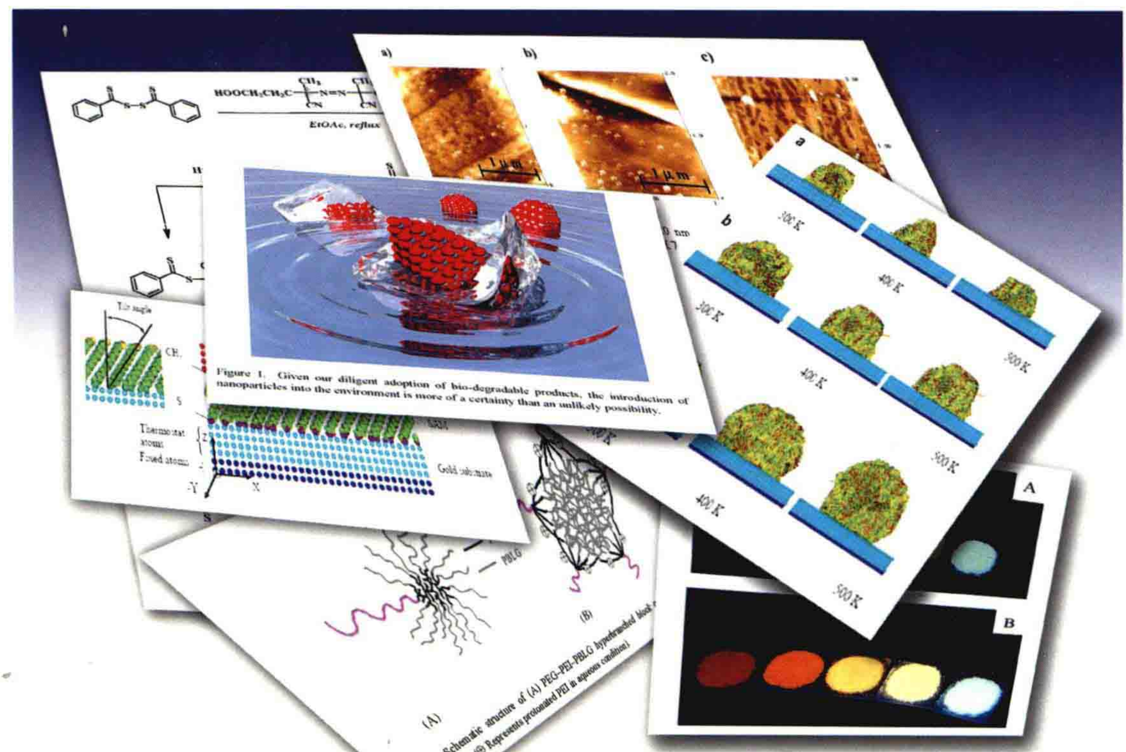
ADVANCES IN NANOTECHNOLOGY

Volume 13



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NOVA

ADVANCES IN NANOTECHNOLOGY

VOLUME 13

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nova publishers
New York

Library of Congress Cataloging-in-Publication Data

ISBN: 978-1-63482-367-8
ISSN: 2159-1490

Published by Nova Science Publishers, Inc. † New York

ADVANCES IN NANOTECHNOLOGY

VOLUME 13

Advances in Nanotechnology

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PREFACE

Nanotechnology is the study of the controlling of matter on an atomic and molecular scale and is also very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly. This book gathers and presents data on nanotechnology, including preparation and characterization of gold nanoparticles in liquid solutions; Nano-ZnO reinforced poly(ether ether ketone) biocomposites; magnetic nanoparticles; nanostructured materials as catalyst supports in olefins polymerization; gold clusters and nanoparticles in zeolites and zeolite-like materials; hybrid dispersed magnetic nanomaterial with core-shell structure based on polydiphenylamine-2-carboxylic acid; hybrid magnetic nanomaterial based on polyphenoxazine and Co nanoparticles; synthesis, characterization and significant applications of PANI-Zr(IV)sulphosalicylate nanocomposite; and synthesis of manganese oxide nanoparticles using similar process and different precursors.

