

# Structural Characterization of Fe-Ag Bimetallic Nanoparticles Synthesized by Chemical Reduction

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## Authors' contributions

*This work was carried out in collaboration between all authors. Author ARB was lead the article, carried out the design and experimental development. Author RP contributed part of the discussion of the results. Authors GR and RE discussed the results and made the image processing. All authors read and approved the final manuscript.*

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## ABSTRACT

**Aims:** The main objective of this research is to establish an efficient route for obtaining dumbbell bimetallic nanoparticles. Likewise, correlating the results of structural characterization with the particles synthesis conditions.

**Methodology:** Fe nanoparticles were obtained using Fe (III) Chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) as precursor and sodium borohydride ( $\text{NaBH}_4$ ) as reducing agent, subsequently, a solution of silver nitrate ( $\text{AgNO}_3$ ) was added to their action.

**Results:** Bimetallic particles were obtained in an aqueous medium and were later studied using the technique of high-resolution transmission electron microscopy (HREM), ultraviolet visible spectroscopy (UV-is) and quasi-elastic light scattering (QELS).

**Conclusion:** Particles with semi-spherical morphology were observed, likewise, a particle size distribution of 20nm was recorded for the particles of Fe and 7nm in the case of Ag additionally inter planar distances corresponding to oxides of Fe were found.

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**Keywords:** *Chemical synthesis; nanoparticles; transmission electron microscopy.*

## **1. INTRODUCTION**

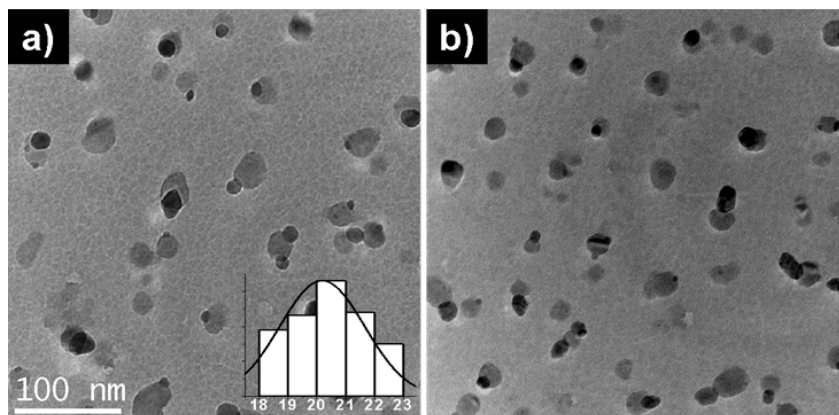
The metallic nanoparticles have a special interest due to the wide range of properties and potential applications in the fields of physics, chemistry, materials science, biology and catalysis [1-4]. Specifically, bimetallic nanoparticles offer a feasible alternative for the potentiation of the metallic properties of the nanoparticles. This is due to these composites consist of two combined nanoparticles with different functionalities with a common interface. Interfacial interactions in these systems lead to changes in the physical and chemical properties of the bimetallic nanoparticles. Consequently, research of new synthesis routes bimetallic nanoparticles is fundamental in the development of nanotechnology. Specially the Fe-Ag dumbbell-like nanoparticles possess the surface character of Ag and the magnetic property of Fe and hence might have great potential applications in biological targeting, biological separation, high-density magnetic recording, catalysis and targeting therapy fields in the near future [5]. Moreover, the preparation and properties of Fe-Ag composite magnetic nanoparticles have been reported a few [6]. Different experimental methods to produce dumbbell-like nanostructures have been reported in the literature [7,8]. However, the chemical method has been employed too successfully in the synthesis of these bimetallic nanostructures [9-11]. In this work, a chemical synthesis was carry on to produce Fe-Ag dumbbell-like nanoparticles by the reduction of  $(\text{FeCl}_3 \cdot 6\text{H}_2\text{O})$  and  $\text{AgNO}_3$  using sodium borohydride ( $\text{NaBH}_4$ ) as a reducing agent.

