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Research Article

Characteristics of Silver-Hydroxyapatite/PVP Nanocomposite

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Abstract Metal nanoparticles play an important role in many different areas such as catalysis, electronics, sensors, and cancer therapy. Silver, in its many oxidation states (Ag^0, Ag^+, Ag^{2+}, and Ag^{3+}), has long been recognized as having an inhibitory effect towards many bacterial strains and microorganisms commonly present in medical and industrial processes. Silver was introduced in various materials including hydroxyapatite due to its biocompatibility. The unique size-dependent properties of nanomaterials make them superior and indispensable. In this work, nanohydroxyapatite/polyvinylpyrrolidone composite was doped with 2 different concentrations of silver nanoparticles prepared by reduction method. Several techniques like TEM, XRD, FT-IR, and SEM with EDS were used to characterize the prepared samples. The bioactivity test (soaking in SBF) at different short time intervals was characterized by using inductively coupled plasma-optical emission spectroscopy (ICP-OES) method. It is demonstrated that silver-doped nanohydroxyapatite obviously improves the bioactivity of the apatite at the early stages of immersion. The antibacterial inhibition over 3 types of bacteria (*Staphylococcus aureus, Streptococcus mutans, and Pseudomonas*) is under investigation.

Keywords hydroxyapatite; silver; nanobiomaterials; bioactivity

1 Introduction

Technologies utilizing nanoparticles are based on the notion that materials constructed from particles below a critical length dimension display very unique chemical and physical properties [4]. The properties of a "building block" nanomaterial are highly dependent upon the nanoparticles size, shape, and composition. However, it is the size dependence which allows nanoparticles to be engineered to have specific properties to serve various functions, including medical applications [1,6]. Nanoscale silver materials are also extremely chemical durable [2,5]. In the case of colloidal silver suspensions, smaller particles contain more active surface sites for liquid-solid interactions and are, therefore, more likely to remain dispersed. For thousands of years, it has been known that silver ions exhibit strong inhibitory effects towards a broad spectrum of bacterial strains [2]. In our previous work, (Mostafa et al. 2009) [3], we studied the effect of two types of polymers polyvinyl alcohols (PVA) and polyvinylpyrrolidone (PVP) on the synthesis of nanohydroxyapatite. The results showed that the polymer affected the crystal morphology and not the phase composition of the product. This work describes the physical characteristics of silver nanoparticles when it is conjugated with nanohydroxyapatite polymer matrix composite. Also, it describes how silver affects the bioactivity of the nanohydroxyapatite.

2 Materials and method

In situ preparation method of nanohydroxyapatite was carried out in the presence of polyvinylpyrrolidone HA-PVP named HAP (Mostafa et al. 2009). Powders obtained were about 50 nm. Silver nanoparticles were prepared by the borohydride reduction method. A solution of 0.03 M citrate was stirred vigorously, then a solution of 7×10^{-4} M PVP was added. Addition of a solution of 1.4×10^{-3} M $AgNO_3$ (25 mL) with a slow stirring for about 10 minutes was added. Few drops of $NaBH_4$ solution were added with continuous stirring for another 10 minutes. The Silver nanoparticles prepared were brownish and had absorption maximum at 400–408 nm by UV spectroscopy. Transmission electron microscope (TEM) was used to determine the size and monodispersity of the resulting nanoparticles (data not shown).

Two different volumes of Ag solution (1.5 mL and 5 mL) (named P1.5 and P5, resp.) were added to 1 g of the prepared nanohydroxyapatite/PVP composite left to dry at 50 °C over night. The analyses of powders used are presented in Table 1.

Sample symbol	[Ca] ppm	[P] ppm	[Ag] ppm	Molar (Ca/P)
HAP	30.68	12.82	—	1.85
P1.5	37.96	15.39	0.006	1.90
P5	26.75	10.8	0.01	1.91

Table 1: Concentrations (ppm) of the Ca, P, and Ag elements in powders prepared and the corresponding Ca/P molar ratios.

The as-dried prepared powder samples were characterized by using TEM Philips CM-20 operated at 200 KV, ICP-OES, and X-ray diffraction (XRD) technique using Philips PW3710 diffractometer with Cu Kα radiation. For estimation of the "*in-vitro*" bioactivity, the powders were immersed in SBF. After soaking in SBF at different times (30 minutes, 9 hours, 12 hours, 48 hours and 120 hours), the granules were filtered, cleaned with ethanol, and dried in air. The physico-chemical properties of the filtered granules were studied by XRD. In addition, the ICP-OES (spectro) was measured over the solution in the goal to evaluate the variations of calcium and phosphorus concentrations versus soaking time in SBF liquid. "*In vitro*" test was realized by soaking 30 mg of powder into 60 mL of simulated body fluid with mineral composition nearly equal to those in human blood plasma at 37 °C. The ionic concentrations of SBF solution were presented in Table 2.

	Ionic concentrations, ppm						
	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	HPO_4^{2-}
Conc. Ppm	326	195	100	36	256	5274	96

Table 2: Concentrations of the SBF solution.

3 Results and discussion

Figure 1 showed the TEM of silver hydroxyapatite/PVP composite material. It can be seen that no agglomeration. The particles seemed to be like fibers with at least more than 100 nm in length and 10–20 nm in diameter. Table 1 showed the results obtained by using ICP-OES method.

XRD diagrams show the effects of SBF on crystalline structure of silver-HA/PVP (P1.5) and silver-HA/PVP (P5), 14 days after immersion. The intensities of peaks at 2 theta 33°, 40°, 50°, and 57° increase after 14 days after immersion in SBF. However, the weight of all peaks increases with the time of immersion. This phenomenon is due to different interactions between chemical composition in the presence of silver and mineral composition of SBF. This effect is induced particularly from the presence of silver at different amounts. In the HA/PVP (HAP) without silver, no modifications were registered in Figure 2.

