Synthesis and Characterization of Silver/Clay Nanocomposites by Chemical Reduction Method

[1]Mansor Bin Ahmad, [1]Kamyar Shameli, [2]Majid Darroudi,
[1]Wan Md Zin Wan Yunus and [1]Nor Azowa Ibrahim
[1]Department of Chemistry, Faculty of Science, University Putra Malaysia,
43400 UPM Serdang, Selangor, Malaysia
[2]Advanced Materials and Nanotechnology Laboratory, Institute of Advanced Technology,
University Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

Abstract: Problem statement: Silver Nanoparticles (Ag-NPs) have been synthesized by using chemical reduction method into the interlayer space of a Montmorillonite (MMT) as a solid support which is used to antibacterial application and polymer nanocomposites for fabrication of medical devices. **Approach:** $AgNO_3$ and $NaBH_4$ were used as a silver precursor and reducing agent, respectively. The properties of Ag/MMT nanocomposites were studied as a function of the $AgNO_3$ concentration. The crystalline structure, d-spacing of interlayer of MMT, the size distributions and surface plasmon resonance of synthesized Ag-NPs were characterized using Powder X-Ray Diffraction (PXRD), Transmission Electron Microscopy (TEM) and UV-vis spectroscopy. **Results:** The results obtained from UV-vis spectroscopy of synthesized Ag-NPs showed that the intensity of the maximum wavelength of the plasmon peaks were increased with the increasing in the $AgNO_3$ concentration. The obtained information from UV-vis spectra of Ag-NPs was in an excellent agreement with the obtained microstructures studies performed by Transmission Electron Microscopy (TEM) and their size distributions. The prepared Ag/MMT nanocomposites are very stable over a long period of time in aqueous solution. **Conclusion:** The synthesized Ag/MMT nanocomposites are very stable in aqueous solution over a long period of time without any sign of precipitation. Silver nanoparticles in MMT suspension could be suitable to use antibacterial applications, since MMT is viewed as ecologically and environmentally inert material and used for biological application such as cosmetics and pharmaceutical usage.

Key words: nanocomposites, silver nanoparticles, montmorillonite, powder X-ray diffraction

INTRODUCTION

Nanoparticles are important materials for fundamental studies and diversified technical applications because of their size dependent properties or highly active performance due to the large surface areas, but when pure nanoparticles are used alone, they present some common problems, e.g., agglomeration between nanoparticles[1]. To overcome agglomeration, preparation of nanoparticles based on clay compounds, in which nanoparticles are supported within the interlamellar spaces of clay and/or on its external surfaces, is one of the most effective solutions[2-4].

Recently, the preparations of metal nanoparticles were discussed in a great number of publications due to their unique physical and chemical properties which lead to many potential applications[5]. There are many preparation methods for the synthesis of metal nanoparticles such as the photo reduction or chemical reduction in aqueous medium with various polymer surfactants[6,7], chemical reduction in soft matrixes e.g., reverse micelles[8] or in solid matrices e.g., mesoporous silicate[9] and chemical vapor deposition[10]. Some of metal nanoparticles have also been synthesized in the two-dimensional interlayer space of Montmorillonite (MMT)[11-13]. MMT as lamellar clay has intercalation, swelling and ion exchange properties. Its interlayer space has been used for the synthesis of nanoparticles materials and biomaterials, as support for anchoring transition-metal complex catalysts and as adsorbents for cationic ions[14]. Silver Nanoparticles (Ag-NPs) are widely used as photosensitive components[15], catalysts[16-20], photo-catalysts[21-24] and in surface enhanced Raman spectroscopy[25-27] as well as in

Corresponding Author: Mansor Bin Ahmad, Department of Chemistry, Faculty of Science, University Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia Tel.: (603)89466044 Fax: (603)89466043

chemical analysis. In this research, we have synthesized Ag-NPs into interlayer of MMT in aqueous solutions by using $NaBH_4$ as a reducing agent at room temperature.

MATERIALS AND METHODS

Materials: All reagents were of analytical grades and were used as received without further purification. $AgNO_3$ (99.98%), used as silver precursor, was supplied from Merck, Germany. MMT, used as a solid support for Ag-NPs, was purchased from Kunipa-F, Japan. $NaBH_4$ (98.5%, Sigma-Aldrich, USA) was used as a reducing agent. All aqueous solutions were prepared with double distilled water (DD-water).

