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The effect of carbon nanotubes as a support on morphology and size of silver nanoparticles

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Abstract

In this study, direct precipitation technique was used to synthesize Ag nanoparticles supported by carbon nanotubes. After distinguishing the best situation in the synthesis of Ag nanoparticles, carbon nanotubes as the support were used to control the Ag nanoparticle size. The prepared carbon nanotubes and Ag nanoparticles were investigated by using X-ray diffraction, transmission electron microscopy, and scanning electron microscopy. The results showed that carbon nanotubes can play an important role in controlling the morphology and size of the obtained powders, and the size of Ag nanoparticles synthesized on the carbon nanotubes is smaller.

Keywords: Carbon nanotubes, Morphology, Silver nanoparticles, Ag/CNT Nanocomposite powder, Size

Background

In recent years, the synthesis, characterization, and functionalism of nanoparticles have attracted vast and persistent interest because of their unique properties and significant potential application. The properties of the nanoparticles closely depend on the crystal size, morphology, aspect ratio, and even crystalline density [1,2]. On the other hand, the specific activity of nanoparticles is strongly related to their size and distribution. Highly distributed nanoparticles with small size and narrow size distribution are ideal for high physical and chemical activity, owing to their large surface-to-volume ratio [2,3]. Today, researchers focus on Ag nanoparticles for their catalytic [4], antibacterial [5], and optical [6] properties. To further enhance these properties, the size, morphology, and the structure of nanoparticles must be controlled. The size and morphology of Ag nanoparticles are affected by different parameters [7,8]. Therefore, the number of studies on different parameters is increased. Meanwhile, the exceptional electrical, chemical, and mechanical characters [9,10] made carbon nanotubes (CNTs) widely used in the construction of chemical sensors and biosensors [11,12], especially in the field of supporting materials [13]. The high surface area of CNTs made it possible to load nanoparticles to enhance their properties [8,11-13]. Fabricating nanomaterial-CNT composites is thereby desirable since it combines both the advantages of CNTs and nanomaterials which may be helpful in widening the applications. Much effort has been made to acquire these hybrid nanomaterials [13]. Many researchers are trying to improve and modify CNT walls to achieve high dispersion of metal nanoparticles on the CNT surface [8,10,11,13,14]. However, there are three problems regarding the application of CNTs as a support for the nucleation of nanoparticles. First, nanotubes are destroyed when they are coated. Second, there are nonhomogenous distributions of nanoparticles on the surface of nanotubes. Third, there is no sufficient connection between the carbon atoms on the surface of nanotubes and the atoms of nanoparticles [15]. In order to obtain the physical properties of nanoparticles, there should be sufficient connections between nanoparticles and nanotubes. Nanotubes are neutral in their chemical properties and have strong molecules; thus, the connection between nanoparticles and nanotubes is hard [16]. Therefore, modifying the CNT surface with desired functional groups by chemical treatments is a good strategy to get well-dispersed catalyst nanoparticles on CNTs. Usually, the chemical oxidation processes functionalize the surface of CNTs. It leads to the formation of some active groups like -OH, -C=O, -C-O, and COOH. They can act as the location for the formation of the ions of nanoparticles [17,18]. It is shown that some chemical processes damage the

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structure of nanotubes and increase their use as the support for nucleation of nanoparticles. Therefore, researchers try to find an appropriate procedure for synthesizing and activating the surface of CNTs.

In this paper, the appropriate procedure is used to fabricate Ag-CNT nanocomposites by attaching Ag nanoparticles on to the surface of CNTs and to study the CNTs' effect on the size and morphology of Ag nanoparticles. More importantly, the content of Ag nanoparticles supported on CNTs can be well controlled by simply tuning the relative ratio of Ag to CNTs.

The resulting CNTs and Ag/CNT nanocomposite were characterized by analyzing the scanned electron microscopy images (SEM; Philips, MAG 15 kV, 30000X, SE detector microscope, FEI Co., Hillsboro, OR, USA) and Fourier transform infrared (FT-IR) spectra (Shimadzu 8400 s, Shimadzu Corporation, Kyoto, Japan). The X-ray diffraction pattern (XRD; Cu(Kα) spectra, λ = 1.54 Å, GBC Scientific Equipment, Braeside, Australia) was used to determine the crystalline structure and average size of Ag nanoparticles and the composition of the Ag/CNT nanocomposite powders.

