



## **Comparison of Pure and Hybrid Nanoparticles using Ionic Liquid as a Capping agent**

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**Abstract :** Ionic liquids are exceptional chemical compounds that are used in many areas of modern science. Due to their highly adjustable nature and incomparable properties, ionic liquids have become key players in the areas of synthesis, catalysis, extraction, electrochemistry, analysis, biotechnology, etc. In addition to the physical and chemical properties of ionic liquids, their high biological activity has attracted considerable attention from biochemists, ecologists and medical professionals. Due to the properties mentioned above, an imidazolium ionic liquid solvent was used for the synthesis of nanostructure nanoparticles. In the present work, cubic form of pure Fe<sub>2</sub>O<sub>3</sub>, spherical nature of pure Ag (0) and hexagonal shaped hybrid Ag- Fe<sub>2</sub>O<sub>3</sub> were successfully synthesized by a simple co-precipitation, reduction and co-precipitation processes. The synthesized nanoparticles were characterized in detail by spectral studies such as IR, XRD, SEM, EDX and TEM analysis. The size and shape of the particles were performed by X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) techniques and Transmission Electron Microscope (TEM) techniques. Quality quantity and purity of the products was checked by Energy Dispersive X-Ray Analysis (EDX).

**Key words :** Iron oxide nanoparticles, Silver nanoparticles, hybrid nanoparticles, Ionic liquid, TEM analysis.

### **Introduction**

In the past few years, synthesis of iron oxide nanoparticles have been carried out because of their function to finding tumors, acts as the targeted delivery vehicle, an important component in coatings, plastics, nanowires, nanofibers, textiles, in specific alloys and acts as the catalyst in many reactions<sup>1</sup>. Silver nanoparticles have attracted a great deal of interest in recent years because of its good antibiotic property and are biocompatible nature. Therefore, many researchers have designed the properties of two particles at the same time in a single

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compound by synthesizing hybrid nanoparticles. Moreover, many researches have been focused on the preparation of composite magnetic nanoparticles. Various composite materials has been successfully synthesized and some of the obtained hybrid nanoparticles are shown here such as Magnetic Core-Shell  $\text{Fe}_3\text{O}_4/\text{Ag}$  Nanoparticles<sup>2</sup>, Ag-  $\text{Fe}_3\text{O}_4$  nanoparticles<sup>3</sup>, Ag@  $\text{Fe}_3\text{O}_4$  core-shell nanoparticle<sup>4</sup>, Ag-  $\text{Fe}_3\text{O}_4$  catalysts derived from MOFs<sup>5</sup>, Ag-ZnO nanoparticles<sup>6</sup>,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , Ag/  $\text{Fe}_3\text{O}_4$  and Ag/  $\text{Fe}_2\text{O}_3$ <sup>7</sup>, magnetic trimetallic Au-Ag- $\gamma$ -  $\text{Fe}_2\text{O}_3/\text{rGO}$  nanocomposites<sup>8</sup> and Dumbbell-Like shaped Bifunctional Au- $\text{Fe}_3\text{O}_4$  Nanoparticles<sup>9</sup>. Irregular shaped  $\text{Fe}_2\text{O}_3$  nanoparticles have been synthesized by the green synthesis method using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and plant extracts *C.rotundus*<sup>10</sup>. Likewise, Zhang et al. prepared agglomerated nanoparticles, when they prepared  $\text{Fe}_2\text{O}_3$  nanoparticles using iron pentacarbonyl and [EMIM][hCOO]- by sonochemical method<sup>11</sup>. Moreover,  $\text{Fe}_2\text{O}_3$ -Ag hybrid nanoparticles was synthesized by using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NaBH}_4$  and PVP as a stabilizing agent, dumbbell shaped nanoparticles was obtained<sup>12</sup>. Here an attempt was made to check the role of ionic liquid as a capping agent in the production of nanoparticles. For that 1,4-Bis(3-methylimidazolium-1-yl)butane chloride ionic liquid was used for the synthesis of pure and hybrid nanoparticles. Hexagonal hybrid  $\text{Fe}_2\text{O}_3$ - Ag (0) nanoparticles not previously obtained were obtained from ionic liquid application.

## Experimental

### Chemicals

AR grade 1-Methylimidazole, 1, 4-dichlorobutane, Ammonium hydroxide, Ferric chloride hexa hydrate, Tetra hydro furan (THF), Acetonitrile, Ethanol, Sodium citrate, De-ionized water, Silver nitrate, Sodium carbonate were purchased from Sigma Alrich and used without further purification. The consistency of the products was checked on TLC plates.