Obtained results by using ICP-OES method, presented in Figure 3, correspond to the kinetic of ionic exchanges between all compounds and SBF. It shows that the releasing

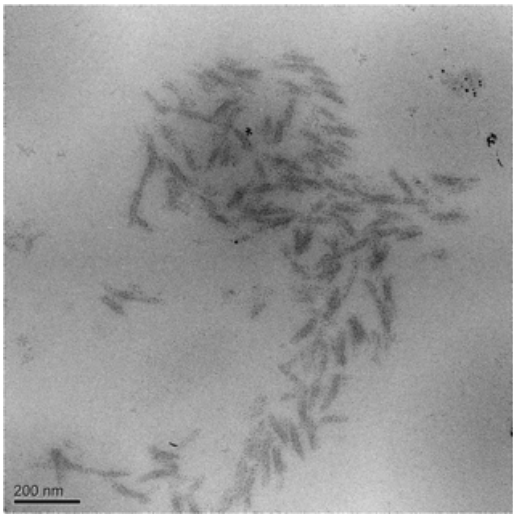

Figure 1: TEM of silver hydroxyapatite/PVP composite material.

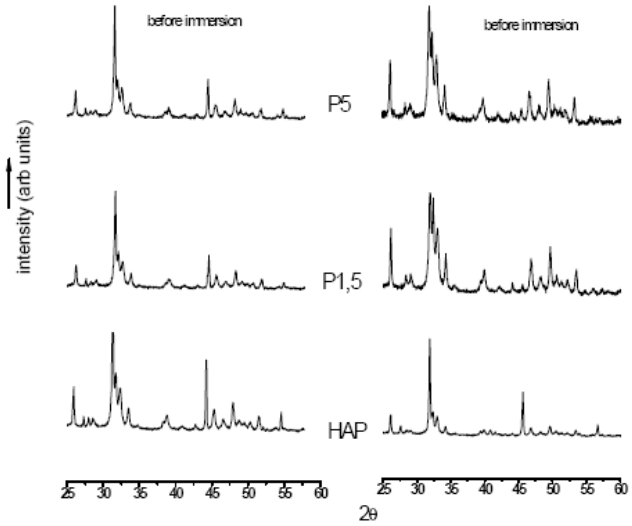

Figure 2: XRD of HA/PVP (HAP), silver-HA/PVP (P1.5), and silver-HA/PVP (P5) before and after 14 days of immersion.

of Ca and P in silver-HA/PVP (P1.5) and in silver-HA/PVP (P5) is slower than that in HA/PVP (HAP). This is an important result because some biomedical applications need the slowing of the releasing of Ca, P, and other atomic elements in biological environment. It depends on many factors like site of implantation, age, and other parameters.

4 Conclusion

This study highlights the effect of HA/PVP doped with silver. It offers more applications to surgeons. They can adapt the implanted biomaterial according to the site which presents the bone defect. The controlled kinetic of releasing of some chemical elements from used biomaterial to biological fluids can be controlled.

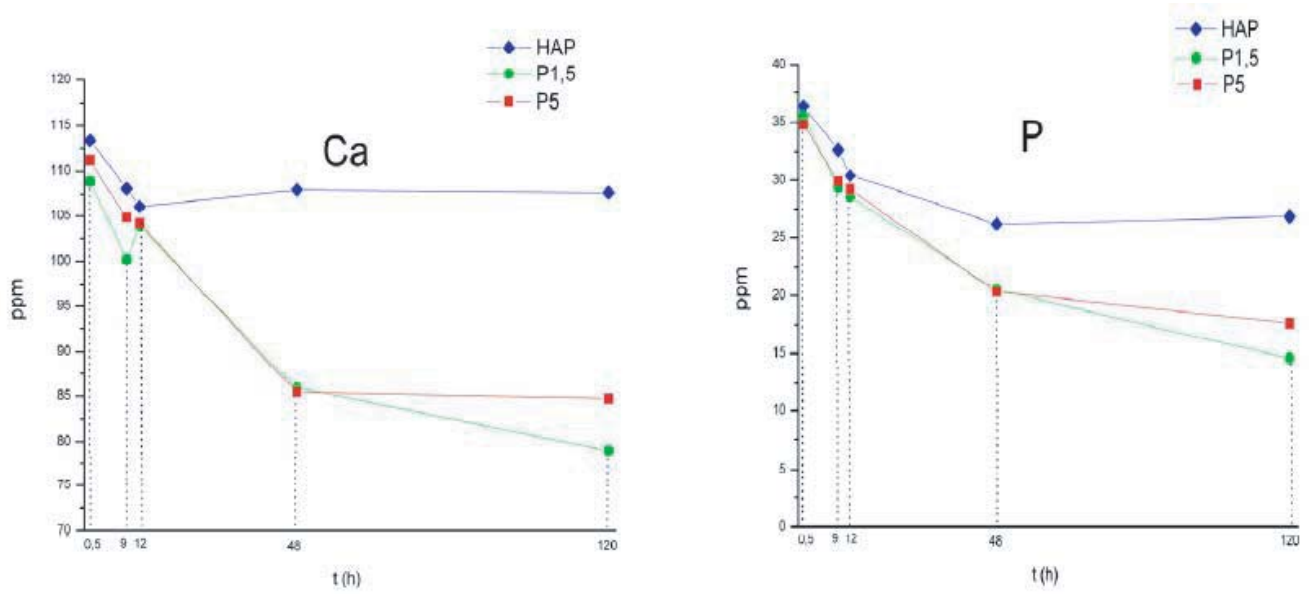

Figure 3: Evolution of elemental concentrations of Ca and P in SBF after soaking time.

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