Methods

The preparation of Ag nanoparticles

In this research, $AgNO_3$ and NaOH (99%) were used as the initial materials to synthesize Ag nanoparticles. The solutions were prepared with some concentrations in distilled water at 25°C. The NaOH solution is stirred on a hot plate, and the $AgNO_3$ solution is dropped on it with a rate of 0.5 mL/min. Black sediment was made after adding more $AgNO_3$ solution. The solution was filtrated and washed with distilled water and ethanol. Finally, the prepared sediment was dried at 120°C on a hot plate for 2 h followed by grinding the product into a fine powder using a mortar until a uniform powder was achieved. For the last treatment, to achieve Ag nanoparticles, the samples were calcinated at 400°C for 2 h.

Synthesis and functionalization of CNTs

To synthesize CNTs, initially 500 mg of Co_3O_4/MgO catalyst powder (prepared by impregnation methods) was placed in the center of a furnace, while argon carrier gas with a flow of 100 sccm has been established in the quartz reaction tube. The synthesis of CNTs was carried out by pyrolyzing the hydrocarbon feed gas flow (in this study acetylene) with a flow rate of 15 sccm for 30 min at 750°C. After synthesizing CNTs, the reactor was turned off and cooled down to room temperature under Ar gas atmosphere. To remove carbon contamination, thermal oxidation was carried out for 1 h at 480°C. It was then refluxed in distilled water for 10 min in the ultrasonic bath, stirred in a mixed solution of HCl (3 M) and HNO_3 (3 M) for 3 h, and finally washed in distillate

Table 1 The concentration of the first solutions for preparing the precursor

| Sample number	Ag(NO_3)·$6H_2O$ (mol/L)	NaOH (mol/L)	Molar ratio Ag (NO_3)·$6H_2O$/NaOH
101	0.25	0.25	1:1
102	0.25	0.50	1:2
103	0.25	0.75	1:3
104	0.25	1	1:4

water and dried at 120°C. Washing CNTs in nitric acid leads to the formation of functional groups (such as -OH, -C=O, -C-O and COOH) on the surface of carbon nanotubes. These functional groups can act as locations for the nucleation and formation of Ag nanoparticles.

### Synthesis of Ag nanoparticles and Ag/CNTs nanocomposites

At first, 0.2 g of CNTs was dissolved in 50 mL NaOH. Then, 2.1 g of $AgNO_3$ was dissolved in 50 mL of distilled water. The solution of NaOH and CNTs was stirred on a hot plate, and the $AgNO_3$ solution was added into the first solution. After saturating the solution, it finally become neutral (pH = 7.2). Then, the sample was dried at 120°C for 1 h, and then it was calcinated at 400°C for 2 h. Finally, Ag nanoparticles were formed on the surface of CNTs.