## **2. EXPERIMENTAL DETAILS**

Fe-Ag dumbbell nanoparticles were produced first by reduction of Fe(III) Chloride hexahydrate with sodium borohydride ( $\text{NaBH}_4$ ) and then by adding silver as nitrate ( $\text{AgNO}_3$ ). The chemical synthesis of iron nanoparticles was carried out using a modification of the Hsing-Lung et al [12] and Zhanhua Guo [13] methods. In this case, we varied the stirring (600 rpm) and temperature conditions ( $25^\circ\text{C}$ ), as a simplification in the use of instrumental and to explore a decrease in the energy incorporation. Two solutions of polyvinylpyrrolidone (PVP) at constant concentration of 1.0M was prepared and mixed and stirred magnetically at 600 rpm for 1h with the precursor (0.1M). The reducing agent ( $\text{NaBH}_4$ ) was added drop wise at a concentration of 0.2M. Finally two solutions of  $\text{AgNO}_3$  at 0.01 and 0.02 M and 0.04 M were added to the Fe nanoparticles. For the structural characterization of bimetallic nanoparticles, a transmission electron microscopy TEM (Phillips Technai F-20) analysis was employed to observe the morphology and sizes of iron-silver nanoparticles. In addition, a UV-vis spectrophotometer (Ocean Optics USB4F01962) was used to identify the presence of individual and bimetallic nanoparticles.

## **3. RESULTS AND DISCUSSION**

Fig. 1 shows low magnification electron microscope images of the nanometric particles obtained with additions of Ag ions to Fe nanoparticles. These images clearly show dispersed nanoparticles with a dumbbell type configuration. The dumbbell type configuration consists of a nanoparticle with a particular composition and size, which is attached another particle whose composition is different and its size is generally smaller. The particles obtained had a light gray.



**Fig. 1. Electron microscope images of the Fe<sub>3</sub>O<sub>4</sub>-Agnanoparticles with a dumbbell type configuration**

This fig. also shows that the morphology of both types of nanoparticles is spherical and the formation of agglomerates is not appreciated. In the past, several investigations have been done to synthesize and analyze the properties of this nanoparticle configuration whose main property is their dual function (bi-functional) [14,15].

The particle size distribution for the colloidal solution is illustrated inset Fig. 1. While for pure Fe, the average particle size is about 20 nm with small dispersion in size for pure Ag the average particle size is small about 7 nm with even less size dispersion. The EDS (Energy-dispersive X-ray spectroscopy) spectrum obtained on dumbbell particles is presented in Fig. 2a and confirms that both Fe and Ag elements are present. Fig. 2b also shows UV-Vis absorption spectra of nanoparticles after chemical procedure.

The curve indicates a discrete characteristic peak of Ag surface plasmon resonance of approximately 455 nm, which indicates the formation of silver nanoparticles [16]. No plasmon resonance peak was observed for Fe particles. There has been previously reported that Fe nanoparticles exhibit no discrete absorption peak [17-19] but the absorption decreased with an increase of wavelength.

Fig. 3(a-c) shows, in particular, some additional structural features of dumbbell nanoparticles obtained by bright field TEM images. According to the mechanism of mass/thickness contrast in TEM, in the case of BF image, thicker or higher Z regions scatter more electrons; therefore, these areas are darker than thinner or low Z regions (light contrast). Thus, in the BF image the dark particle correspond to silver element, while lighter particle has a chemical composition based on Fe. We can notice that from the iron particle has a greater thickness should be less contrast, however, the smallest particle has low contrast due to have the highest atomic number. In addition, Fig. 3d show a Z-contrast image (HAADF) which illustrates that higher contrasts region (lighter) correspond to particle with high Z value (Ag), on contrary, darker region corresponds to nanoparticle with low Z (Fe). In this way, these TEM analyses confirm the presence of Fe-Ag particles dumbbell type.

