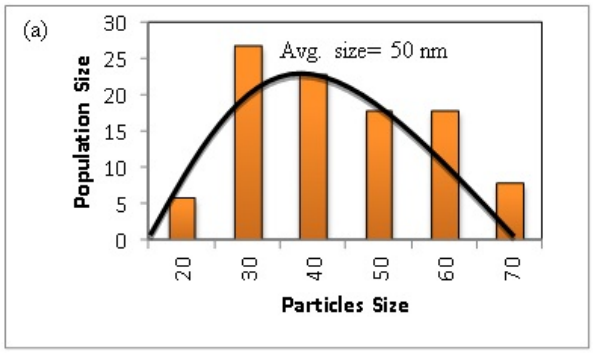
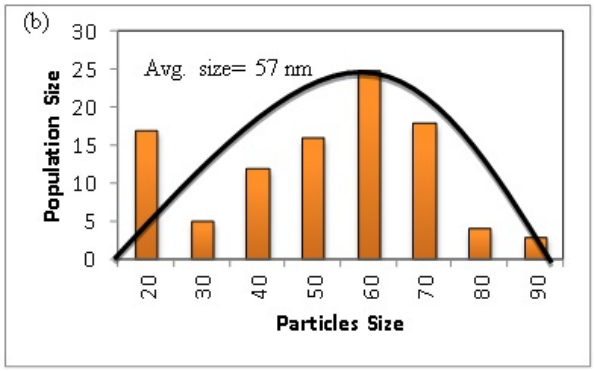
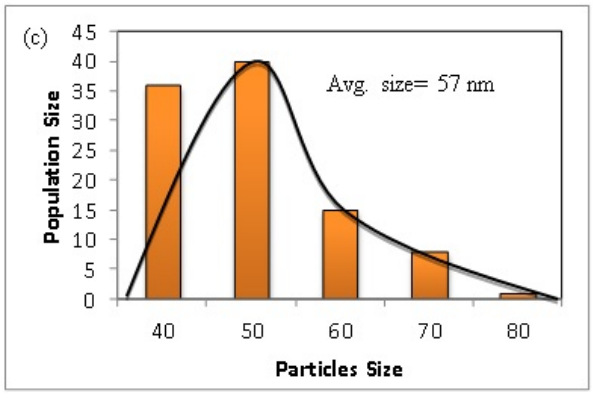


Figure-6. FESEM Morphology of AgNPs at temperature (a) 45 °C (b) 60 °C (c) 75 °C (d) 90 °C.







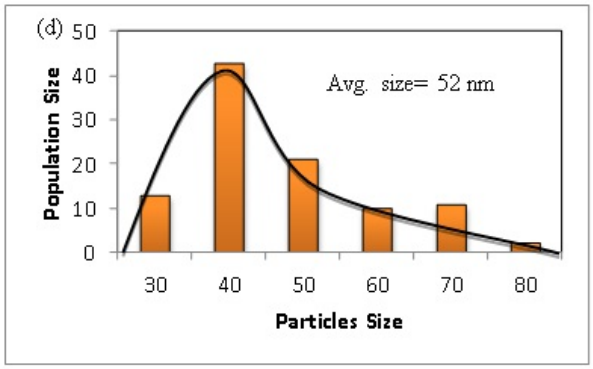


Figure-7. Histogram of population size on AgNPs at temperature (a) 45 °C (b) 60 °C (c) 75 °C and (d) 90 °C.

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