Results and discussion

Table 1 shows the samples with four different molar ratios. The X-ray of Ag nanoparticles is presented in Figure 1. All peaks concern Ag nanoparticles. It is shown that if the concentration of the initial materials is high, the width of the peak decreases, and if the concentration of NaOH is high, Ag nanoparticles become larger. In
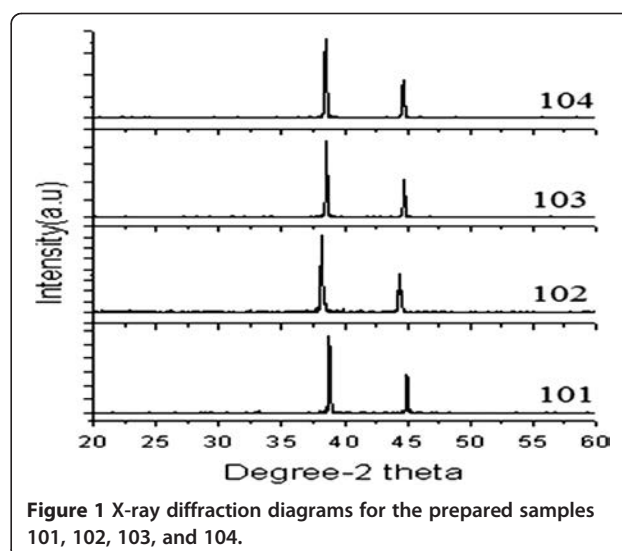
Figure 1 X-ray diffraction diagrams for the prepared samples 101, 102, 103, and 104.
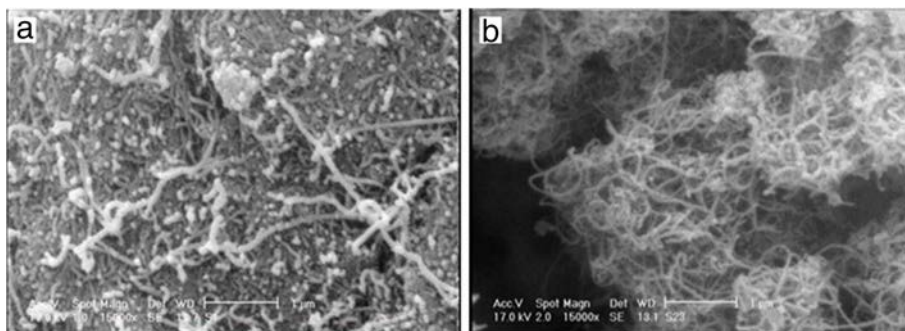
Figure 2 SEM images of CNTs (a) before and (b) after purification process.

addition, if the concentration of NaOH is low, the size of Ag nanoparticles becomes smaller.

The XRD patterns of all samples of Ag powder obtained at different ratios of concentration are shown in Figure 1. The average size of nanoparticles (D) was obtained by measuring the width of diffraction lines and applying the Debye-Scherrer formula [19]: $D = k\lambda/(\beta \cos \theta)$, where λ is the wavelength of Cu(Kα) radiations (1.54 Å), β is the full width at half maximum (FWHM) of the peak corresponding to the plane, θ is the angle obtained from the 2θ value corresponding to maximum intensity peak in the XRD pattern, and k, which is 0.9, is the constant and its content is related to the shape of nanoparticles. The average size of Ag nanoparticles for the samples 101, 102, 103, and 104, is 48, 50, 56, and 57 nm, respectively. Results show that 48 nm is the lowest amount that we can produce using chemical precipitation method on the surface of CNTs. This method cannot be used to produce smaller particles. The result shows that if the concentration of NaOH doubled from 0.25 to 0.5 M, the sizes of nanoparticles increase by 2 nm. That is,

making the first particles is faster than adding ions to the last ones, and then their sizes increase.

Figure 2 shows CNTs before and after purification process. Figure 2a shows carbon nanotubes between the high volumes in purified carbon nanotubes. After purification process (Figure 2b), impure materials are destroyed in high temperature and the number of carbon nanotubes increases.

In order to study the process, transmission electron microscopy (TEM) images of CNTs were prepared (Figure 3).There was not any carbonic pollution on the surface of nanotubes. The appearance of a metallic catalyst between nanotubes shows suitable purification of this synthesis. All of the nanotubes have empty structures that are good for making carbonic fibers. The determination of the diameters of some nanotubes shows that the average diameter of nanotubes is 20 nm.

FT-IR spectra are applied to detect the appearance of functional group types on the surface of carbon nanotubes [18]. Figure 4 shows the FT-IR spectra of CNTs before and after purification in HNO_3 solution. FT-IR spectra show that the absorbance peaks in 1,211, 1,462, and 1,514 cm^{-1} are related to O-C=O, C-O, and C=O banding (Figure 4b). Therefore, purification of CNTs in the HNO_3 solution caused the formation of functional groups like C=O, C-O, and O-C=O [14,18-20]. On the other hand, the height of the peak shows the high density of oxygen groups on the surface of nanotubes; it plays an important role in determining the number of nanoparticles that match with the surface. Figure 5 shows the formation of functional groups on the surface of carbon nanotubes.