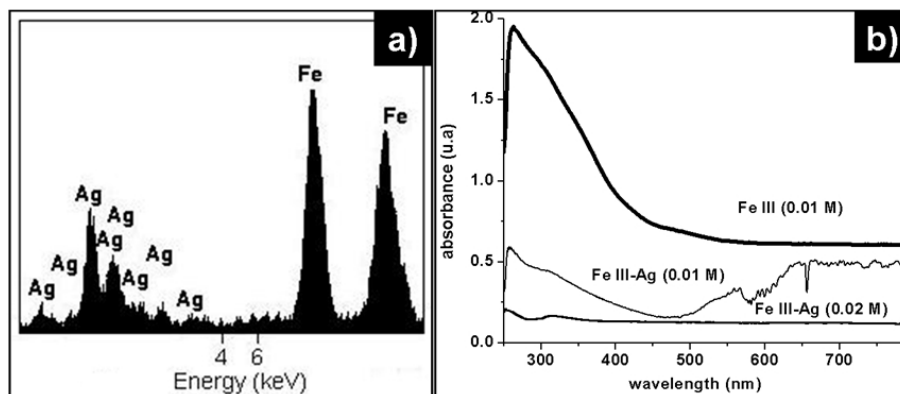


Fig. 2. (a) EDS spectrum obtained of  $\text{Fe}_3\text{O}_4$ -Agdumbbell particles (b) UV-Vis absorption spectra of nanoparticles after chemical procedure.

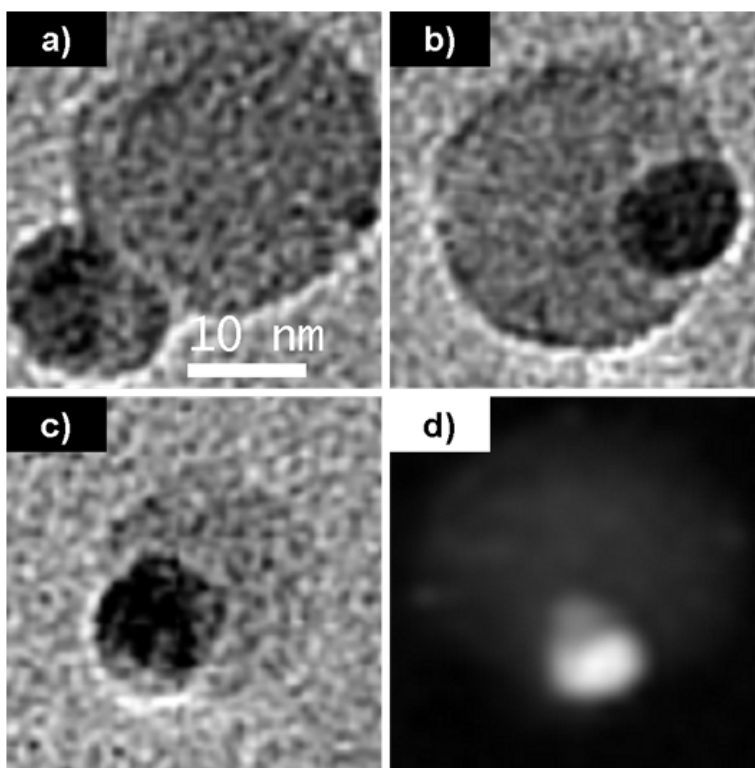


Fig. 3. (a-c) Structural features of dumbbell nanoparticles obtained by bright field TEM images and (d) Z-contrast image (HAADF) of  $\text{Fe}_3\text{O}_4$ -Agdumbbell particles

In order to determine the structure and crystallinity of the nanoparticles HRTEM images have been analyzed as shown in Fig. 4 (a-b). These images confirmed the structure of bimetallic nanoparticles. The inter-plane lattice measurement for the small particle is about 2.28 Å, which is consistent with the 2.3 Å lattice spacing for the (111) planes face cubic center (FCC) of silver. However, the inter plane spacing probed for larger particle corresponds to

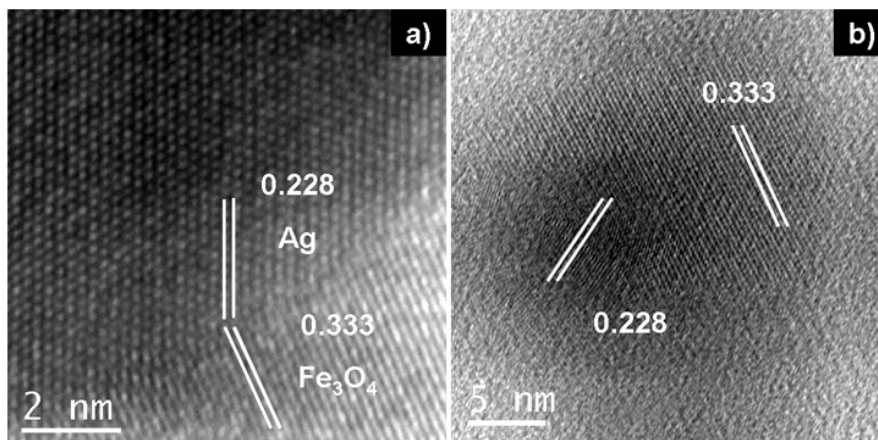
3.33 Å, which closely agrees with value for the (112) plane of the Fe<sub>3</sub>O<sub>4</sub>, indicating that iron particles were oxidized. Several previous studies have confirmed that iron nanoparticles are easily oxidized [20]. Therefore, the particles synthesized here have a Fe<sub>3</sub>O<sub>4</sub>-Ag chemical composition.