The ILs used in this study was synthesized according to the procedures reported in the literature<sup>13</sup>.

### Synthesis of $\text{Fe}_2\text{O}_3$ Nanoparticles:

Iron oxide nanoparticles ( $\text{Fe}_2\text{O}_3$ ) were fashioned by a simple co-precipitation process. At first, 0.03 mole of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 0.015 mole of IL were dissolved in 50 mL of de-ionized water. Keep stirring the solution for an hour. About 0.03 mole of ammonium hydroxide dissolved in 25mL of de-ionized was added to the former one by drop-wise under vigorous stirring. The stirring process was continued for another three hours at room temperature. After adjusting the pH to 8, the brown dispersion was formed, the resultant precipitate was washed with de-ionized water and ethanol several times until the solution was neutral. The obtained  $\text{Fe}_2\text{O}_3$  NPs were finally heated at 60°C for 12 hours for further characterization.

### Synthesis of Ag(0) Nanoparticles:

Ag (0) nanoparticles were prepared as same as reported in the journalism<sup>14</sup>.

### Synthesis of $\text{Fe}_2\text{O}_3$ -Ag(0) nanoparticles

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.03mole) and 0.015 mole IL were dissolved in 50 mL deionized water. The solution was stirred for uniform concentration for an hour. At the same time, 0.03mole of silver nitrate and 0.015 mole of ionic liquid dissolved in 25mL of de-ionized water was slowly added to the above stirring mixture. The solution was heated for about 40°C. 0.03 mole of sodium citrate solution dissolved in 25mL of de-ionized water was then slowly added drop wise to the reaction mixture under vigorous stirring. The addition process was conducted for 0.5 hour and the solution was continuously stirred for another 3 hours. Subsequently, 0.03 mole of Ammonium hydroxide solution (0.03mole in 25mL of deionized water) was then added drop wise to the resultant stirring mixture. After adjusting the pH at 8.0, the precipitated out of the hybrid nanoparticles was collected by centrifugation and washed three times with de-ionized water and ethanol alternately. The obtained  $\text{Fe}_2\text{O}_3$ -Ag NPs were finally heated at 50°C for 12 hours for further characterization.

## Results and Discussion

### FT-IR Study

Table 1 shows the FT-IR results of the pure and hybrid nanoparticles synthesized by 1,4-Bis(3-methylimidazolium-1-yl)butane chloride ionic liquid. Comparison of the results shows that the frequency of the  $\text{Fe}_2\text{O}_3$  of the hybrid nanoparticles differs from that of the pure  $\text{Fe}_2\text{O}_3$ , the reason for the above is due to the entry

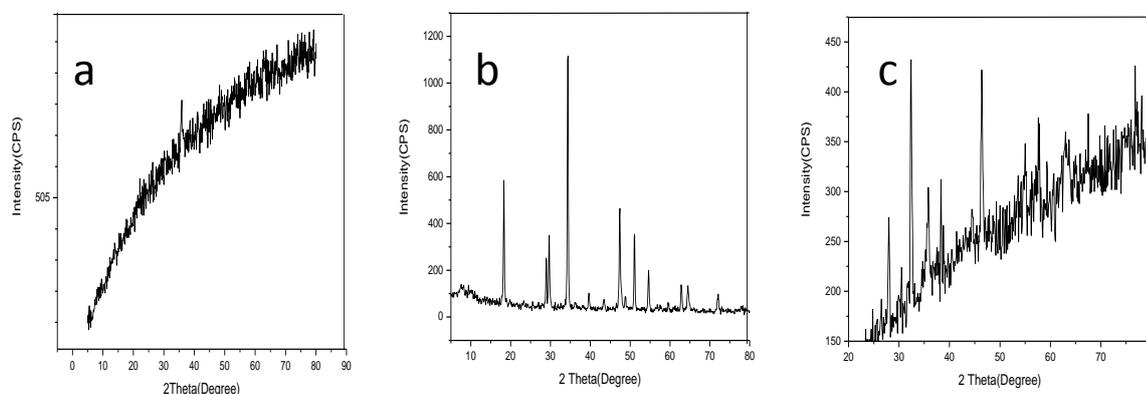
of the Ag(0) into the Fe<sub>2</sub>O<sub>3</sub>. This makes the remarkable changes to the Fe<sub>2</sub>O<sub>3</sub> frequency. The same effect can be observed in the pure Ag(0) and hybrid Fe<sub>2</sub>O<sub>3</sub>.Ag(0) frequencies also. Here the entry of Fe<sub>2</sub>O<sub>3</sub> makes a change to the Ag(0) frequency. From the FT-IR studies it is clearly indicates that introduction of foreign substance makes the remarkable changes in the frequencies of the parent compound.