Due to the formation of an -OH group on Ag [21,22] and the C-O, C=O, and O-C=O groups on functionalized CNTs, as mentioned above, Ag/CNT composites are formed naturally by some physicochemical actions such as Vander Waals force (physical), H bonding, and other bindings. For example, the -OH group on Ag may react with the -OH and -COOH groups on CNTs when removing H_2O in wet fresh composites. Thus, the bonds
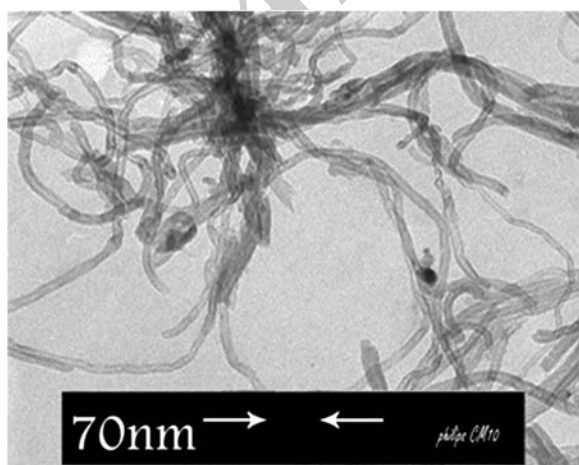
Figure 3 TEM image of carbon nanotubes after purification process.
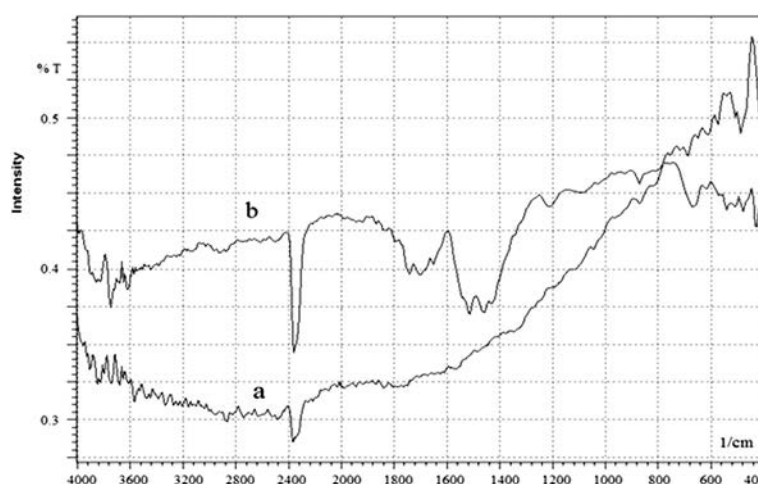
Figure 4 FT-IR spectra of CNTs (a) before and (b) after purification process in HNO$_3$ (5 M) solution.

C-O-Ag and O=C-O-Ag might be formed by the dehydration reaction occurring among the functional groups on the interface of two materials. However, the high specific surface area of CNTs was also the basis for the formation of uniformly dispersed composites.

In order to study the morphology of synthesized Ag nanoparticles on the surface of CNTs, we prepared SEM images from Ag nanoparticles and Ag/CNT nanocomposite powder (Figure 6). In this image (Figure 6a), we can see the high volume of Ag nanoparticles that aggregate together.

Figure 6b shows the typical SEM image of silver nanoparticle-decorated CNTs. Therefore, the prepared Ag nanoparticles can easily be assembled onto the surface of the functionalized CNTs by using a direct precipitation technique.

As a result, we herein conjecture that for the Ag/CNT nanocomposite powder under precipitation conditions, the redox reaction between Ag ions will take place on the surface of CNTs. Ag ions were attached on CNTs due to the coordination reaction between Ag ions and polar oxygenated functional groups in the precipitation process. Consequently, Ag nucleated heterogeneously via

precipitation deposition because CNTs have prevented Ag from growing into aggregated nanoparticles.

