

Research Article

Spectroscopic Study of Polyaniline/AgCl@Ag Nanocomposites Prepared by a One-Step Method

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Polyaniline (PANI)/Ag@AgCl nanocomposites were successfully synthesized by one-step method, which consists of mixing aqueous solutions of silver nitrate with aniline chloride and delaying the evolution of reaction. By this way, aniline chloride represents a monomer for PANI and a source of Cl^- anions necessary for the formation of AgCl, and silver nitrate acts simultaneously as oxidant initiator for aniline polymerization and precursor for AgCl@Ag phase. The formation of polyaniline has been identified by the change of color to black green and from RAMAN and FTIR spectroscopy while AgCl@Ag phase has been highlighted from XRD and RAMAN. The application of Debye-Scherrer theory allows us to measure the crystallite sizes of Ag and AgCl which were, respectively, 23 and 52 nm. The AC conductivity showed a regime of constant DC conductivity at low frequencies corresponding to 0.4 S/cm^{-1} and a crossover to a frequency-dependent regime of the type $A\omega^s$ at high frequencies.

1. Introduction

Polyaniline is one of the most promising intrinsic conducting polymers because of its relatively high electrical conductivity after doping, its environmental stability in the doped and neutral states, its ease of synthesis, and the relatively low cost of the starting materials [1, 2]. In general, conductive polymers can be synthesized electrochemically or by chemical oxidation of the corresponding monomers in various organic solvents and/or in aqueous media. The interest in the development of new inorganic/organic nanocomposites has increased in recent years due to a wide range of potential use of these materials. These hybrids can be used in the optical, electrochemical, electronic, mechanical, photoelectrochemical, and other fields. An important class of hybrid materials is that in which the organic fraction is composed of conductive polymers such as polyaniline or polypyrrole. These materials become more pronounced when at least one of the fractions occurs at the nanoscale [3].

In order to improve the structural and physical properties, various materials such as metals or metal salts are

doped in conductive polymers by different experimental protocols. The incorporation of Ag nanoparticles into conducting polymers is of great interest in virtue of their synergetic physicochemical properties. Particularly, PANI/Ag composites have received significant attention because of their excellent antibacterial activity and electrochemical property [4]. However, less attention has been paid to the study of silver halide/polyaniline nanocomposites and the exploration of their possible new properties.

Silver halide is well known as photosensitive materials and is employed as raw materials in photographic films. In particular, silver chloride (AgCl) is a typical photosensitive semiconductor material with an indirect band gap (3.25 eV), which accordingly has intrinsic light response in the UV region. To obtain high absorption coefficient in a broad visible spectra region, AgNPs doping on AgCl surface has been introduced to change the band structure of AgCl and to improve its visible light sensitivity. Ag@AgCl/polyaniline nanocomposite represents multifunctional materials having unique properties and wide varieties of potential applications in various areas. Many attempts have been carried out

in order to elaborate Ag@AgCl/polyaniline nanocomposite; however, all these attempts include two steps of preparation [5, 6], consisting of preparation of Ag nanoparticles separately and mixing it with AgCl/polyaniline composite. In this work, we report our contribution for the preparation of PANI/Ag@AgCl ternary nanocomposite using a one-step simple method.

2. Experimental

2.1. Materials. Silver nitrate (AgNO_3) and aniline chloride (AnCl) were purchased from Sigma-Aldrich. These reagents were used as received without further treatment. The aqueous solutions throughout the experiments were prepared with deionized water.

2.2. Synthesis of PANI/AgCl@Ag Nanocomposites. PANI/AgCl@Ag ternary nanocomposite was prepared by mixing 50 mL aqueous solutions of silver nitrate and aniline chloride at ambient temperature with a molar ratio of Ag^+ to AnCl corresponding to 3. The mixture is kept under stirring for one hour, and then it was left in the laboratory at room temperature. After 13 days of ageing, the formed dark green precipitate has been washed with deionized water/ethanol several times until its filtrate was colorless and neutral, and finally dried at 60°C for 24 h.

