

Research Article

A Simple Approach for the Synthesis of Gold Nanoparticles Mediated by Layered Double Hydroxide

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The present work introduces a new procedure to obtain gold nanoparticles (AuNPs). AuNPs (77–213 nm) were obtained in the absence of any classical reducing agents in a medium containing Mg^{2+}/Al^{3+} layered double hydroxide (LDH) and *N,N*-dimethylformamide. XRD analysis showed the presence of crystalline phases of gold in the Au/LDH composite. The 2θ values of peaks corresponding to the LDH interlayer distance indicated that metallic NPs were deposited on the surface of the material. Furthermore, atomic force microscopy (AFM) analysis showed that AuNPs tend to agglomerate in a nonclassical halter-like shape.

1. Introduction

Metal nanoparticles (NPs) have a large surface-to-volume ratio [1–4]; therefore a large fraction of the metal atoms is on the surface available for catalysis [5]. Therefore a nanoparticle of 10 nm diameter has about 10% of its atoms on the surface, in contrast to a nanoparticle of 1 nm that has 100% [6]. This characteristic usually indicates electronic and chemical properties that differ from those of the bulk materials [7]. Gold nanoparticles (AuNPs) are promising because they have electronic, magnetic, and optical properties [8]. AuNPs also have therapeutic potential as drug-delivery carriers due to their characteristics such as size, stability, and biocompatibility [9]. Recent works have shown that the AuNP functionalization with different molecules has many applications in biomedical imaging, clinical diagnosis, and therapy, including cancer treatment [10–13].

Layered double hydroxides (LDHs) have many applications in heterogeneous catalysis as catalysts or catalyst precursors [14–17]. They are also known as anionic clays and hydrotalcite-like compounds, because structurally they are very similar to brucite $[Mg(OH)_2]$, where magnesium is

octahedrally surrounded by six oxygen atoms in hydroxide form. Layers are formed by sharing the edges of adjacent octahedral units, creating two-dimensional sheets that stack together to form three-dimensional structures through hydrogen bonding [18, 19].

Many reactants can act as reducing agents for the formation of gold nanoparticles such as cyclodextrins [8, 20, 21], sodium citrate [22, 23], hydrazine sulfate [24], and sodium borohydride [25, 26]. Obtaining gold nanoparticles in the absence of these reactants would reduce process costs and be environmentally benign.

Herein we report an unprecedented method for the synthesis of gold nanoparticles in *N,N*-dimethylformamide (DMF) mediated by layered double hydroxide materials (LDHs).

2. Experimental

2.1. Materials. All chemicals were reagent-grade or analytical-grade substances when available and were used without further purification. All aqueous solutions were prepared in Milli-Q water.

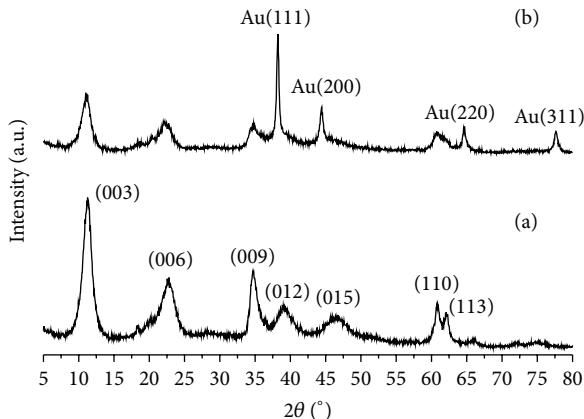


FIGURE 1: XRD patterns of (a) LDH and (b) Au/LDH composite.

2.2. Synthesis of LDH. The Mg/Al layered double hydroxide was obtained using a solution containing 0.006 mol of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Vetec, 99%) and 0.003 mol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Vetec, 99%) ($\text{Mg}(\text{II})/\text{Al}(\text{III}) = 2$) in 100 mL of Milli-Q water. Under vigorous stirring, LDH was prepared by coprecipitation at constant pH (≈ 10) with a 1.0 mol L^{-1} solution of NaOH (Vetec, 99%) at room temperature. The suspension thus obtained was filtered, washed with Milli-Q water, and dried over a stove. The LDH was obtained as a white solid.

2.3. Synthesis of Au/LDH Composite. AuNPs were prepared by adding LDH in a solution of 0.025 mol L^{-1} $\text{AuCl}_4 \cdot 2\text{H}_2\text{O}$ (Aldrich, 99%) in N,N -dimethylformamide (Aldrich, 99.8%) ($\text{Au:LDH} = 1:4$) at 80°C for 24 h. Initially, the DMF gold solution was yellow; 15 minutes after LDH addition to the system, the mixture started to darken, and after about 1 hour of reaction a black colored precipitate appeared. After 24 hours of reaction, the entire solution became dark. The lightly purple solid obtained was filtered, washed with portions of DMF, and dried in a properly stove.