**Table 1: IR spectral comparison studies of pure and hybrid nanoparticles**

Peak Assignment	Frequencies of absorption bands, cm <sup>-1</sup> of Fe <sub>2</sub> O <sub>3</sub> nanoparticle by IL	Frequencies of absorption bands, cm <sup>-1</sup> of Ag(0) nanoparticle by IL	Frequencies of absorption bands, cm <sup>-1</sup> of Fe <sub>2</sub> O <sub>3</sub> -Ag(0)nanoparticle by IL
Vibrational frequency for Fe <sub>2</sub> O <sub>3</sub> Nanoparticles	1560, 1335, 1155, 581, 523	-	1561, 1332, 1156, 616, 545
Vibrational frequency for Ag(0) Nanoparticles	-	3063, 580	3066, 544

### IL-1,4-Bis(3-methylimidazolium-1-yl)butane chloride

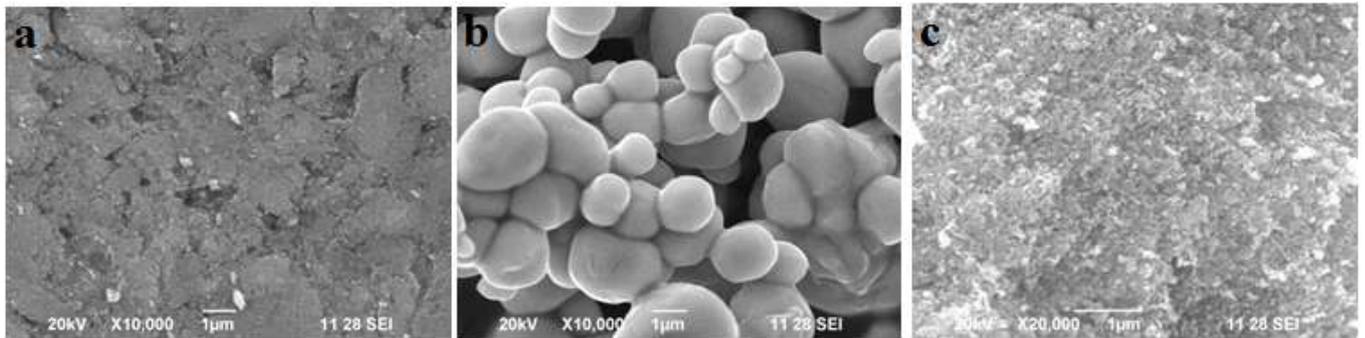
### XRD Analysis



**Figure 1: XRD pattern of (a) Pure Fe<sub>2</sub>O<sub>3</sub>; (b) Pure Ag (0); (c) Hybrid Fe<sub>2</sub>O<sub>3</sub>-Ag nanoparticle by IL**

The powder XRD model of synthesized pure Fe<sub>2</sub>O<sub>3</sub>, pure Ag (0) and hybrid Fe<sub>2</sub>O<sub>3</sub>-Ag nanoparticles by IL are shown in figure 1a-c. All reflection peaks of the nanoparticles in pure Fe<sub>2</sub>O<sub>3</sub> are indicated as a rhombohedral form, which agrees well with the value of JCPDS file No. 89-0596. The synthesized pure Ag(0) show reflections indexed to hexagonal (primitive) which are in good accordance with the values on the standard card (JCPDS No. 87-0598)). For Fe<sub>2</sub>O<sub>3</sub>-Ag hybrid nanoparticles, all reflection peaks could be indicated to orthorhombic crystal structures (JCPDS NO 21-1080). The size of the crystals of the nanoparticles produced was calculated from the Debye-Scherrer equation  $D = K\lambda / \beta \cos \theta$  using Bragg's law. The average sizes of the prepared iron oxide, silver (0) and iron oxide- silver hybrid nanoparticles were 16.7, 26.5 and 18.5 nm respectively.