2.3. Characterization. X-ray diffractograms were carried out with powder samples by a Panalytical X'Pert Pro MPD diffractometer equipped with a copper tube of wavelength $k\text{-alpha } 1.54060 \text{ \AA}$ and a filter $k\text{-beta}$ in nickel ($2\theta = 25^\circ\text{--}90^\circ$). FTIR analyzes were performed by a Perkin-Elmer spectrometer, and the spectra were obtained using KBr pellets. Raman spectra were collected using a Raman LabRam HR spectrometer from HORIBA Jobin Yvon with a laser HeNe of 633 nm. We used a Perkin-Elmer UV-vis spectrometer (Lambda 950) to determine the type of formed polyaniline, and the samples are used in their solid form. The Quanta 200 JEOL scanning electron microscope was used to evaluate the morphologies of various elaborate nanocomposites. The electrical properties were determined using an Agilent Technologies branded conductivity meter (impedance meter), model 4294 A.

3. Results and Discussions

3.1. DRX Diffractogram. The composition and the structure of the product were characterized by XRD. Figure 1 shows the XRD pattern of nanocomposites. In XRD pattern, it is obvious the coexistence of two well-crystallized phases: metallic nanoparticle Ag^0 and AgCl. The peaks at $\theta \approx 38^\circ$, 44° , 64° , 76° , and 81° represent, respectively, the diffraction of the reticular hkl planes (111), (200), (220), (311), and (222) of the face-centered cubic metallic silver nanoparticles (ASTM sheet 01-087-0720 [4]). On the other hand, the peaks at $2\theta \approx 28^\circ$, 32° , 46° , 55° , 57° , 67° , 74° , and 85° represent, respectively, the diffraction of the reticular hkl planes (111), (200), (220), (311), (222), (400), (331), (420), and (422) of

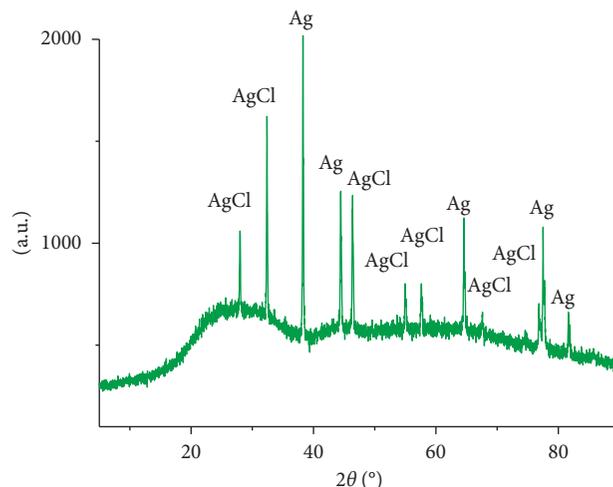


FIGURE 1: XRD pattern of the formed nanocomposite.

AgCl with face-centered cubic structure phase (ASTM sheet: 01-085-1355). The amorphous character of polyaniline is given by a wide curvature located around $2\theta \approx 24.9^\circ$ [7, 8].

Using Scherrer's equation,

$$D = \frac{k\lambda}{\beta_e \cos \theta} \quad (1)$$

where D is the average size of the crystallites, θ is the diffraction angle, λ is the excitation wavelength (1.54 \AA), k is the form factor (0.9), and β_e is the width at midheight of the line (hkl) considered which is given by

$$\beta_e = \sqrt{\beta^2 - \beta_0^2} \quad (2)$$

where β represents the half-height width observed on the XRD pattern and β_0 represents the experimental enlargement of the device, evaluated on each device using a reference single crystal.

It is possible to calculate the crystallite sizes of Ag^0 and AgCl which are, respectively, 23 and 52 nm.