Chapter 1 – Gold nanoparticles and their applications are currently intensively studied materials with promising properties that are used in many fields, including optoelectronics or catalysis. They are used in modern nanobiotechnology for the production of biosensors, visualization of cellular structures, targeted transport of drugs. Colloid solutions of nanoparticles are studied for their unique physical and chemical properties that are different from the "bulk" materials. In all applications of nanotechnology the size and shape of the nanoparticles play an important role. Numerous studies describe the unique properties of gold nanoparticles, which can be used in applications such as fuel cells, environmental and other chemical processes. In this chapter we summarized the basic techniques of preparation of nanoparticle solutions. Principles of applications on the basis of nanoparticle solutions (unique optical properties, in particular a localized surface plasmon resonance LSPR (localized surface plasmon resonance)) are described. The study of their optical properties depending on a stability and aggregation mechanisms of colloids is also presented. Change of the solutions stability may be accompanied by significant external change (shrinkage, discoloration) indicating adverse changes in properties (increase distribution, aggregation).

The particles with desirable properties can be synthesized by various approaches, as the result we can obtain the desired particle size, shape and distribution. To maintain the properties of the solutions we use different techniques (stabilized by electrostatic forces, polymer stabilization, chemical coating). Much attention is devoted to the method of preparation of ultrapure gold nanoparticles in solution by cathode sputtering directly onto polyethylene glycol or glycerol. This method allows to obtain the stable colloidal metal solutions ready for use without using of chemical reactions and stabilizing or reducing agents with wide applications based on theirs unique optical properties and anti-bacterial applications.

Chapter 2 – Poly(ether ether ketone) (PEEK) is a high-performance semicrystalline thermoplastic widely used as biomaterial for medical applications owed to its superior mechanical and tribological properties, biocompatibility, non cytotoxicity and bioactivity comparable to that of bio-inert titanium alloys. However, the characteristics of PEEK have to be tailored to match specific tissue properties. In this chapter, we describe the preparation of PEEK/ZnO nanocomposites with a view to use them as biomaterials for load-bearing applications like orthopaedic and trauma implants. For such purpose, raw and silane-modified ZnO nanoparticles at various loadings have been incorporated in the biopolymer matrix following a processing route based on cryogenic ball-milling and compression moulding. A detailed characterization was carried out to evaluate the effect of nanoparticle content and surface treatment on the morphology, thermal, mechanical, tribological and antibacterial properties of these bionanocomposites. Samples with silane-treated ZnO showed higher stiffness, strength, ductility, toughness and glass transition temperature whereas reduced coefficient of friction and wear rate compared to neat PEEK and composites with bare nanoparticles. Further, they displayed superior antibacterial activity against human pathogen bacteria *Escherichia coli* and *Staphylococcus aureus,* and the antimicrobial effect increased upon raising nanoparticle content.

Chapter 3 – Magnetic nanoparticles are well-fabricated nanomaterials that offer controlled size, shape, monodispersity as well as their stability towards oxidation, ability to be manipulated externally, enhancement of contrast in magnetic resonance imaging and versatile applications in biomedicine. Developing methods such as co-precipitation, thermal decomposition and/or reduction, micelle synthesis, and hydrothermal synthesis has made significant progress in the size and shape control of magnetic nanoparticles. The physicochemical properties of magnetic nanoparticles need to be well understood to improve their ability of hybrid interaction with various molecules. Magnetic nanoparticles could have many applications in biology and medicine, including protein purification, drug delivery, and medical imaging. Due to the potential benefits of multifunctional nanoparticles in biomedical applications, recent advances in nanotechnology have improved the ability to specifically tailor the features and properties of magnetic nanoparticles for these biomedical applications. Magnetic nanoparticles continue to garner widespread interest in biomedical applications, such as visualization agents in MRI, therapeutic vehicles for drug delivery and heat mediators in hyperthermia. Recent advances in colloidal synthesis and surface-functionalization techniques have greatly contributed to the design of functionalized magnetic nanoparticles with controlled properties and multifunctional capabilities. In general, surfactant/polymer coating, silica coating and carbon coating of magnetic nanoparticles or embedding them in a matrix/support are employed in the modification of magnetic nanoparticles. The surface-functionalization methods, in particular, have aided in obtaining magnetic nanoparticles coated with molecules with tailored functionalities that enhance their applications. We will review examples of the design and biomedical application of multifunctional magnetic nanoparticles. After their conjugation with proper ligands, antibodies, or proteins, the biofunctional magnetic nanoparticles exhibit highly selective binding.