2.4. Materials Characterization. Powder X-ray diffraction patterns were recorded on a Rigaku Ultima IV diffractometer using $\text{Cu K}\alpha$ radiation. Scans were performed over 2θ range from 5° to 80° , using a resolution of 0.05° and count time of 1 s at each point.

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet Magna-IR 760 spectrophotometer with a resolution of 4 cm^{-1} and a number of 16 scans using wavenumber range from 400 to 4000 cm^{-1} . Samples were prepared by mixing the powdered solids with KBr.

Scanning electron microscope (SEM) images and energy-disperse X-ray spectroscopy were performed on a JEOL JSM 6460-LV microscope operating among 10–20 kV and equipped with an energy-disperse X-ray spectrometer.

The atomic force microscope used was the Alpha300 AR model (WITec Instruments, GER). Images were obtained by performing noncontact AFM mode.

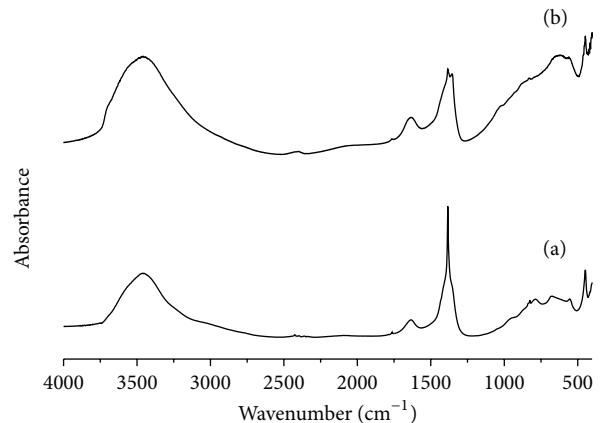


FIGURE 2: FTIR spectra for (a) LDH and (b) Au/LDH composite.

3. Results and Discussion

So far, the synthesis and support of gold nanoparticles on layered double hydroxide were carried out using cyclodextrins, sodium borohydride or citrate, and hydrazine sulfate as reducing agents [20–26]. When experiencing other means of metal reduction, we observed that N,N -dimethylformamide was not capable of reducing Au(III) from NaAuCl_4 precursor. Layered double hydroxide was first thought as an intercalation matrix for the AuCl_4^- anion; thus at first sight, DMF would be a proper medium for this process. However, after the addition of LDH to the medium, the mixture changed its color and a dark precipitate was obtained at the end of the process. We managed to characterize this dark solid to obtain its chemical composition and microstructural and short-long range structural characteristics.

3.1. Powder X-Ray Diffraction. Figure 1 shows the XRD patterns of LDH (a) and Au/LDH composite (b). The LDH pattern (Figure 1(a)) is typical of a hydrotalcite-like material having been indexed according to the American Mineralogist card no. 0014738.

The XRD pattern of Au/LDH composite (Figure 1(b)) showed four additional peaks: a high intensity peak at $2\theta = 38.2^\circ$ and three additional peaks at $2\theta = 44.4^\circ, 64.7^\circ$, and 77.8° . These reflections correspond respectively to the four planes (111), (200), (220), and (311) indicating that crystalline phases of gold were formed in the material [26, 27]. Applying the Scherrer formula:

$$t = \frac{0.9\lambda}{\sqrt{Bm^2 - Bs^2} \cos \theta}, \quad (1)$$

where λ is the X-ray wavelength, Bm is the observed peak width, Bs is the peak width of a crystalline standard, and θ is the angle of diffraction; an estimate of the mean crystallite size (t) of 22 nm for the gold phase could be obtained by considering full width at half the maximum of the four most intense reflections.