Generally, for AgCl@Ag nanocomposite prepared by simple precipitation and by photoreduction of Ag metal by light, the XRD peaks of Ag^0 phase are very low, and they are invisible in XRD diffractogram. This is caused by their high dispersity at the surface of AgCl. However, in our case, it is interesting to note that the intensity of Ag^0 is remarkably intense. This is evidence that Ag nanoparticles have been formed essentially through reduction of Ag^+ cations by aniline to form PANI.

3.2. FTIR Spectroscopy. The evolution of the reaction between silver nitrate and aniline chloride during ageing has been detected by FTIR spectroscopy. Figure 2 presents the FTIR spectra of product isolated from reaction medium after 30 minutes of agitation without ageing and after 3, 7, and 13 days of ageing. It can be seen that the bands of aniline dominate the spectra for products without ageing and those characterized after 3 and 7 days of ageing: the band at 1384 cm^{-1} is attributed to C-N stretch of aniline hydrochloride and the

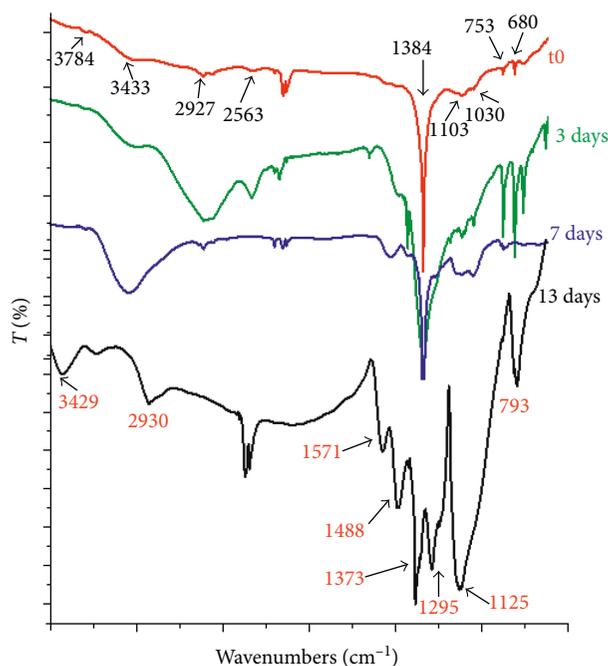


FIGURE 2: FTIR spectra of the nanocomposite during the polymerization reaction.

bands at 3784 cm^{-1} and 3433 cm^{-1} are attributed to N–H stretching vibration. The band corresponds to asymmetric C–H stretching vibration appear at 2927 cm^{-1} , and the band at 753 cm^{-1} is assigned to the vibration of N–H. With ageing, it can be seen that these bands loses intensity until total disappearance and appearance of new bands on the 13th day. The band of a pure PANI usually appears at 1294 cm^{-1} ($\nu_{\text{C-N}}$ in secondary aromatic amine), 1555 cm^{-1} ($\nu_{\text{C=C}}$, quinoid ring), 1469 cm^{-1} ($\nu_{\text{C=C}}$, benzenoid ring), and 1120 cm^{-1} (vibrational mode of $\text{B-NH}^+ = \text{Q}$ structure) [2]. All these bands appear at the spectrum of product ageing for 13 days; however, we noted a slight shift caused essentially by the interaction between polymer chains and silver metals. The band at 2930 cm^{-1} is attributed to the vibration stretching of the aromatic nucleus, C–H [6]. The C–N stretching vibration is located around 1373 cm^{-1} . The band at 793 cm^{-1} represents the out-of-plane bending C–H [3, 5, 7]. The relative intensity of the band at 1571 cm^{-1} and the band at 1488 cm^{-1} indicates the oxidation state of the material [7].

3.3. Raman Spectroscopy. We have noticed that the FTIR spectra do not continue all the characteristic polyaniline bands. This may be due to the complexity of the matrix forming this nanocomposite [7]. On the other hand, the metallic silver chloride and silver chloride bands are located in the low frequencies of or the utility of analysis by Raman spectroscopy.