## SEM Analysis



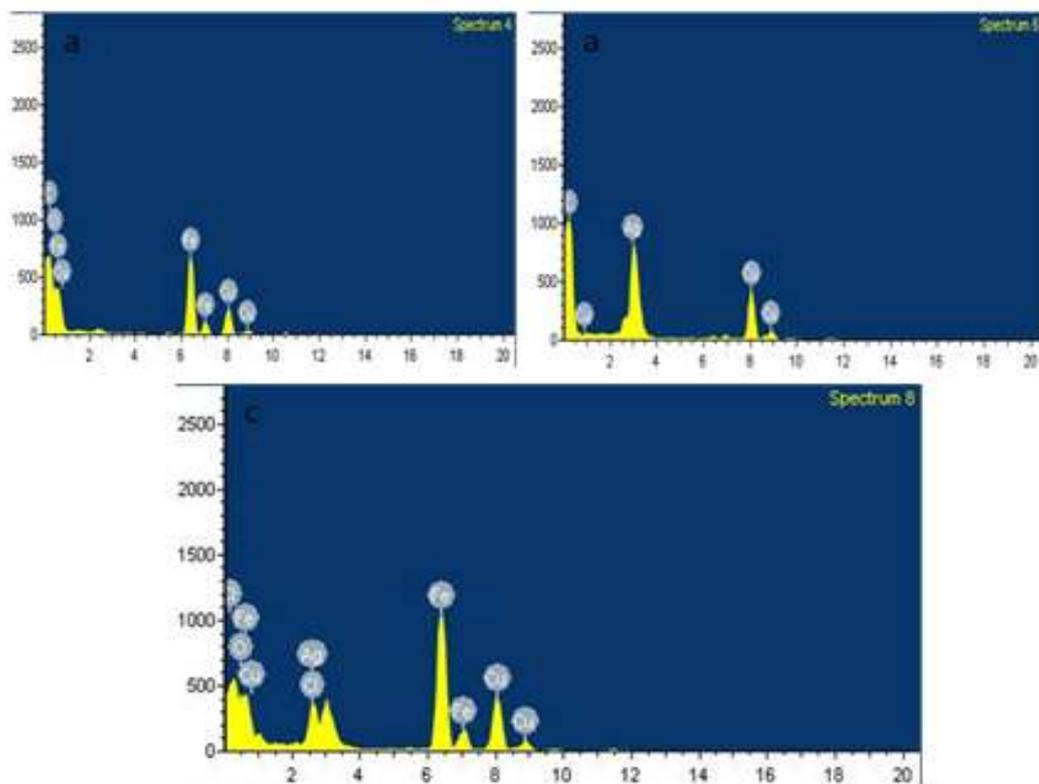
**Figure 2: SEM image of (a) Pure Fe<sub>2</sub>O<sub>3</sub>; (b) Pure Ag (0); (c) Hybrid Fe<sub>2</sub>O<sub>3</sub>-Ag nanoparticle by IL**

The structure and morphology of pure Fe<sub>2</sub>O<sub>3</sub>, pure Ag(0) and hybrid Fe<sub>2</sub>O<sub>3</sub>-Ag nanoparticles produced by IL are shown in figure 2a-c. As seen from Fig. 2(a), the flake shape of the agglomerated nanoparticles was formed when Fe<sub>2</sub>O<sub>3</sub> nanoparticles were prepared in the pure state. Moreover spherically shaped nanoparticles was produced by pure Ag(0) and granule shaped particles was generated by Fe<sub>2</sub>O<sub>3</sub>-Ag hybrid nanoparticle.

## EDX pattern

The purity and composition of pure Fe<sub>2</sub>O<sub>3</sub>, pure Ag(0) and hybrid Fe<sub>2</sub>O<sub>3</sub>-Ag nanoparticles are displayed in figure 3a-c. Synthesized Fe<sub>2</sub>O<sub>3</sub> shows only iron and oxygen signals other than copper and carbon, Ag(0) displays only silver signal other than copper and carbon, moreover the synthesized Fe<sub>2</sub>O<sub>3</sub>-Ag hybrid nanoparticles shows iron, oxygen, silver, copper and carbon signals. The other peak in the figure, which corresponds to copper, was due to the carrier material and was not taken into account in the elementary analysis of the products. Spectral evidence shows that the synthesized nanoparticles were sufficiently pure.