Another important detail observed when comparing these XRD profiles refers to the fact that the same interlayer distance of 8 \AA was obtained for both LDHs. This may

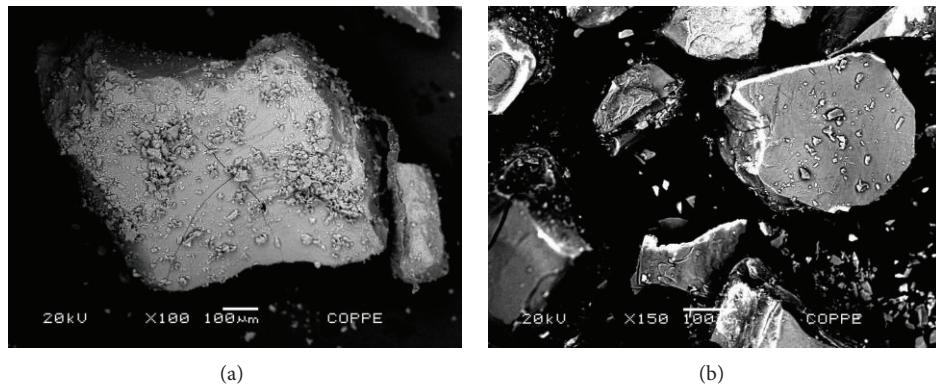


FIGURE 3: Backscattered electron images from LDH ((a) magnification: 100x) and Au/LDH composite ((b) magnification: 150x).

TABLE 1: CHN elemental analysis of LDH and Au/LDH composite.

	C (%)	H (%)	N (%)
LDH	1.25	3.73	3.56
Au/LDH composite	0.68	4.14	1.44

indicate that gold particles were located primarily on the surface of LDH and not in the interlayer region [25].

3.2. Fourier-Transform Infrared Spectroscopy. Figure 2 shows the FTIR spectra for LDH and for Au/LDH composite in the region of 400–4000 cm⁻¹. Both of them exhibit a broad band at 3500 cm⁻¹ that can be assigned to O-H stretching, a band at 1630 cm⁻¹ that is typical of the angle deformation vibration of the water molecule, and a band at 450 cm⁻¹ that can be assigned to the vibrations of octahedrally coordinated Al-O bonds. Concerning the strong band centered at 1384 cm⁻¹ in LDH spectrum, it can be assigned as the asymmetric stretching of nitrate ion (NO₃⁻). As the absorbance of this band appeared to be reduced in the spectrum of Au/LDH (Figure 2(b)) it may be inferred that ion exchange process occurred, corroborating the CHN elemental analysis (Table 1), which indicated a decrease in the amount of nitrogen (from NO₃⁻) for Au/LDH composite in face of LDH.

3.3. Scanning Electron Microscopy and X-Ray Energy Dispersive Spectroscopy. Both micrographs in Figure 3 are visualizations of LDH and Au/LDH composite using backscattered electrons signals. Both images show agglomerates greater than $100\text{ }\mu\text{m}$. The left micrograph was obtained from LDH, and no phase contrast was detected while the right image was taken from the Au/LDH composite and showed different phases by evidence of different shades of gray. The bright spots seen are related to the metallic phase (Au). This was confirmed by EDX analysis of Au/LDH composite (Figure 4) which reveals heterogeneous distribution of gold in the material (Figure 4—Pt.1). Here it is also important to note that Mg intensity is always greater than that of Al, as expected by the proposed synthesis of LDH. Another important feature

is related to the unexpected presence of chloride ion in the Au/LDH material (see EDX spectra of Figure 4). In addition, the chloride ion seems to be homogeneously distributed in the LDH matrix since it was detected for all the three regions probed. One explanation for this considers that chloride ion was intercalated by ion-exchange process with nitrate ion, considering that FTIR and CHN analysis showed a decrease of NO_3^- in Au/LDH composite in face of LDH sample.

3.4. Atomic Force Microscopy. In order to gain some microstructure information concerning the gold particles deposited on LDH, we managed to obtain atomic force micrographs. Figures 5(a) and 5(b) correspond to the phase and topography images, respectively. It is clearly shown that black spots in the phase image correspond to the highest heights in the topography image (the “whiter” spots), and therefore it is possible to identify them as the gold nanoparticles deposited on LDH matrix. These particles present size distribution from 77 to 231 nm and are constituted by agglomeration of smaller gold crystallites, considering the mean crystallite size of 22 nm obtained from the XRD pattern of Au/LDH composite.

In Scheme 1, we show a proposal for the mechanism of the formation of gold nanoparticles in which we suggest that DMF, besides being the solvent, is the reducing agent in a redox process mediated by LDH.