To have a precise investigation, TEM analysis was used to observe the Ag and Ag/CNT nanopowders. Figure 7 shows TEM images of Ag nanoparticles, synthesized with and without the presence of carbon nanotubes during the process. According to Figure 7a, in the absence of carbon nanotubes, silver nanoparticles are stuck together in a longer cluster form with diverse morphology. The dimension of the synthesized nanoparticles is diverse, and their average size is 10 to 30 nm. The presence of carbon nanotubes in the solution during the synthesis process causes the synthesis of nanoparticles with dimensions ranging between 4 to 15 nm averaging at about 6 nm on the surface of the nanotubes (Figure 7b). Also, the presence of nanotubes prevents the nanoparticles from forming larger clusters. The separation between nanoparticles can improve the physical and chemical properties of nanoparticles. Thus, CNTs are an appropriate infrastructure to control the dimensions of nanoparticles during their synthesis, using chemical solution process. In conclusion, the nanotubes can cause a great decrease in the dimensions of silver nanoparticles, help control their morphology, and prevent them from agglomerating. This conclusion is caused by performing an appropriate experimental process in the purification of the nanotubes and functionalization of their surface with functional groups, which was used in this research.

In order to study the structure of Ag nanoparticles, we prepared XRD patterns from Ag and Ag/CNT powders in the range of (2θ = 20° to 60°) (Figure 8). The small peak (2θ = 26.5°) corresponds to the interlayer space of MWCNTs, and the other peaks (2θ = 20° to 60°) are related to the structure of Ag nanoparticles. The intense
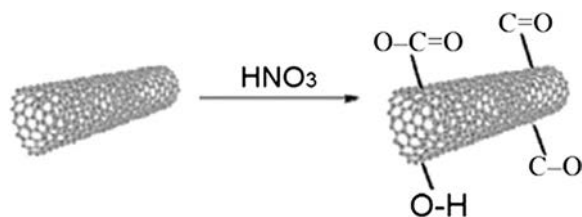
Figure 5 The schematic of functional groups on the surface of CNTs.
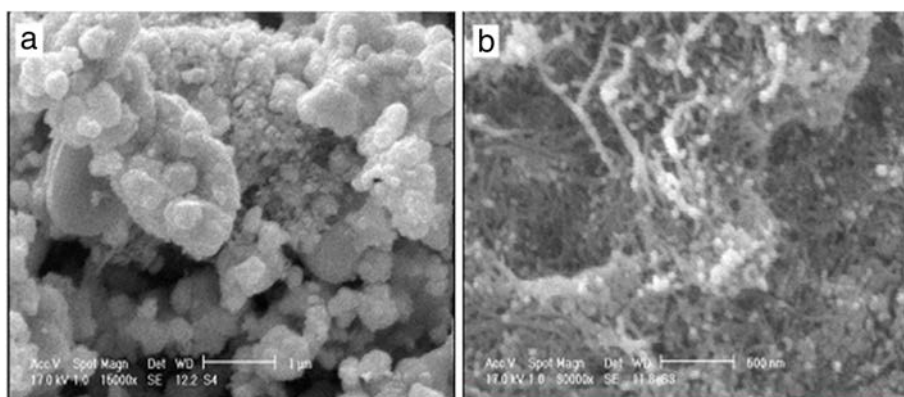
Figure 6 SEM images of Ag nanoparticles and Ag/CNT nanocomposite powder. (**a**) Ag nanoparticles without applying CNTs. (**b**) The synthesis of Ag nanoparticles on the surface of CNTs and preparation of Ag/CNT nanopowder.

peaks were observed at 37.5° and 45° and indicate the crystalline nature of the synthesized Ag nanoparticles with spherical structure. Ag nanoparticles are composed of pure crystalline Ag since no other impurity peaks are observed in the XRD patterns.