**Figure 3: EDX pattern of (a) Pure Fe<sub>2</sub>O<sub>3</sub>; (b) Pure Ag (0); (c) Hybrid Fe<sub>2</sub>O<sub>3</sub>-Ag nanoparticle by IL**



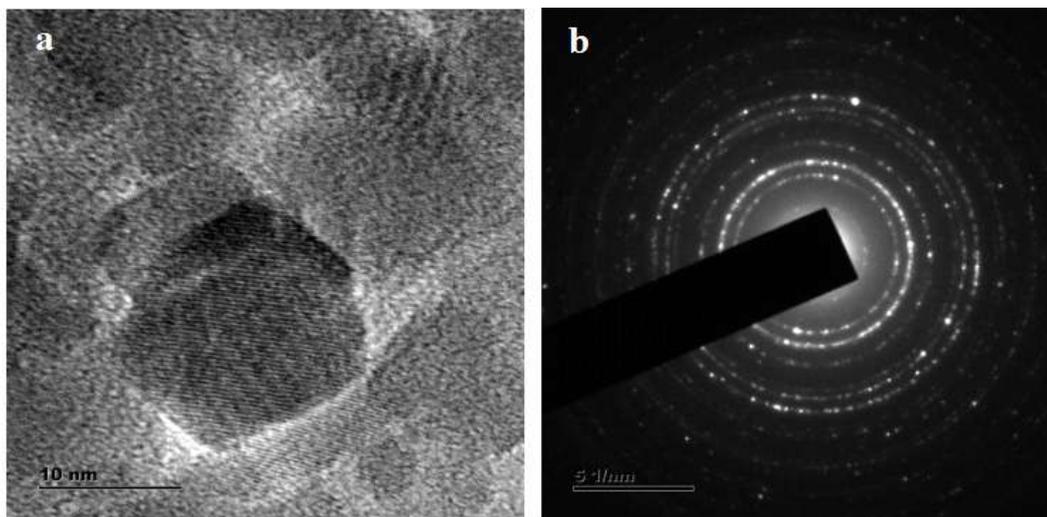
To confirm the formation of Fe<sub>2</sub>O<sub>3</sub>-Ag nanoparticles, an EDX analysis was carried out. The details of the three EDX spectra of the electrospun values, measured in atomic and weight %, are shown in Table 2. From the EDX spectrum and Table 2 results it has been confirmed that in the hybrid nanostructure synthesis, Ag was incorporated into Fe<sub>2</sub>O<sub>3</sub>.

**Table 2: EDX weight ratio of pure and hybrid nanoparticles**

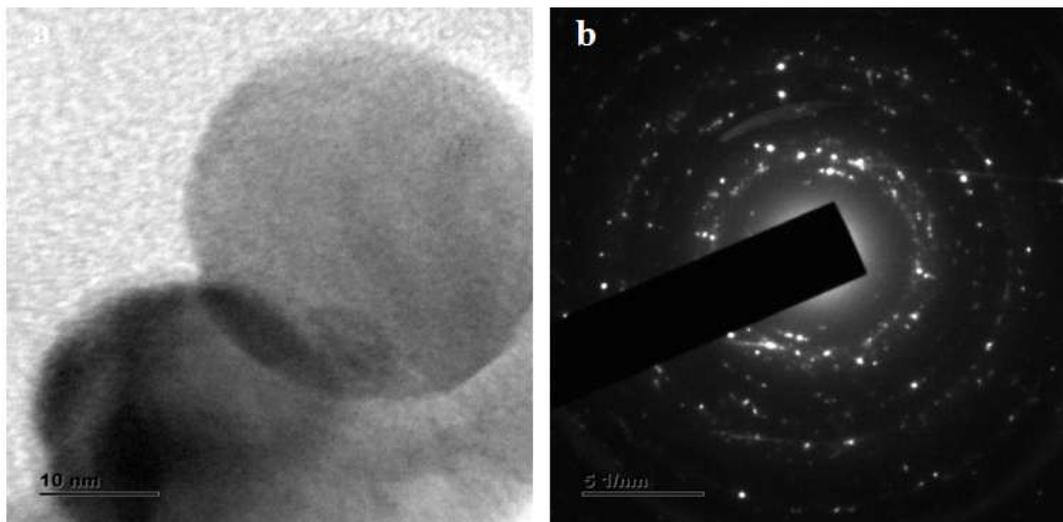
Compound	Fe		O		Ag	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
Pure Fe <sub>2</sub> O <sub>3</sub> nanoparticles	49.29	26.3	6.59	12.28	-	-
Pure Ag(0) nanoparticles	-	-	-	-	43.44	14.43
Hybrid Fe <sub>2</sub> O <sub>3</sub> - Ag nanoparticles	47.87	48.62	2.38	8.42	16.28	8.56