HRTEM images also show Ag particles with poor crystallinity associated with the presence of defects in the structure. Twinning is a characteristic crystalline defect observed in the Ag particle structure. On the contrary, it was found that the Fe-based nanoparticles are free of defects being FCC type. It is important to note that the amount of silver added was varied with the aim of establishing different conditions for the heterogeneous nucleation. Further HRTEM analysis of synthesized particles reveals that the amounts of Ag ions added affect the dumbbell morphology and the size of the particles. For example, large concentration of Ag additions leads to larger Ag particles with more crystalline defects in comparison to those of iron.

On the other hand, the heterogeneous nucleation of Ag on Fe particles was aided by the presence of small amounts of reducing agent (sodium borohydride) and depending on amounts of Ag ions addition. The obtained dumbbell type nanoparticles are the result of the use of small amounts (0.01 M) of silver ions added to the iron nanoparticles. Silver particles nucleation occurs preferentially in sites where there is another solid formed, not following an independent nucleation (homogeneous). This result suggests that Ag solution atoms nucleate in regions where the energy barrier is lower (Fe particles, heterogeneous nucleation) than other regions of the solution. It is well known that Ag and Fe atoms are immiscible in the solid state. In this sense, the formation of these pairs of particles could be influenced by the poor or null solid solubility between iron oxide and silver particles in the nanometric scale, favoring the mechanism of heterogeneous nucleation of silver on iron.

As the concentration of Ag ions was increased from 0.01 to 0.02M, the size of Ag particles nucleates on Fe takes similar dimensions. However, when the concentration of Ag ions added was 0.04M, Ag nanoparticles follow a homogeneous nucleation. The silver nanoparticles have average size of 50 nm which is greater than those of Fe particles (25 nm). In this way, it is easily to deduce that the chemical reduction rate of Ag nanoparticles is higher than iron. Both the highest concentration of silver ions added, as the higher chemical reduction rate of silver nanoparticles may be the factors which under these conditions the particles of silver follow a homogeneous nucleation instead heterogeneous nucleation. After homogeneous nucleation of Ag particles, their particle size and structure observed by HRTEM images easily denote their presence. This is because that they are greater than Fe particles and have commonly multiply twinning instead FCC type of Fe-based nanoparticles. Thus, the formation of these pairs of particles (dumbbell) could only be occurring when the amount of silver added was relatively smaller.

Thus, we can deduce that four factors are contributing to the formation of Fe<sub>3</sub>O<sub>4</sub>-Ag dumbbell nanoparticles: first, smaller amount of reducing agent remainder after the homogeneous nucleation of Fe-based nanoparticles; second, the used of small amounts of Ag added to Fe colloidal solution, third the poor solubility of Ag in Fe-based particles and finally the nucleation of silver particles on the existing Fe particles (heterogeneous nucleation).



**Fig. 4(a-b). HRTEM images of bimetallic nanoparticles with inter-plane lattices of 2.28 and 3.33 Å corresponding to Ag and Fe<sub>3</sub>O<sub>4</sub> respectively**

#### 4. CONCLUSION

The chemical reduction by NaBH<sub>4</sub> offers an effective synthesis route to the formation of Fe<sub>3</sub>O<sub>4</sub>-Ag dumbbell nanoparticles. The dumbbell particles formation is the result of the use of small amounts of silver added to the seeded particles of Fe (0.1 M Fe: 0.01M Ag). HREM analysis confirms that iron particles during the Ag reduction process were oxidized. We also reported that the dumbbell nanoparticles formation is influenced by the low solubility of these two materials and their different nucleation rates.

#### ETHICAL APPROVAL

All authors declare that all experiments and the results obtained are accurate and made according to the rules of ethics followed by the Michoacán University of San Nicolas of Hidalgo.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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