Synthesis of Ag/MMT nanocomposites: For the synthesis of Ag/MMT nanocomposites, the silver contents of the samples were 0.5 (S1), 1.0 (S2), 1.5 (S3), 2.0 (S4) and 5.0 g (S5) Ag/100 g MMT. Constant amounts of MMT were suspended in different volumes of 1×10^{-3} M $AgNO_3$ solution and stirred for 24 h. Freshly prepared $NaBH_4$ (4×10^{-2} M) solution was then added to the suspensions under continuous stirring to reach a constant $AgNO_3/NaBH_4$ molar ratio (1:4). After the addition of the reducing agent stirring was continued for another one hour. The suspensions were finally centrifuged, washed with DD-water twice and dried under vacuum overnight. All experiments were conducted at ambient temperature.

Characterization methods and instrumentation: The prepared Ag/MMT nanocomposites were characterized by using Ultraviolet-Visible (UV-vis) spectroscopy, Transmission Electron Microscopy (TEM) and Powder X-Ray Diffraction (PXRD). The UV-vis spectra were recorded over the range of 300-700 nm by a Lambda 25-Perkin Elmer UV-vis spectrophotometer. TEM observations were carried out on a Hitachi H-7100 electron microscopy and the particle size distributions were determined using the UTHSCSA Image Tool software, Version 3.00 program. The structures of produced Ag/MMT nanocomposites were carried out on a Philips PXRD (X'pert, Cu K_α radiation). The change in interlamellar spacing of MMT and Ag/MMT nanocomposite were also studied by using PXRD in the small angle range of $2°<2\theta<12°$. The interlamellar space was calculated from the PXRD peak positions using Bragg's equation. A wavelength equal to 0.15418 nm was used for these measurements. The PXRD patterns were recorded at a scan speed of $2°$ min^{-1}. After reactions the samples were centrifuged by using high speed centrifuge machine (Avanti J25, Beckman).

RESULTS

The formation of Ag-NPs was followed by measuring the surface plasmon resonance (SPR) of the MMT suspensions containing Ag-NPs at the wavelength ranged from 300-700 nm (Fig. 1). TEM images and their size distributions of Ag-NPs show the mean diameter of the nanoparticles ranged from about 4-9 nm (Fig. 2). The comparison between PXRD patterns of MMT and prepared Ag/MMT nanocomposite under chemical reduction route in the small angle range of 2θ ($2°<2\theta<12°$) indicate the formation of the intercalated structure (Fig. 3). The PXRD patterns were also employed to determine the crystalline structures of the synthesized Ag-NPs (Fig. 4). The stability of synthesized MMT suspensions containing Ag-NPs was found to be stable over a long period of time (>2 months) without any sign of precipitation.
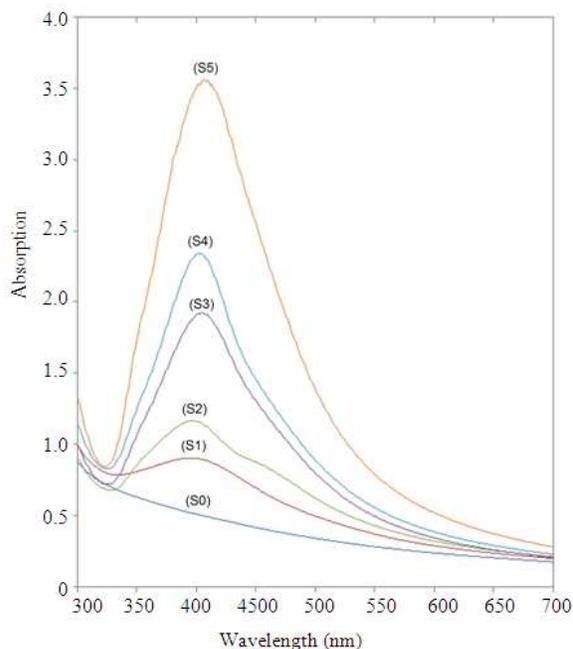