### TEM Analysis

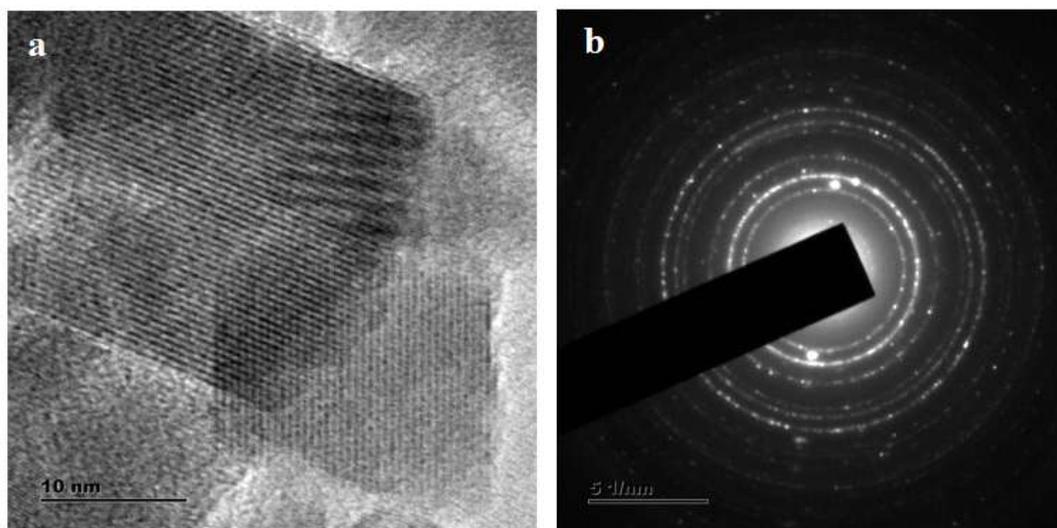
The morphologies of as prepared pure and hybrid nanoparticles are shown in figure 4-6. Figure 4a shows the transmission electron microscopy (TEM) image of the pure iron oxide (Fe<sub>2</sub>O<sub>3</sub>) nanoparticles. Analysis of the micrographs indicates that the morphology of the nanoparticles are cubic in shape. The obtained nanoparticles are in the range of sizes approximately 15-18nm.



**Figure 4: (a) TEM image and (b) SAED image of Fe<sub>2</sub>O<sub>3</sub> nanoparticle by IL**



**Figure 5: (a) TEM image and (b) SAED image of Ag(0) nanoparticle by IL**



**Figure 6: (a) TEM image and (b) SAED image of Fe<sub>2</sub>O<sub>3</sub>-Ag nanoparticle by IL**

Figure 5a shows the TEM image of the pure Ag(0) nanoparticles. From this structure, it is manifest that the structure of the nanoparticles are nanospheres with a diameter of about 12-15nm. TEM images of the hybrid nanoparticles (Fe<sub>2</sub>O<sub>3</sub>-Ag) are shown in figure 6a. It is clearly evident that the particles appeared hexagon shape with a diameter ranging between 15 nm to 20 nm. Figure 4b, 5b and 6b shows the selected area electron diffraction (SAED) pattern of nanoparticles. From the SAED pattern of these three samples it is clear that all the three synthesized nanoparticles are crystalline (bright spots) in nature. TEM analysis of hybrid nanoparticles shows that when Ag (0) was introduced into Fe<sub>2</sub>O<sub>3</sub>, the organization of Fe<sub>2</sub>O<sub>3</sub> was converted from cubic to hexagon, and during this process the active site of the nanoparticles was increased from four to six. In addition to that when Ag(0) was incorporated into the Fe<sub>2</sub>O<sub>3</sub> the size of hybrid Fe<sub>2</sub>O<sub>3</sub>-Ag nanoparticles were increased approximately by 1-2 nm.

## Conclusion

From the IR report it has been shown that significant changes are observed in pure and hybrid nanoparticles. From the EDX analysis, it is clear that the Fe<sub>2</sub>O<sub>3</sub>, Ag(0) and Fe<sub>2</sub>O<sub>3</sub>-Ag(0) nanoparticles prepared were sufficiently pure. In the present investigation XRD results revealed that the size of the synthesized

nanoparticles was in good agreement with the TEM results. In the present investigation, it could be confirmed that from TEM results, during hybrid, active site of the compound increases. Because of this increase in active site its activity also increases.

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