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Synthesis and characterization of silver-copper core-shell nanoparticles using polyol method for antimicrobial agent

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Abstract. Silver and copper nanoparticles are well-known as the good antimicrobial agent. The nano-size of particles influences in enhancing the antimicrobial activity. This paper discusses the effect of molarity on the microstructure and morphology of silver-copper core-shell nanoparticles prepared by a polyol method. In this study, silver-copper nanoparticles are synthesized through the green approach of polyol method using ethylene glycol (EG) as green solvent and reductant, and polyoxyethylene-(80)-sorbitan monooleate (Tween 80) as a nontoxic stabilizer. The phase and morphology of silver-copper nanoparticles are characterized by X-ray diffraction (XRD) and Field emission scanning electron microscope (FESEM) and Transmission electron microscope (TEM). The results XRD confirm the pure crystalline of silver and copper nanoparticles with face-centered cubic (FCC) structure. FESEM and TEM analysis confirm the existence of Ag and Cu nanoparticles in core-shell shape.

1. Introduction

Combination of two different metals nanoparticles were known as bimetallic nanoparticles. In recent years the unique properties of bimetallic nanoparticles had lead to a new applications and the possibility of making new products, for example catalyst, sensors, and substrates for surfaceenchanced Raman scattering [1]. This area of nanoscience was gaining mounting attention in the field of catalysis also due to the synergistic effects [2].

Bimetallic nanoparticles have four types of mixing patterns which are core-shell nanoparticles, subcluster nanoparticles, mixed (alloy) nanoparticles and multi-shell nanoparticles [3]. Bimetallic nanoparticles, either as alloys or as core-shell structures, exhibited unique electronic, optical and catalytic properties compares to pure metallic nanoparticles [4,5]. Silver-copper bimetallic nanoparticles have attracted much attention because of its high electron conductivity and its use for preparation of lead-free solder alloy [6]. There has been wide-ranging research into the synthesis of metal particles such silver and copper by the polyol method [7,8]. Over the past decade the polyol process has been used to prepare elemental Co, Ni, Cu, Ag, Au, Pt, Pd, Cd, and Fe and also bimetallic alloys of Co-Ni, Ag-Pd, Au-Pt, Ag-Cu and Fe-Pt [9]. The polyol involved in the reaction acted as solvent, stabilizer and reducing agent which limits particles growth and avoid agglomeration [10].

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Ag-Cu nanoparticles were emerging as another important material in this new era due to its great variety applications in electronic devices, dental and biological. Both Ag and Cu nanoparticles have great potential in variety applications due to their outstanding electrical and thermal properties resulting great demand in the market. Ag nanoparticles have received great attention because of their excellent broad-spectrum antimicrobial activity, while silver nanoparticles have proved to be most effective as it has good antimicrobial agent against bacteria, viruses and other eukaryotic microorganism[1,11]. According to Carroll et al., the metal nanoparticles such as Ag and Cu were found to have antibacterial activity. The bactericidal influence of metal nanoparticles was attributed by their high surface to volume ratio and small size, which allow them to interact closely with microbial membranes and it was not just due to the release of metal ions in solutions. The antibacterial properties of the metal nanoparticles have the properties of microbe inactivation and heavy metal removal. The nano antimicrobial metals can be used effectively by coating them on the sufaces that require antimicrobial functions in water treatment filters and medical devices [12].

However, Ag nanoparticles in huge ratio retarded the antimicrobials life time. Also, Cu nanoparticles were often easily get oxidize and unstable in atmosphere [13]. Bimetallic Ag-Cu nanoparticles were reported to successfully prevent Cu nanoparticles from oxidation and thus enhance the antibacterial activities. Moreover, bimetallic Ag and Cu nanoparticles were also shown higher surface reactivity and therefore being used to improve interfacial and catalytic process [14].

In this study, the Ag-Cu nanoparticle were synthesized through the polyol method using ethylene glycol (EG) as solvent and reductant, and polyoxyethylene-(80)-sorbitan monooleate (Tween 80) as a nontoxic stabilizer. The core-shell nanopaticles was studied because of the less widely researched regarding this type of pattern. The crystal lattice information of the system as well as morphology and size of crystallite were investigated using XRD, while FESEM and TEM analysis were conducted to study the morphology and physical size and shape of the Ag-Cu nanoparticles.

2. Experimental Procedure

2.1. Materials and Synthesis Procedure

Silver nitrate (AgNO₃) and copper nitrate (Cu(NO₃)₂.3H₂O) were purchased from Sigma Aldrich Malaysia and were used as precursors. Ethylene glycol (EG, Sigma Aldrich) was used as solvent and reducing agent. Tween 80 (Sigma Aldrich) was used as stabilizer. Acetone (Merck Malaysia) was used as a solvent. All chemical were used as purchased without any further purification.