The hybrid nanostructures, which combine magnetic nanoparticles with other nanocomponents, exhibit paramagnetism alongside features such as fluorescence or enhanced optical contrast. Such structures could provide a platform for enhanced medical imaging and controlled drug delivery. We expect that the combination of unique structural characteristics and integrated functions of multicomponent magnetic nanoparticles will attract increasing research interest and could lead to new opportunities in nanomedicine.

Chapter 4 – Polyolefins are the most widely used thermoplastic commodity nowadays due to their chemical and physical properties. The total production of polyethylene and polypropylene was over 100 million tonnes in 2009, accounting for more than 60% of all industrial polymer production in the world. Polyolefins production has been based on the Ziegler Natta and Phillips catalyst for many years, but these catalysts have been substituted for metallocene catalysts in some applications, since metallocene catalysts can produce polymers with specific and uniform microstructures. However, metallocenes are homogeneous catalysts and they have to become heterogeneous catalyst in order to be used in current plants on an industrial scale. Also, production of some materials such as bimodal polyolefins requires two or more kinds of catalysts linked on a support.

Support has an important role in the heterogeneous catalyst of modern polyolefins due to its direct influence in catalytic activity of metallocenes and in the final properties of the polymers obtained. Amorphous silica is the most used support and other materials such as zeolites, aluminum, clays, mesoporous, synthetic polymers and their combinations have been also used, looking for the best performance of the catalytic system. This chapter reviews and describes nanostructured materials as supports in catalytic systems to produce polyolefins with specific physical and mechanical properties. Synthesis methods for nanostructured materials based on mesoporous materials, zeolites, modified clays and other inorganic oxides are discussed. Also, techniques to anchor Ziegler Natta and metallocene catalyst on supports are described, with an emphasis on application of nanostructured material supports to obtain bimodal polyolefins and olefin copolymers.

Chapter 5 – The recent data related to the preparation and catalytic applications of gold nanoparticles supported onto zeolites and zeolite-like materials (MOFs) are reviewed. The most perspective reactions for the Au/zeolite systems are CO oxidation, partial oxidation of organic substrates, hydroamination and valorization of renewables.

Chapter 6 – Hybrid magnetic nanomaterial with core-shell structure, where particles of Fe_3O_4 form the core and polydiphenylamine-2-carboxylic acid is the shell, was obtained for the first time in the interfacial process. According to TEM data Fe_3O_4/polydiphenylamine-2-carboxylic acid nanoparticles have size $2 < d < 14$ nm. It was found by IR spectroscopy that the polymer shell is formed by C–C - joining into 2- and 4-positions of phenyl rings with respect to nitrogen. The obtained hybrid nanomaterial is superparamagnetic and thermally stable.

Chapter 7 – During the IR heating of polyphenoxazine (PPhOA) in presence of cobalt (II) acetate $Co(CH_3CO_2)_2{\cdot}4H_2O$ in the inert atmosphere at the temperature $T = 500–650$ °C the growth of the polymer chain via the condensation reaction of phenoxazine olygomers happens simultaneously with the dehydrogenation of phenyleneamine structures with the formation of conjugated C=N bonds. Hydrogen emitted during these processes contributes to the reduction of Co^{2+} to Co^{o}. As a result the nanostructured composite material in which Co nanoparticles are dispersed into the polymer matrix is formed. According to TEM Co nanoparticles have size $4 < d < 14$ nm. The investigation of magnetic and thermal properties of Co/PPhOA nanocomposite has shown that the obtained nanomaterial is superparamagnetic and thermally stable.

Chapter 8 – PANI supported novel PANI-Zr(IV)sulphosalicylate nanocomposite material has been synthesized via sol-gel method. The nanocomposite material was characterized on the basis of FTIR, XRD, SEM, TEM and Raman studies. Physiochemical properties of the material have also been determined. Bifunctional behavior of the material has been indicated by its pH titrations curves. The nanocomposite material exhibits improved thermal stability, higher ion-exchange capacity and better selectivity for toxic heavy metals. The ion-exchange material shows an ion-exchange capacity of 1.8 meq g^{-1} for Na^+ ions. Sorption behavior of metal ions on the material was studied in different solvents systems. The cation exchanger was found to be selective for Pb(II), Hg(II) and Zr(IV) ions. Analytically important separations of heavy metal ions in synthetic mixtures as well as industrial effluents and natural water were achieved with the exchanger. The observed band gap for the different samples was found to be in the range of 3.19 to 3.65eV which shows that nano-composite materials cover semiconducting range. Activation energy was also calculated using thermo gravimetric analysis. Membrane potentials of monovalent electrolytes namely KCl, NaCl and LiCl have been studied at different concentrations to examine the relationship between effective fixed charge density and transport properties of the membrane. Effective fixed charge densities were found to follow the order $K^+ > Na^+ > Li^+$. Nano-composite material has also been tested against the various bacterial and fungal strains and relatively higher activities were observed than the known antibiotics.

