

NEW BIONANOPARTICLES AND THEIR APPLICATION IN NANOMEDICINE

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Abstract. Biomedical nanotechnology presents revolutionary opportunities in the field against many diseases such as cancer, neurodegenerative diseases, as well as detecting microorganisms and viruses associated with infections. There has been enormous interest in the field of preparation of nanostructured advanced materials by physical methods have become an important branch of high technological materials. In this paper the use of nanocomposites of inorganic materials in organic matrices or photosensitizer-stabilised gold or silver nanoparticles for photodynamic therapy of cancer, is presented. A combination between typical properties of organic polymers (specific absorption of light) with the advantages of nanoparticles, particularly the high specific surface and the high ratio of surface atoms to inner sphere atoms, is discussed. For both types of nanoparticles, gold and silver, the changed topography of the film surface after deposition is caused by a local material transport and a material separation between formed particles (probably AgNO₃) and the embedding polymer matrix. It is assumed that small particles of Ag are formed by a thermal redox process between Ag⁺ and the polymer. The structure of the prepared hybride nanocomposites by means of X-ray diffraction, IR, XRD, XRF and optical spectroscopy, etc. will be evaluated.

Keywords: Nanotechnology, nanocomposites, nanoparticles, nanomedicine, PVP, PVA.

1. INTRODUCTION

The development of nanomaterials, i.e. compounds in which an inorganic solid is associated with organic entities interacting at molecular level, is a new and innovative direction for the preparation and application of new materials. Few examples of experimental procedures used in order to obtain stable nanomaterials involve:

- intercalation processes;
- the grafting of organic groups onto the surface;
- inorganic solids, or the entrapment of molecules in organic matrices by different methods.

The organic-inorganic systems resulting from the interactions of different organic species with inorganic matrices show controlled properties useful for selective nanocomposite materials design. The combination of organic/inorganic compounds has the power to produce highly complex structures and functionalities.

Metallic nanoparticles of definite size are easily synthesized via a “bottoms-up” approach and surface-modified with special functional groups. As a result of such plasmon absorption bands the optical properties of copper, silver and gold nanoparticles in solution have received considerable attention. It has been shown that the colour of noble metal nanoparticles depends on the size and the shape of the particles, as well as on the refractive index of the surrounding medium. In addition, it has been documented that bimetallic nanoparticles generally show different physico-chemical properties as compared to their individual particles.