The Raman spectra are given in Figure 3. All bands are regrouped and assigned in Table 1.

The most interesting bands are located around 250 cm^{-1} and 311 cm^{-1} related, respectively, to the stretching vibrations of bridging halogen metal and to thermal halogen atoms stretching vibration [13].

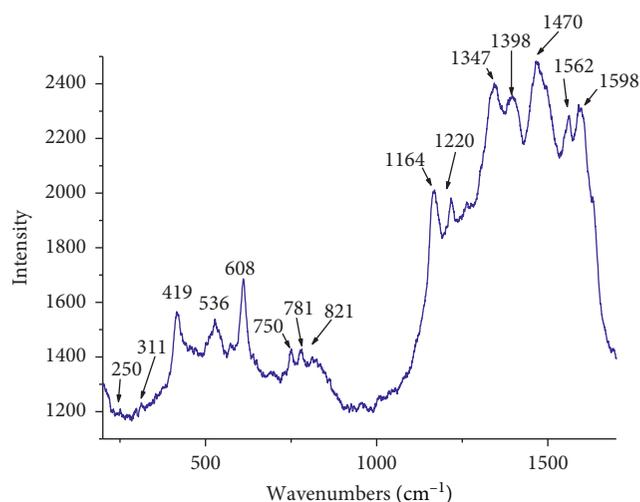


FIGURE 3: Raman spectra of ternary nanocomposite PANI/Ag@AgCl.

TABLE 1: Assignments of the Raman bands of prepared nanocomposites.

Raman shift (cm^{-1})	Assignments
1598	$\nu_{\text{C=C}}$ stretching vibration in the quinonoid rings [2, 9, 10]
1562	N–H deformation vibration of the semiquinoid structures [2, 11]
1470	$\nu_{\text{C=N}}$ stretching vibrations in quinonoid unit [11, 12]
1398	$\nu_{\text{C-N}^+}$ ring-stretching vibrations of substituted N-phenylphenazines [2, 4]
1347	Symmetric $\nu_{\text{C-N}}$ stretching [3, 4, 11]
1220	$\delta_{\text{C-H}}$ bending vibration [2, 3, 11]
1164	
821	
781	
750	Various deformations modes of polyaniline [9, 12]
608	
526	
419	
311	Terminal halogen atoms stretching vibrations ($\nu_{\text{Ag-Cl}}$) [8]
250	Stretching vibrations of the bridging halogen metal ($\delta_{\text{Cl-Ag0}}$ and/or $\delta_{\text{N-Ag0}}$) [8, 13]

3.4. UV-Vis Spectroscopy. The UV-vis spectrum of nanocomposite (Figure 4) shows the existence of three characteristic bands (335 nm, 482 nm, and 563 nm). The bands at 335 nm and 563 nm are the standard polyaniline bands [14, 15]. The first is associated with the $\pi-\pi^*$ electronic transition in the benzenoid segment. The second is associated with the excitation produced at the quinonoid rings [16, 17]. The third band at 482 nm is associated with the plasmonic resonance absorption of electrons on the Ag metal surface [18, 19]. This plasmonic band is due to the excitation of the electrons of polymer-metal interface by luminous photons. The nanoparticles of AgCl are not identified by this analysis because they are immediately transformed into metal Ag by the light photons. These

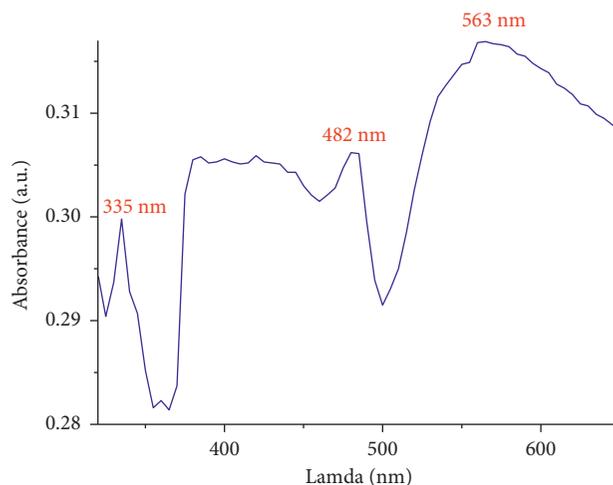


FIGURE 4: UV-vis absorption spectrum of synthesized nanocomposites.