Chapter 9 – The aim of the present work is to compare the outcomes of sol gel synthetic technique with oxalic acid. The sol gel synthetic technique would be used on two different precursors: manganese acetate and manganese chloride. In a synthesis method using manganese acetate as a precursor, manganese oxalate dihydrate is first produced via the sol–gel process and then decomposed in the air, at high temperatures. The decomposition process leads to the emergence of Mn_3O_4. In other methods, Mn_2O_3 nanoparticle powder has been prepared using similar sol-gel processes and manganese chloride as a precursor. A comparitive study has been done on structural analysis by X-ray diffraction (XRD), surface analysis by scanning electron microscopy (SEM), and magnetic properties using a superconducting quantum interference device (SQUID) magnetometer.

CONTENTS

In: Advances in Nanotechnology. Volume 13
Editors: Zacharie Bartul and Jérôme Trenor
ISBN: 978-1-63482-367-8

Chapter 1

PREPARATION AND CHARACTERIZATION OF GOLD NANOPARTICLES IN LIQUID SOLUTIONS

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ABSTRACT

Gold nanoparticles and their applications are currently intensively studied materials with promising properties that are used in many fields, including optoelectronics or catalysis. They are used in modern nanobiotechnology for the production of biosensors, visualization of cellular structures, targeted transport of drugs. Colloid solutions of nanoparticles are studied for their unique physical and chemical properties that are different from the "bulk" materials. In all applications of nanotechnology the size and shape of the nanoparticles play an important role. Numerous studies describe the unique properties of gold nanoparticles, which can be used in applications such as fuel cells, environmental and other chemical processes. In this chapter we summarized the basic techniques of preparation of nanoparticle solutions. Principles of applications on the basis of nanoparticle solutions (unique optical properties, in particular a localized surface plasmon resonance LSPR (localized surface plasmon resonance)) are described. The study of their optical properties depending on a stability and aggregation mechanisms of colloids is also presented. Change of the solutions stability may be accompanied by significant external change (shrinkage, discoloration) indicating adverse changes in properties (increase distribution, aggregation).

The particles with desirable properties can be synthesized by various approaches, as the result we can obtain the desired particle size, shape and distribution. To maintain the properties of the solutions we use different techniques (stabilized by electrostatic forces, polymer stabilization, chemical coating). Much attention is devoted to the method of preparation of ultrapure gold nanoparticles in solution by cathode sputtering directly onto polyethylene glycol or glycerol. This method allows to obtain the stable colloidal metal

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solutions ready for use without using of chemical reactions and stabilizing or reducing agents with wide applications based on theirs unique optical properties and anti-bacterial applications.

INTRODUCTION

One of the most important areas and challenges of modern science is preparation of colloidal solutions of metal nanoparticles. Gold nanoparticles and their applications are currently one of the most studied materials that are used in many areas including catalysis or optoelectronics [1]. Gold nanoparticles are used in modern nanobiotechnology, for the production of biosensors, visualization of cellular structures [2], targeted drug delivery [3]. Colloidal nanoparticles are studied because they have unique physicochemical properties which differ from bulk [4]. The size and shape of nanoparticles plays an important role in all applications of nanotechnology [5]. Numerous studies [6] described the unique properties of gold nanoparticles which can be used in applications such as fuel cells, in environmental and other chemical processes [7]. The basic principles of applications concerning metal nanoparticles lie in their unique optical properties, in particular a localized surface plasmon resonance (LSPR) [8]. Great importance is the study of optical properties of metal nanoparticles, stability and aggregation mechanisms of colloids. Changing the stability of the solutions may be accompanied by significant external change (shrinkage, discoloration) indicating unfavorable change of properties (increase distribution, aggregation). To obtain particles having desirable properties, the result can be achieved by various approaches for the preparation of desired particle size, shape and distribution [9]. To maintain the properties of the solutions different approaches can be used (stabilization aid of electrostatic forces, the polymer stabilization, chemical treatment of the surface). The development of science in the field of nanotechnology is focused on improving of these methods.