Silver-copper nanoparticles were prepared by using polyol method involving reaction of 0.8M silver nitrate (AgNO₃) and 0.2M copper nitrate (Cu(NO₃)₂.3H₂O). The preparation of Ag-Cu core-shell nanoparticles has been carried out in two steps. The first step was the synthesis of Cu inner core, and the second step was the preparation of Ag outer shell. At first, 0.2M copper nitrate trihydrate (Cu(NO₃)₂.3H₂O) was dissolved in 100mL of EG solution where EG was used both as a solvent and reducing agent. Then, Tween 80 was added to the solution as a stabilizer that prevents the mixture from oxidation or agglomeration. The mixture was heated and vigorously stirring for one hour with temperature of 140°C. 0.8M silver nitrate (AgNO₃) was added and the mixture was continuously heated for another 4 hours. Then, the solution was cooled to room temperature. The solution in order to separate the precipitated and the surfactant. The precipitate silver-copper nanoparticles were then rinsed with deionized water and were dried thoroughly at room temperature. The experiment were repeated for other samples by varying the molarity of the two precursors of AgNO₃ and Cu(NO₃)₂.3H₂O of 7:3M and 6:4M, respectively.

2.2. Characterization

The phase and crystal structure of Ag-Cu nanoparticles were characterized using X-Ray diffraction (XRD, Rigaku Ultima IV), with Cu K α radiation (λ = 1.54056 nm). Scans of 20 were taken in the range between 30°-80° at scanning rate of 1.2′/min. The mean crystallite size of the catalyst was estimated using the Williamson-Hall method by referring to the most prominent peak (111). The surface morphology of Ag-Cu nanoparticles was characterized using a DSM 982 Gemini Supra 40 VP FESEM. Particle morphology and size distribution were determined by TEM. Specimens were prepared by placing a drop of sample onto a 200-mesh holey carbon copper grid. The excess liquid was removed from grids with tissue paper and air-dried before examined with a TEM (JEOL 200CX).

3. Results and Discussion

3.1. XRD analysis

The phase and crystal structure of the synthesized nanoparticles are studied using XRD analysis. XRD patterns of Ag-Cu nanoparticles with different molarity ratios of 6:4M, 7:3M and 8:2M at the temperature of 140°C and reaction time 4 hours are shown in Figure 1.



Figure 1. XRD patterns of Ag-Cu nanoparticles with different molarity Ag-Cu at (a) 8:2M, (b) 7:3M and (c) 6:4M.

As can be seen in the pattern, at molarity ratios of 7:3M and 8:2M, the main characteristic diffraction peaks for silver are observed at $2\theta = 38.141$, 44.34, 64.499 and 77.40 with correspond to crystallographic planes of (111), (200), (220) and (311), respectively for 7:3M and at $2\theta = 38.06$ (111), 44.278 (200), 64.4 (220) and 77.36 (311) for 8:2M. There are three main characteristic diffraction peaks for copper observed for 7:3M which are at $2\theta = 43.338$ (111), 50.54 (200), and 74.137 (220). While, for 8:2M sample, the main characteristic diffraction peaks for copper are observed at $2\theta = 43.279$ (111), 50.356 (200) and 74.157 (220). The results are similar to the results as reported by Min Huang et al., where all seven characteristic diffraction peaks of silver and copper appeared. The Miller indices are specified above the peaks and in the bracket. All the peaks are well indexed to face centered cubic (fcc) phase of crystalline Ag (JCPDS card no.4-783) and fcc phase of

crystalline Cu (JCPDS card no. 4-836). The silver nanoparticles contain high atomic density facet as (111) in all samples that are known to be highly reactive [6].

At molarity ratio of 6:4M, four main characteristic diffraction peaks are observed at $2\theta = 38.121^{\circ}$, 44.301°, 64.46°, and 77.419°, they are assigned to the (111), (200), (220) and (311) crystallographic planes of fcc silver crystals. However, no characteristic diffraction peaks for copper are observed. This is predicted due to the low concentration of copper in the precipitated as the effect of the insufficient reaction. As the concentration of copper are invisible in the pattern. Moreover, the invisible of copper peaks is also contributed by the peaks intensity of silver is more strength than copper due to the different crystal size. Hence, the low concentration of copper causes the difficulty in observing the copper peaks in the pattern.