Comparing the peaks of X-ray diffraction for two samples of Ag and Ag/CNTs, it is observable that the peak of Ag nanoparticles is sharper than the peak of Ag/CNTs. The FWHM related to Ag/CNT powders is more than that related to Ag nanoparticles. Then, the determination of the average size of Ag nanoparticles shows that the size of nanoparticles on the surface of CNTs is smaller than that of Ag nanoparticles. The sizes of Ag nanoparticles on the surface of CNTs decrease from 48 to 35 nm since CNTs have the high area and prepare active places for nucleation of Ag nanoparticles.

The results indicate that the presence of carbon nanotubes in the solution not only can change the morphology of Ag nanoparticles, but also is able to decrease the average size of the nanoparticles. Then, the surface of CNTs is a suitable place for nucleation of nanoparticles. We believe that the nucleation and growth processes of Ag nanoparticles were significantly influenced by the introduction of CNTs, which have altered the size and shape of Ag aggregated nanoparticles. Consequently, Ag nucleated heterogeneously via precipitation deposition because CNTs have prevented Ag from growing into aggregated nanoparticles [23,24]. The dense and entangled Ag/CNT hybrid nanostructures form a three-dimensional network structure.

Conclusion

In this research, Ag/CNT powder was synthesized on the surface of carbon nanotubes in a chemical process with $AgNO_3$ salt. The results show that the surface of nanotubes was decorated with Ag nanoparticles. The coating of CNTs with functional groups, such as O-H, C-O, -C=O, and O=C can bond with the -OH group on the surface of Ag nanoparticles. It causes Ag nanoparticles to connect with the surface of CNTs. The results show that nanotubes are the suitable support for synthesizing and controlling the sizes and morphology of aggregated Ag nanoparticles, too. When we use CNT, the average size of Ag nanoparticles is decreased from 48 to 35 nm.
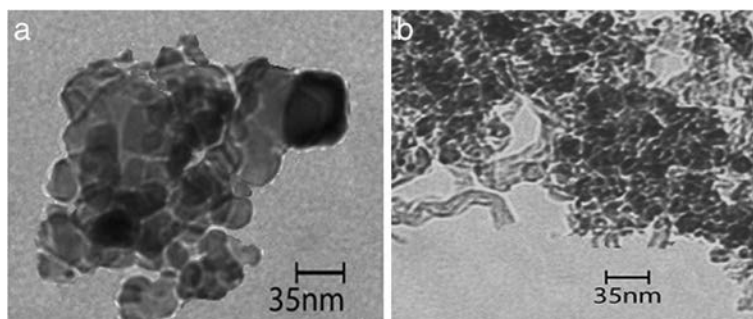
Figure 7 TEM images of Ag nanoparticles. (**a**) Synthesized Ag nanoparticles. (**b**) The synthesis of Ag nanoparticles on the surface of CNTs and preparation of Ag/CNT nanopowder.
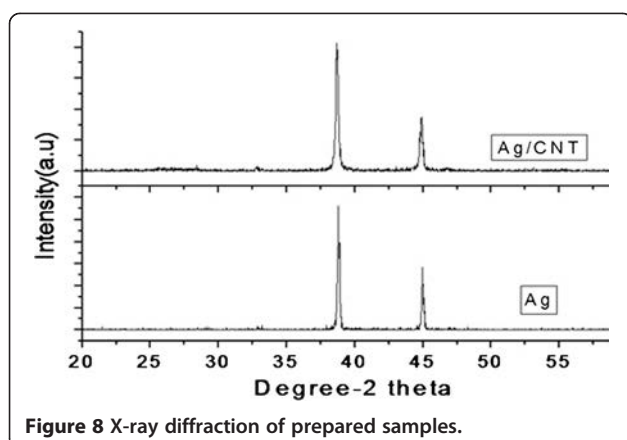
Figure 8 X-ray diffraction of prepared samples.

Therefore, the nanotubes have the highest area cause; the sizes of nanoparticles are decreased to 13 nm. The comparison of SEM images of Ag nanoparticles shows that the presence of CNTs causes Ag nanoparticles not to be aggregated together to form larger particles.

Competing interests

The authors declare that they have no competing interest.

Authors' contributions

Both authors provided the same contributions in this article. Both authors read and approved the final manuscript.

Acknowledgment

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