1. HISTORY OF NANOPARTICLE PREPARATION

Colloidal metal solutions (from the Greek, "Kólla", means "glue") provide the best examples of nanotechnology throughout antiquity, the Middle Ages and modern times. The colloidal system may be called a system in which one substance is in the form of particles of different sizes distributed in another. The continuous phase is called the dispersion medium and dispersed material is called the dispersed phase. Metal colloids are "finely divided" components of catalysts, colored glass, dyes, photographic materials, and eventually, the "ancestors" of quantum dots [10]. Lycurgus Cup is an excellent example of late Roman culture and the use of "nanotechnology" in practice. Exceptional case of Roman glass, dated to the fifth century, clearly shows one of the greatest examples of nanotechnology in antiquity.

Lycurgus Cup is in the collections of the British Museum in London. If the cup is lit from the outside, it appears as green. When it is lit from the inside, the color changes to red, except for the king who looks violet. Characterization of cup was performed by methods TEM (transmission electron microscopy) and SEM (scanning electron microscopy). The researchers found that "wonderful" dichroism is present thanks to nano-sized particles of silver (66.2 %), gold (31.2 %) and copper (2.6 %), up to 100 nm in size were dispersed in a glass matrix. Most of nanometals have size 20-40 nm [10-11]. After the Romans also medieval craftsmen added metal components into the glass to create a beautiful stained-glass windows. Johann Kunckel in the middle of the 16th century created a beautiful glass that had a ruby color, method of infusion (blanching) of gold in the glass [12].

Colloidal gold salts were described in paper L'arte Vertraria by glassmaker and alchemist Antonio Neri in 1612, and because of this paper in the middle of the 17th century colloidal gold began to be used for the production of red ruby glass and painting on porcelain. "Purple of Cassius" is a mixture of colloidal gold nanoparticles and the tin dioxide, in a glass matrix [13]. A similar example can be seen in the use of silver nanoparticles for the production of lemon-yellow glass in the cathedrals of Europe. Formation of nanosilver in glass production was carried out *in situ*. In 1718 Hans Heicher published a summary of the use of gold for medical purposes, which describes the solutions and the gold stabilization with boiled starch, which is an example of stabilization of gold with ligands. In 1857 Faraday synthesized colloidal gold by reduction of aqueous $HAuCl_4$ and described its optical properties. It is important that the Faraday proved that the gold colloids are in the metallic state. He was also the first who registered the relationship between metal colloids, their environment, and optical properties and who described the protective effect of gelatin and other macromolecular compounds. The solutions of colloidal gold prepared it is still located at the Royal Institution in London.

At the turn of the 19th and 20th century Richard Zsigmondy described methods for the preparation of colloidal gold solutions using various reducing agents: hydrogen peroxide, white phosphorus and formaldehyde. Zsigmondy also suggested that the stability of solutions is due to the charge of colloidal particles. Along with Smoluchowski Zsigmondy calculated at what distance should be the gold nanoparticles to aggregate. For contributions to the theory of colloidal solutions received in 1925 the Nobel Prize. Another Nobel laureate Theodor Svedberg had a number of fundamental studies on the preparation and study of the sedimentation properties of solutions of colloidal gold. In his works Svedberg used more than 25 different reducing agents and formulated the mechanism of chemical condensation particle colloidal gold.

For a long time it was believed that gold can be a catalyst, but Bone and Wheeler in 1906 showed that gold foil accelerate the reaction between hydrogen and oxygen to form water. Colloidal solutions of gold ^{198}Au with a half-life of 65 h are used in oncology. We use non-radioactive nanoparticles today. Colloidal nanoparticles are also used for example in phototermic therapy. It is a promising direction in the treatment of tumors and infectious diseases. Gold nanoparticles have an absorption maximum in the visible or near infrared region when irradiated with light of the appropriate wavelength and are strongly heated. In the case that the nanoparticles are located inside the target cell (which can be achieved by surface modification, or by conjugation to an antibody [15]), the cells die. This method allows to selectively destruction of tumor via photo destruction due to thermal heating of the nanoparticles by means of laser pulses. There are two types of biosensors - biological and chemical. The principle of biosensor is to identify interactions between molecules. Receptor molecules which have affinity for the analysis of proteins and DNA can be prepared on the surface of nanoparticles. Gold is used as an underlayer, as it is an inert material in this case. If the solution in which the modified nanoparticles are located also contains the target molecules which interacts with the nanoparticles it results to an amplification of the electric dual layer.