1.1. Plasmon Resonance (PR) in Silver Nanoparticles

PR – collective oscillations of conducting electrons in metal nanostructures

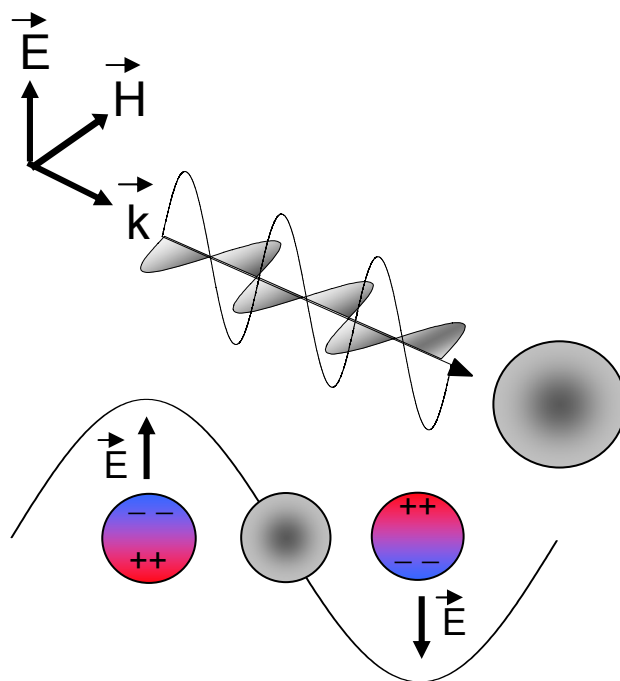


Figure 1: Ag nanoparticles exhibit PR in the visible spectral range

$$\omega_p = (\mathbf{ne}^2/\epsilon_0\mathbf{m}_e)1/2 \quad (1)$$

$$\epsilon_{\text{metal}}(\omega_p) = 0$$

1.2. Optical properties of Silver Nanoparticles

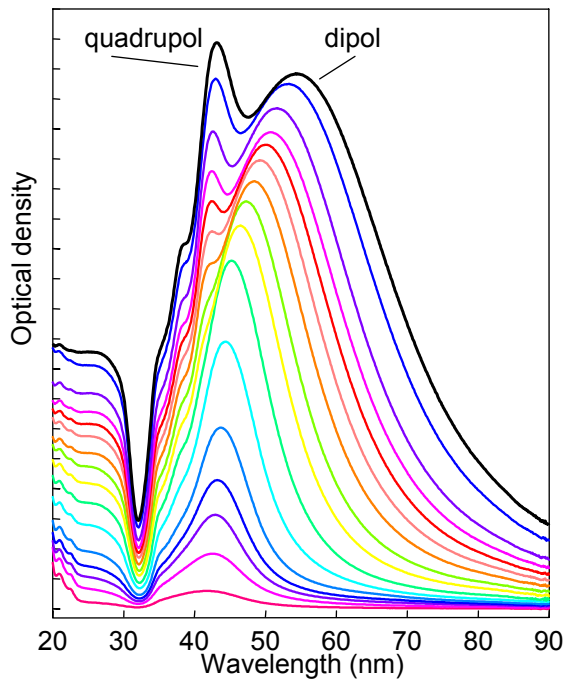


Figure 2: Extinction Spectra of Ag Nanoparticles as a Function of Size

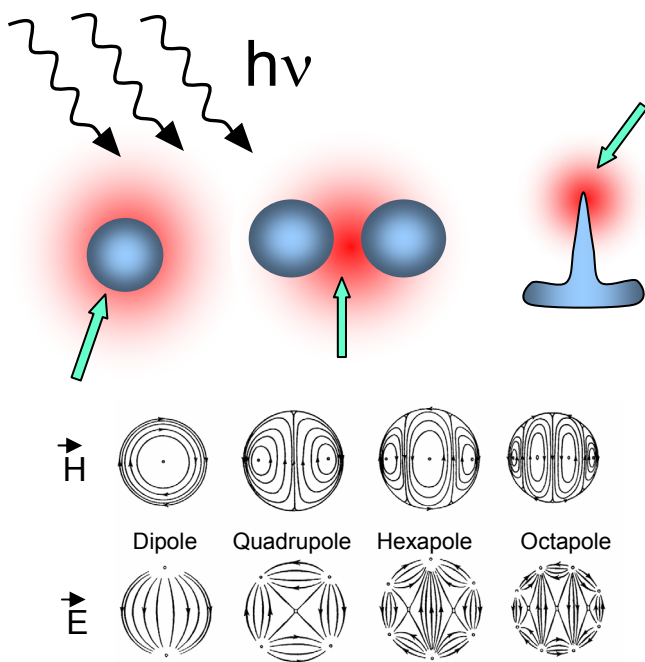


Figure 3: Local field in enhanced. Several orders of Magnitude.

2. PROCESSES

Chemical reduction of noble metal salts in aqueous medium or organic solvents with capping agents such as poly(vinyl pyrrolidone) (PVP) and poly(vinyl alcohol) (PVA) has been used to prepare shape-controlled noble metal nanoparticles. Linear polymers and micelles are

potential candidates as capping agents to control the size and shape of metal nanoparticles.

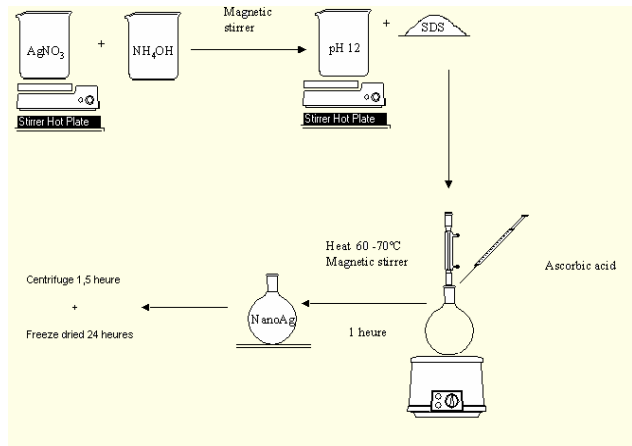


Figure 4: Synthetic chemical of preparation.

In most cases, capping agents such as PVP, PVA are mixed with the solutions of noble metal salts prior to adding reducing agent.