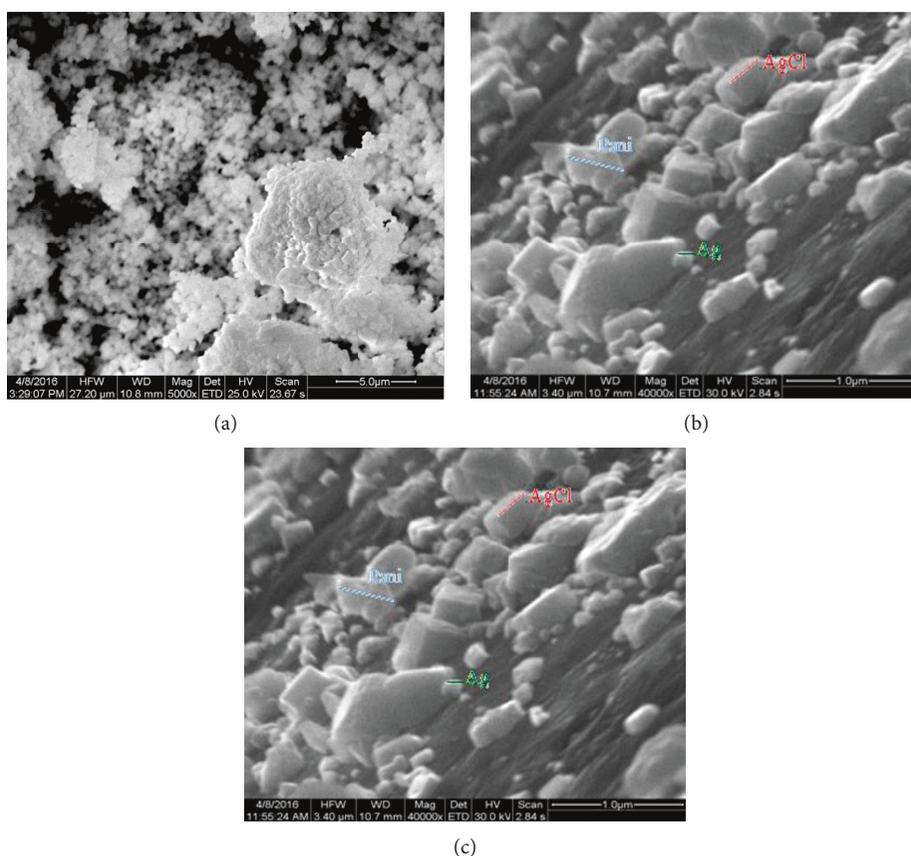


FIGURE 5: SEM images of the elaborated nanocomposite.

interpretations prove that nanocomposites are formed by polyaniline, silver metal, and AgCl nanoparticles.

3.5. Morphology Study. The SEM image of prepared nanocomposite is shown in Figure 5. It can be seen that silver chloride clearly appear in cubic form with a smooth surface. This is in agreement with the results of XRD. The particle sizes of AgCl particles ranged from 50 to 300 nm. On the

other hand, it can be seen that some tiny Ag nanoparticles of 5–20 nm are anchored on the surface of AgCl nanocubes, and Ag@AgCl clusters are agglomerated on that of PANI forming a spongy structure [14].