The average gain is from 0.01 to 0.1 nm. To determine this slight gain we use e.g. SPR (surface plasmon resonance) [16].

2. Properties of Colloidal Solutions

2.1. Optical Properties

The optical properties can be investigated by studying the interaction of light with matter. The behavior of bulk electrons (by volume) of material differs from the behavior of electrons in nanoparticles [17]. Scattering and absorption of light therein has a series of particularities. For example, colloidal nanoparticles can be a different color as a result of specific interaction with the incident light. One characteristic of colloids may be a color that is changing, for example for the gold nanoparticles from ruby to blue, silver nanoparticles are characterized by a yellow color.

The size of nanoparticles is usually comparable to the mean free path of electrons. Electron mean free path for gold and silver is 40-50 nm [18]. LSPR arises not only in the metal nanoparticles, but also in system of "metal needles" or the rough metal surface. This phenomenon is used in optical microscopy, fluorescence microscopy or Raman microscopy [19]. Plasmon resonance is coherent excitation of free electrons in the conduction band, which leads to oscillations in the same phase. It arises when the size of metal nanoobjects is less than the wavelength of the incident radiation. This phenomenon usually occurs for nanoparticles of noble metals (gold, silver), also alkali metals and copper. For gold, silver and copper, the absorbance is in the visible light [20]. The absorption spectrum of gold nanoparticles can be seen in Figure 1. The intensity of absorption is directly proportional to the concentration of metal clusters in the solution. For spherical nanoparticles shows a single peak (Figure 1). The plasmon resonance of spherical nanoparticles is shown in [21]. The figure shows the interaction of the electric field of the incident light with the free electrons. The electric field polarizes the free electrons. Consequently, on opposite sides of the nanoparticles form charges, which leads to restoring force. There is a dipole oscillation of free electrons with the same frequency.

Energy of plasmon resonance depends on the density of free electrons, particle size, their shape, orientation in space, and the dielectric constant of the environment [22]. The larger the particle, the greater the proportion of higher order modes, since light can not homogeneously polarize particle. These higher order modes have maxima at lower energies. Consequently, the plasmon band shifted towards the red region increases with particle size. The width of plasmon bandwidth increases with increasing particle size. Increasing both the wavelength at the absorption maximum, and bandwidth with increasing particle size was confirmed by experiment [23]. When electrons flexibly collide with the surface the coherence is disturbed. The smaller size of the nanoparticles, the faster the electrons reach the surface and dissipate more quickly. Consequently, the peak width of plasmon resonance increases with increasing particle size.

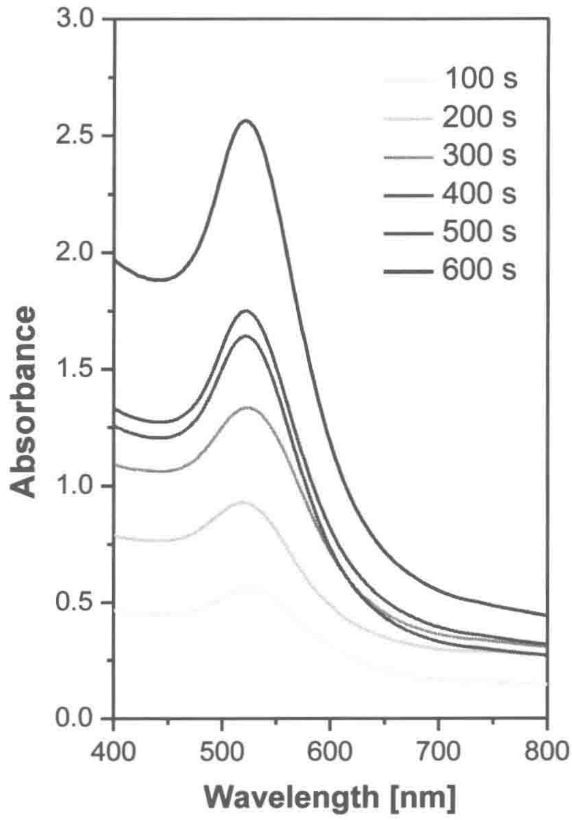

Figure 1. The UV-Vis absorption spectra for AuNPs solution in PEG/H_2O at a ratio of 1/9, deposition times varied in the interval 100-600 s, the samples were prepared at 30 mA.