Fig. 1: UV-vis absorption spectra of Ag/MMT suspension for different $AgNO_3$ concentrations; (S1) 0.5%, (S2) 1.0%, (S3) 1.5%, (S4) 2.0%, (S5) 5.0% and (S0) $AgNO_3$/MMT suspension in the absence of $NaBH_4$
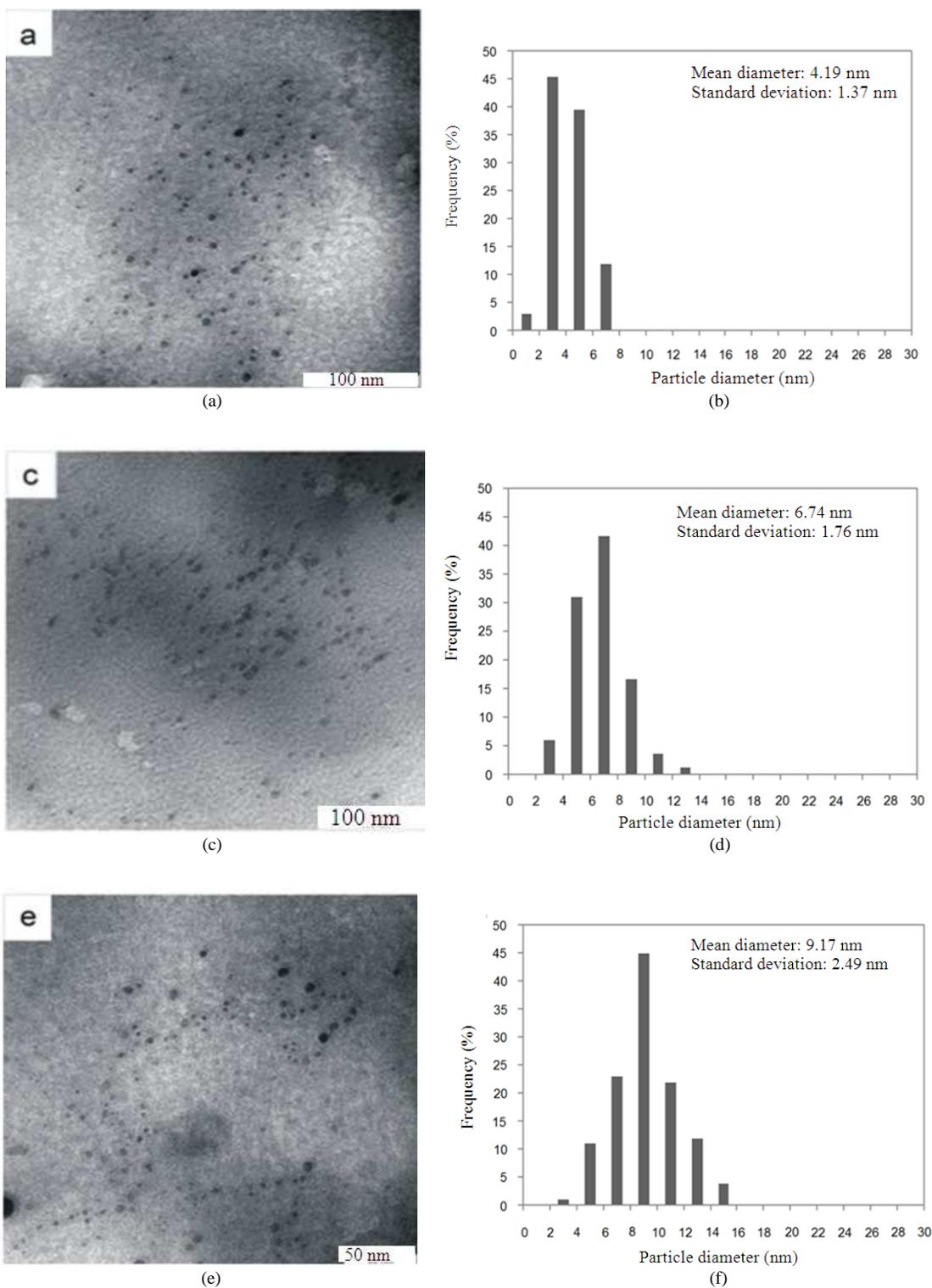
Fig. 2: TEM images and their corresponding particle size distributions of Ag/MMT nanocomposites at different AgNO$_3$ concentrations [1.0% (a-b), 2.0% (c-d) and 5.0% (e-f)]
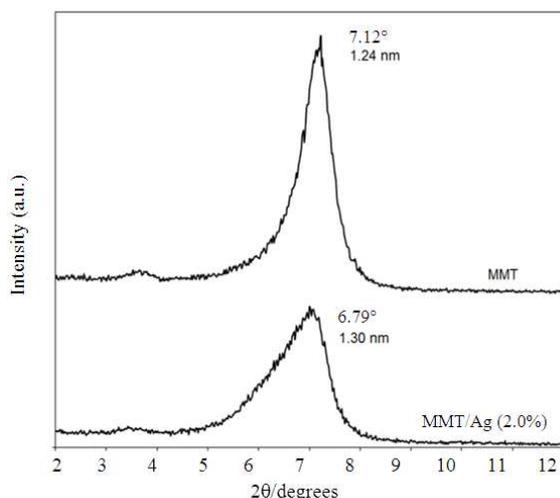
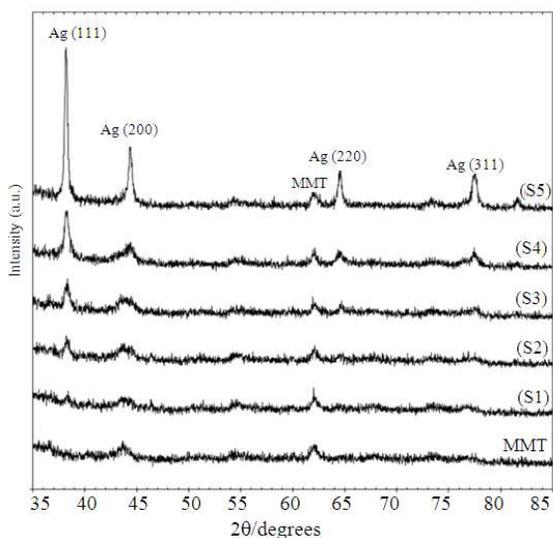Fig. 3: PXRD patterns of MMT and Ag/MMT nanocomposite for determination of d-spacing (d_L)