4. Conclusion

So far this work is the first attempt to prepare gold nanoparticles without an effective reducing agent in the reaction. We believe that metal reduction occurred by means of reaction with the solvent, *N,N*-dimethylformamide, mediated by layered double hydroxide. This can be affirmed based on the experimental observation that while no color change was observed even in a long period after mixing NaAuCl₄ with DMF, a dark heterogeneous mixture began to form immediately upon addition of LDH. As a parallel process, chloride ion generated from AuCl₄⁻ was intercalated in the LDH matrix by the ion-exchange process with nitrate ion. This work described the method to constitute in a simple way gold nanoparticles supported on LDH that can be applied as

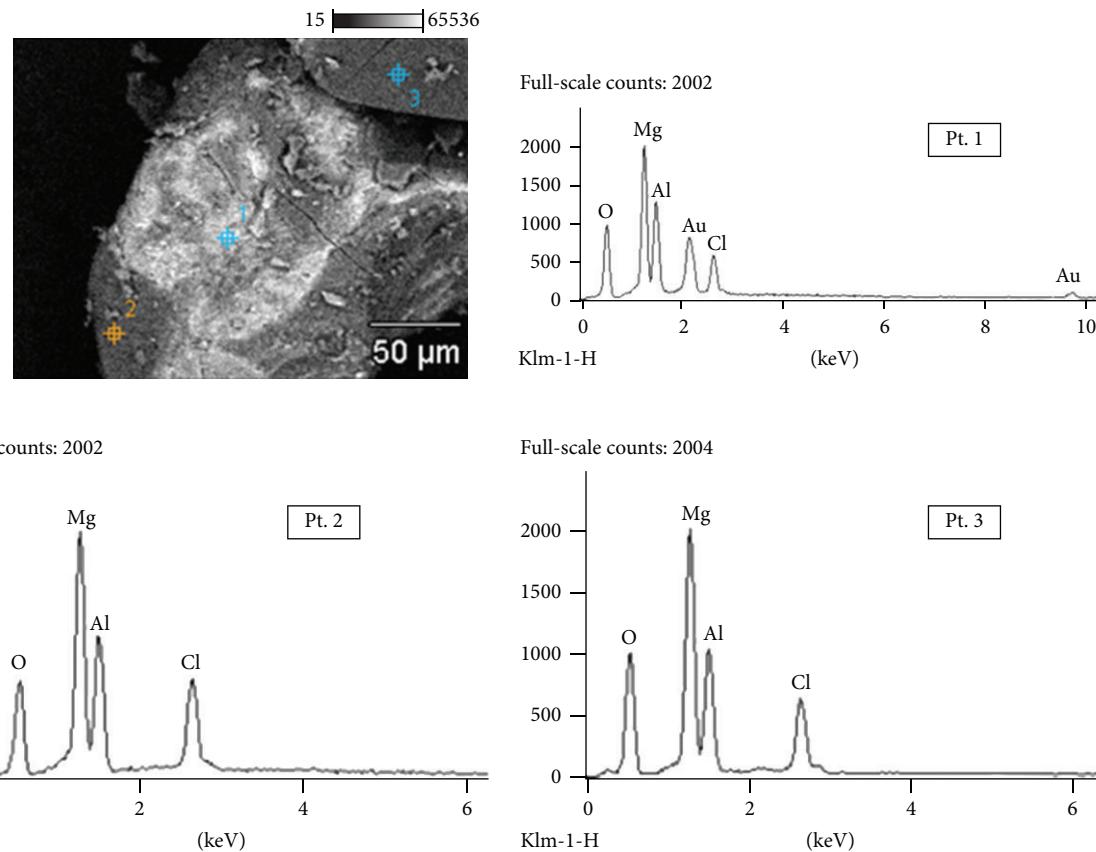


FIGURE 4: EDX spectra related to the three points probed in the SEM image of Au/LDH composite.

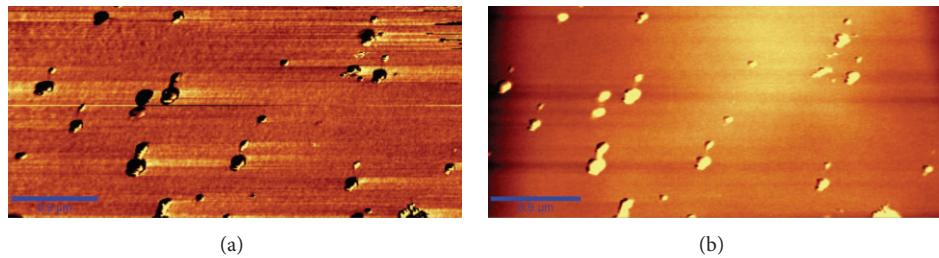
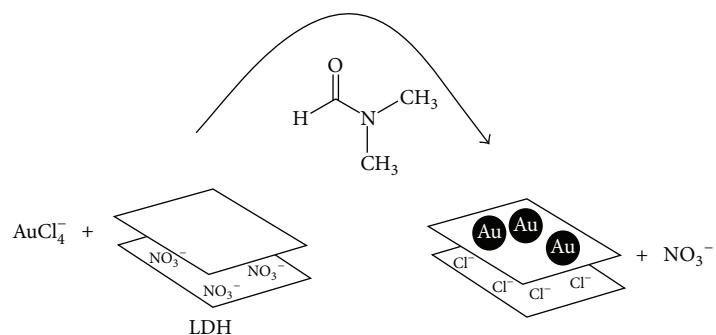


FIGURE 5: (a) Phase and (b) topography images obtained for Au/LDH composite with atomic force microscopy.