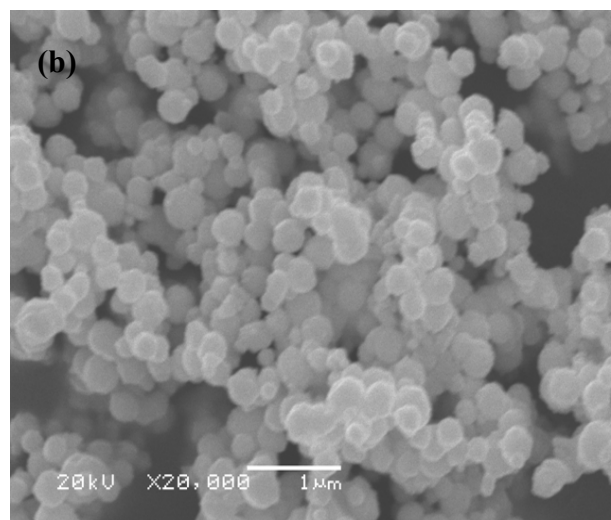
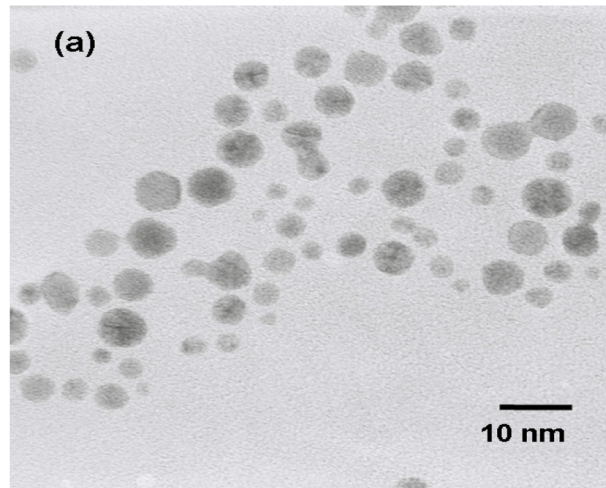


Figure 5: Nanoparticles: (a) gold and (b) silver.

This procedure leads to the change of the relative concentration of capping agent with time and therefore leads to a wide range of sizes of the resulting nanoparticles as the reaction proceeds. Here we present a new and simple chemical protection– reduction technique for producing shape-controlled Au nanostructures at room temperature, using $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ as the gold source or AgNO_3 as the silver source and PVP or PVA, as the capping agent.

The reducing agent and the capping agent were mixed prior to addition to the solution above solution was then added dropwise to a 5 ml aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}/\text{AgNO}_3$ at a rate of 5 ml min⁻¹ and stirred for 36 h. The reaction product was isolated by centrifugal separation and then immersed into oleic acid for later use. The resulting pale green colloidal dispersion of Au/Ag nanoparticles is stable for several months at room temperature. The formation of Au nanoparticles were monitored by UV–Vis spectra recorded by UV-Vis spectrophotometry.

Here, a classical route for the synthesis of gold colloids (*i.e.*, the alcoholic reduction of gold ions in presence of polymeric stabilizer) has been modified to produce gold-based quantum dots. Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Aldrich, 99.9%) has been used as metallic precursor and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, Aldrich, 99.8%) and polyvinylpyrrolidone (PVP, Aldrich MW = 10,000 a.m.u.) as reducing agent and stabilizer, respectively. A PVP, amount ranging from 2.0 to 8.0 g, was dissolved in 20 ml of ethylene glycol at room temperature. The solution was kept at 60^o C under vigorous magnetic stirring. Then, 5.0 mg of HAuCl_4 , dissolved in 1 ml of ethylene glycol was injected in the hot PVP solution. During the gold nanoparticles formation the solution color changed from yellow to ruby-red. To end the reaction the reactive mixture was cast into 250 ml of acetone and the system was sonicated for a few minutes in order to remove the ethylene glycol from the Au-PVP nanocomposite. The Au-PVP system was used as precursor for the preparation of gold-derivatized nanoparticles. The material was stable for months in air at room temperature.

3. CONCLUSIONS:

In this paper the use of nanocomposites of inorganic materials in organic matrices or photosensitizer-stabilised gold or silver nanoparticles for photodynamic therapy of cancer, is presented. A combination between typical properties of organic polymers (*specific absorption of light*) with the advantages of nanoparticles, particularly the high specific surface and the high ratio of surface atoms to inner sphere atoms, is discussed.

The main objective of the present proposal is the molecular design, synthesis of novel molecular materials capable of energy and/or electron transfer or exhibiting considerable degree of ground state charge transfer. The project will focus on the new chemical procedures for

the synthesis of novel systems with the goal to control electron and/or energy transfer for applications in molecular electronics, photonics, nanotechnology and solar cells.

Two major scientific priorities will be:

- a. Preparation and investigation of immobilized metal nanoparticles as gold, silver in polypyrrole (PPy, PVP, PVA) by reaction between tetrachloroauric acid/silver nitrite and polymer in different media.
- b. structure and morphology characterization of investigated materials.

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