2.2. Stability of Solutions

To maintain the properties of the colloidal solutions the stabilizers are used. The stabilizers are substances which prevent spontaneous growth (coagulation) of colloidal particles. Poorly stabilized nanoparticle aggregate, which limits further use. Nanoparticles may have high affinity for oxygen [24,25]. In this case partially oxidized nanoparticles are formed having a surface chemisorbed ions. Stabilization may be performed in various ways, such as e.g. electrostatic repulsion, steric hindrance, encapsulation of nanoparticles (such as creating a micelle layer on the surface surrounding the thiol groups, ligands, steric stabilization - large-functional polymer or dendrimer) [26]. Ions form a boundary layer between the dispersion medium and the dispersed phase. Macromolecular substances are adsorbed on the nanoparticle surface, creating a mechanical barrier that prevents aggregation.

The efficiency of stabilization can depend on the physical and chemical nature of the polymer [27], concentration, adsorption to the surface of the nanoparticles, its solubility in the dispersion medium. The protective polymer layer may reduce the interfacial tension effect of by interaction of the continuous phase with the dispersion medium. Interaction with the surface of the polymer nanoparticles can affect the growth factor, in the case of strong adsorption the growth on surface may be inhibited. Binding of macromolecule polymer nanoparticles can lead to selective growth of one of its sides. Full coverage of polymeric nanoparticles prevents from the diffusion of other components. On the other hand, the excess of stabilizer may lead to the formation of the second layer of molecules, which also reduces the aggregative stability of the system [28]. An insufficient amount of stabilizer leads to the fact that some nanoparticles may adsorb onto the surface of one of macromolecules resulting in flocculation.

The antibacterial activity of silver and gold nanoparticles depends on the particle size. The formation of aggregates of silver and gold leads to reduction of antibacterial properties of solutions [24]. Stable Au or Ag solutions may exhibit also antibacterial properties [25,29,30-32]. Based on the method of [33] colloidal gold nanoparticles were prepared [34] and it was determined their effect on various kinds of pathogenic Gram-positive and Gram-negative bacteria (Pseudomonas aeruginosa, Klebsiella oxytoca, Enterobacter faecalis, Klebsiella pneumoniae, Vibrio parahaemolyticus, Vibrio cholerae, Escherichia coli, Salmonella Typhim, Salmonella paratyphi, and Proteus vulgaris). Results were compared with the effect of the antibiotic tetracycline. In almost all cases, gold nanoparticles showed growth inhibition zone: highest against E. faecalis (11 mm), the lowest against K. pneumoniae (6 mm). In case of E. Coli gold nanoparticles are more effective than antibiotics.

3. Preparation of Colloidal Solutions

There are physical, chemical, photochemical and biological methods for the preparation of nanoparticles. Further methods for preparing of nanoparticles solutions can be divided into dispersing and condensation. Dispersing methods are based on the destruction of the crystal lattice of the material (laser ablation, cathode sputtering, dispersing arc), belongs to the type of "top-down". Condensation is usually realized by the reduction of salts of noble metals. Each method has its advantages and disadvantages. The classic method of preparing the colloidal solution of gold nanoparticles is based on a reduction of the tetrachloroauric acid with sodium citrate [35]. Due to disproportionation monodisperse nanoparticles are formed which size varies depending on the concentration of reducing agent and the size of the stabilizing ligand. Other methods to stabilize the nanoparticles can be carried out by forming the organic monolayer growth on the surface, size and shape are governed by the concentration of reducing agent and stabilizer. In some cases, the reducing agent is also the stabilizer [36]. As the reducing agent used is sodium citrate, alcohols, Na_2S, B_2H_6, $NaBH_4$, including hydrogen gas [10], sugars (glucose, fructose, sucrose) [37]. We can use white phosphorus or hydrazine, however, these compounds are highly toxic and solutions obtained by these methods can not be used in biological applications.

3.1. Dispergation Methods

(i) Laser Ablation

This method differs from traditional methods of preparing nanoparticles. The method is based on the irradiation of metal target immersed in the surfactant solution or water with laser pulses. Mafuné et al. prepared spherical silver nanoparticles with the distribution of 5-30 nm [38]. E.g. silver nanoparticles were produced by laser ablation of the silver plate in an aqueous solution of $C_{12}H_{25}SO_4Na$. Water acts as a substrate for the formation of