3.6. Mechanism of Formation of PANI/Ag@AgCl Nanocomposite. The possible mechanism of the formation of PANI/Ag@AgCl could be elucidated by the following

explanation. Generally, the preparation of PANI/Ag nanocomposite has been carried out in the literature by the use of aniline liquid which allows the formation of biphasic material formed by PANI and Ag nanoparticles. In our case, by using aniline chloride as a source of aniline instead of aniline liquid, the medium is rich with chloride anions which react with silver nitrate to form AgCl. It is well known that silver halides are instable under light due to their photosensitive property. On absorbing a photon, a silver halide particle generates an electron and a hole, and subsequently the photogenerated electron combines with a Ag^+ ion to form Ag^0 atom. Ultimately, a cluster of silver atoms is formed within a silver halide particle upon the absorption of photons. Since the molar ratio of Ag to Cl^- is corresponding to 3, then unreacted Ag^+ serves as oxidant for the polymerization of aniline; by this way, a ternary nanocomposite is obtained and then AgCl NPs acted as first nucleation of composite and PANI were formed around AgNPs to obtain PANI/AgCl@Ag ternary nanocomposite.

3.7. Electrical Properties. The frequency-dependent electrical conductivity σ_{ac} of the nanocomposite has been determinate by the Almond-West universal power law [15]:

$$\begin{aligned}\sigma_{\text{tot}}(\omega) &= \sigma_{\text{dc}} + \sigma_{\text{ac}}(\omega), \\ \sigma_{\text{ac}}(\omega) &= A\omega^s, \\ \sigma_{\text{tot}}(\omega) &= \frac{lZ'}{(Z'^2 + Z''^2)},\end{aligned}\quad (3)$$

where Z' and Z'' are the real and imaginary parts of the impedance, l is the thickness, A is the electrode area coated on the surfaces of the samples, and s is the frequency exponent which generally is less than or equal to one.

Figure 6 shows the AC conductivity as a function of frequency, and we can observe that the AC conductivity for the formed nanocomposite starts constant and then increases rapidly from a given frequency. This abrupt rise in conductivity is related to the heterogeneity of nanocomposites [14]. This composite material (polymer-metal) is the seat of an intrinsic dipolar polarization, the appearance of mobile charges, and the elaboration of large dipoles on the particles [15]. The conductivity DC can be determined by the extrapolation of conductivity AC towards the zero limit of the frequency. The conductivity DC of our nanocomposite is 0.4 S/cm. We can conclude that our materials belong to the semiconductor class that has wide domains of application.

4. Conclusion

In summary, we have succeeded to prepare bifunctional PANI/AgCl@Ag nanocomposite by a facile and convenient method. The generation of AgCl and PANI was accompanied with the in situ formation of metallic Ag by photo-reduction by light and reduction of Ag^+ by aniline species. From spectroscopy and XRD study, we have shown the coexistence of these three phases. It is interesting to note that

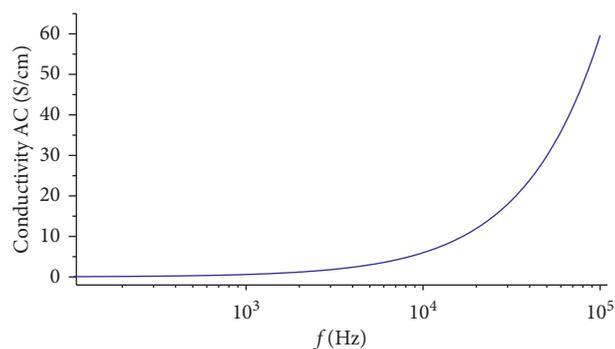


FIGURE 6: AC conductivity spectra of PANI/Ag@AgCl.

Ag nanoparticles coexist with acceptable quantity, and they are dispersed on the nanocubic surfaces of AgCl. On the other hand, the AC conductivity of nanocomposite shows the same behavior of common disordered material.

Data Availability

The authors declare that all data supporting the findings of this study are available within the article and supplementary materials.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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