From the results it can be concluded that, both Ag and Cu phases are clearly identified on the samples at the molarity ratios of 8:2M and 7:3M. Accordingly, there is no obvious XRD peak arising from possible alloy, mixture or aggregates phases of Ag and Cu are observed. However, only silver peaks are visible in the 6:4M sample due to incomplete reaction. Therefore, it is safe to say that the Cu-Ag core-shell nanoparticles are possible to be synthesized using polyol method with the molarity ratios Ag to Cu between 8:2M and 7:3M.

XRD results also found that the crystallite size of the synthesized Ag-Cu core-shell nanoparticles, calculated using Scherrer's equation for the most intense peak in the pattern, is distributed within the range of 27-32 nm for silver and 24-56 nm for copper, as shown in Table 1.

2-Theta	Intensity (%)	FWHM	Crystal size (nm)	Element	(h k l)		
Sample 6:4 M							
38.121	100	0.279	32	Ag	(111)		
44.301	40.9	0.371	24	Ag	(200)		
64.46	25.3	0.372	26	Ag	(220)		
77.419	27	0.418	25	Ag	(311)		
Sample 7:3 M							
38.141	100	0.319	27	Ag	(111)		
43.338	3.3	0.181	56	Cu	(111)		
44.34	34.4	0.376	23	Ag	(200)		
50.54	3.3	0.413	21	Cu	(200)		
64.499	25.7	0.416	23	Ag	(220)		
74.137	1.6	0.372	27	Cu	(220)		
77.401	27.7	0.471	22	Ag	(311)		
Sample 8:2 M							
38.06	100	0.294	30	Ag	(111)		
43.279	5.4	0.286	31	Cu	(111)		
44.278	38.2	0.374	23	Ag	(200)		
50.356	1.7	0.303	30	Cu	(200)		
64.4	26	0.4	24	Ag	(220)		
74.157	1.1	0.346	30	Cu	(220)		
77.36	28.6	0.435	24	Ag	(311)		

Table 1. XRD parameters of Ag-Cu core-shell nanoparticles

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3.2. FESEM and EDS analysis

The FESEM micrographs are taken to support the XRD result and also to study the surface morphology of the Ag-Cu core-shell nanoparticles. Figure 2 shows the enlarged image SEM micrograph of the Ag-Cu nanoparticles at different molarity. It can be seen in Figs. 2(a) and (b) that the surface morphology and roughness of both samples are quite similar. The particles are uniformly distributed in nanoscale size with a narrow size distribution. Almost all particles are found in spherical shape.

However, the shape and size distribution in 6:4 M micrograph cannot be clearly identified. As can be seen in Fig. 2(c), the surface is rough and agglomerates. It is also difficult to identify the individual particles. It is due to the incomplete reaction of reduction of reactants to produce Cu particles. As described above, the high concentration of Cu in solutions made the reduction reaction become incomplete. The findings are good agreement with XRD results.



(a) 8:2 M



(b) 7:3 M



(c) 6:4 M

Figure 2. FESEM images of Ag-Cu nanoparticles prepared at 140°C for varied molarity

The samples were also examined using EDS analysis to determine the actual elemental concentration. The result is listed in Table 2.

Table 2. EDS data of Ag-Cu core-snell hanoparticles						
Sample	Element	Weight	Atomic			
		(%)	(%)			
8:2 M	Cu L	18.25	27.48			
	Ag L	81.75	72.52			
7:3 M	Cu L	13.83	21.42			
	Ag L	86.17	78.58			
6:4 M	Cu L	12.47	19.47			
	Ag L	87.53	80.53			

3.3. TEM analysis

TEM analysis is conducted to investigate the physical size, size distribution and morphology of the synthesized nanoparticles. Figure 3 shows the images of Ag-Cu core-shell nanoparticles at different molarity. It can be seen that at the concentrations of Ag^+ of 0.6 M and 0.7 M, the synthesized nanoparticles exhibit perfect core-shell structures. Interestingly, it is also found that few of Cu encapsulates more than one Ag nanoparticles in one shell. However, as soon as the Ag⁺ concentration increase to 0.8M, the nanoparticles tend to aggregate into chainlike or branchlike structure.



(a) 8:2 M

(b) 7:3 M



(c) 6:4 M Figure 3. TEM images of Ag-Cu nanoparticles prepared at 140°C for varied molarity

4. Conclusions

Silver-copper core-shell nanoparticles were successfully synthesized by a polyol method with wide range of size and various shapes. The synthesized nanoparticles were pure crystalline with face centered cubic structure with the crystallite size distributed in the range of 27 nm to 32 nm for Ag and 24 nm to 56 nm for Cu. Finally, FESEM and TEM techniques confirmed the presence of Ag and Cu nanoparticles.

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