SCHEME 1: Proposal for the formation of gold nanoparticles mediated by LDH and *N,N*-dimethylformamide.

composites for organometallic catalysis [28], drug delivery systems [29] and clinical diagnosis [30].

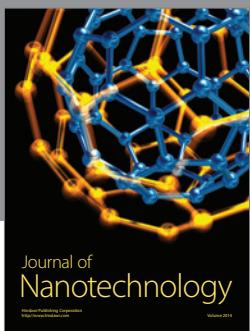
Acknowledgments

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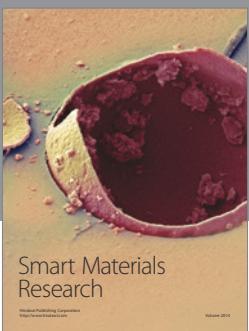
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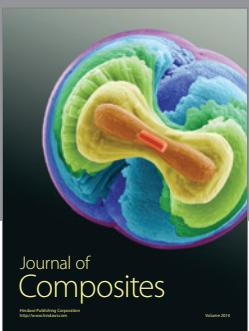
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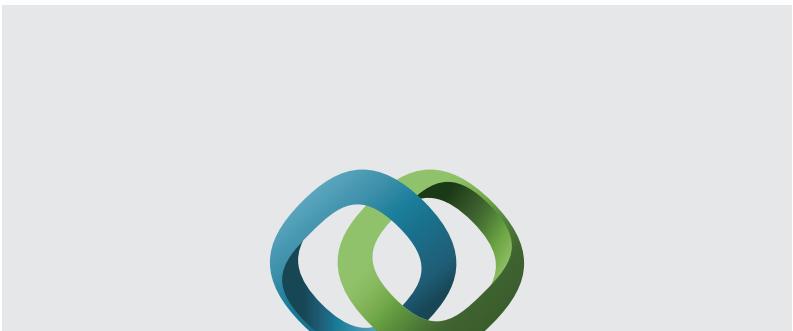
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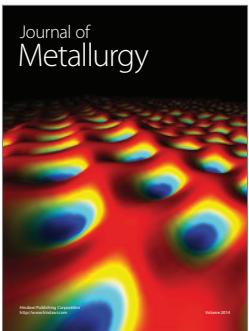


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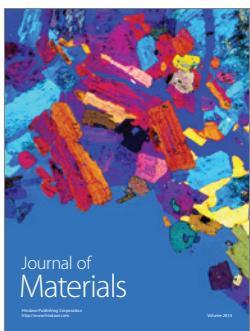
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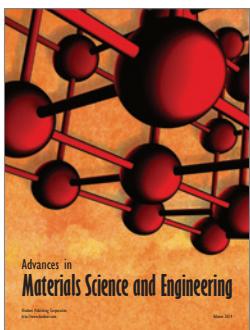
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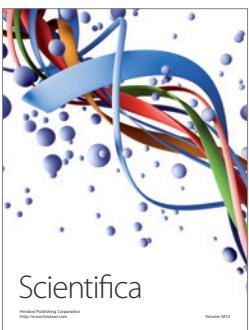
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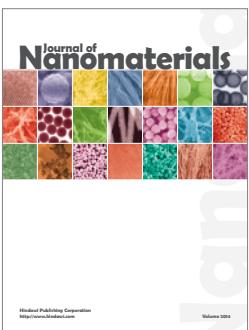
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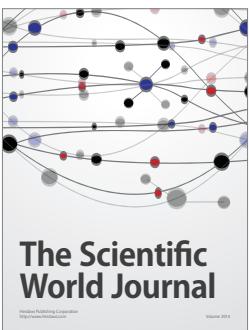
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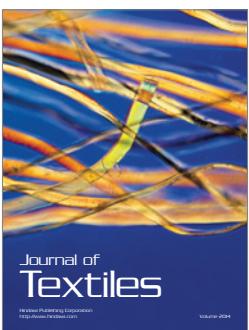
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