Fig. 4: PXRD patterns of MMT and Ag-NPs into MMT as a substrate at different $AgNO_3$ concentrations

DISCUSSION

The color of $AgNO_3$/MMT suspensions through reduction process by $NaBH_4$ changed from colorless to light brown, then to brown and finally to green, indicating the formation Ag-NPs in MMT suspension.

The characteristic silver SPR bands were detected around 400 nm (Fig. 1). These absorption bands were assumed to correspond to the Ag-NPs smaller than 10 nm[6,7]. While there is no characteristic UV-vis absorption of Ag-NPs before addition of $NaBH_4$ (Fig. 1f), growth of the plasmon peak at 396 nm indicates the formation of Ag-NPs in S1 (Fig. 1a). Gradual increase in $AgNO_3$ concentration, from S1-S4, increases the corresponding peak intensities (Fig. 1a-d) in a range of wavelengths from 396-402 nm. In S5, the absorption peak due to SPR of Ag was slightly red-shifted to higher wavelength (404 nm) indicating the increase in the size of Ag-NPs[28]. TEM images and their size distributions of Ag-NPs also confirmed this phenomenon (Fig. 2).

As shown in Fig. 3 the original d-spacing (d_L) of MMT, 1.24 nm is increased to 1.30 nm at smaller 2θ angles ($2\theta = 6.79°$ for S4) by silver intercalation. This d_L value is a direct proof of the fact that, in the path of ion exchange, Ag^+ ions are bound not only on the external surfaces and edges of MMT but also in the interlamellar space. Metallic nanoparticles formed at the latter location are to cause of the increase in basal spacing. In these samples the intensities of the reflections are significantly lower whereas their half-widths are larger than those of undoped clay minerals: the highly ordered parallel lamellar structure of the mineral is disrupted by particle formation[29].

All the nanocomposites have similar diffraction profiles and the PXRD peaks at 2θ of 38.28°, 44.38°, 64.52° and 77.61° (Fig. 4) can be attributed to the (111), (200), (220) and (311) crystallographic planes of face-centered cubic (fcc) silver crystals, respectively[30]. For all samples, the main crystalline phase was silver and no obvious other phases as impurities were found in the PXRD patterns. The PXRD peak broadenings of Ag-NPs are mostly because of existing of nano-sized particles in these nanocomposites[31]. In addition there is a characteristic peak in about $2\theta = 62.1°$ that related to MMT (PXRD Ref. #00-003-0010) as a stable substrate.

CONCLUSION

Synthesis of Ag-NPs in the interlamellar space of MMT in wet chemical reduction method by using $NaBH_4$ as a reducing agent at room temperature is simply possible. The properties of Ag-NPs were studies as a function of $AgNO_3$ concentration which the molar ratio of $AgNO_3$/$NaBH_4$ was constant. When the amount of $AgNO_3$ had been increased, the particles size of Ag-NPs was gradually increased but their size distribution was narrow. The synthesized Ag/MMT nanocomposites are very stable in aqueous solution over a long period of time without any sign of precipitation.

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