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Physico–chemical and mechanical properties and antibacterial activity of silver/poly(vinyl alcohol)/graphene nanocomposites obtained by electrochemical method

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ABSTRACT

Silver/poly(vinyl alcohol) and silver/poly(vinyl alcohol)/graphene nanocomposites in different forms (colloid dispersion, thin films and hydrogel discs) were synthesized by electrochemical reduction of Ag^+ ions at constant current density. CV, Raman, XRD, FT-IR, and XPS analyses were used to characterize the interactions between silver nanoparticles, PVA molecules, and graphene. Ag/PVA/Gr nanocomposites had better mechanical and thermal properties and higher antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* than Ag/PVA nanocomposites. Slow silver release, as well as a high remaining silver content (76%) after 28 days in simulated body fluid confirmed that both Ag/PVA and Ag/PVA/Gr nanocomposites are capable of maintaining sterility over time.

1. Introduction

Graphene (Gr), a single layer of hexagonally arrayed sp^2-bonded carbon atoms, has exceptional mechanical and optical properties, as well as electrical and thermal conductivity [1–3], and has therefore been applied in sensors, tissue implants, wound dressings, and soft transducers to control drug delivery and target cells [4–7]. Graphene in composite materials can be present in a chemically modified form or in a pristine-like state [8,9].

Hydrogels are especially interesting as tissue substitutes because their high water content makes most of them nontoxic, biocompatible, and environmentally friendly [10]. However, hydrogels have poor mechanical properties and/or are too brittle to maintain shape. Poly(vinyl) alcohol (PVA) is a water-soluble synthetic polymer with high hydrophilicity, biocompatibility, and nontoxicity. It has excellent film-forming, emulsifying, and adhesive properties, so it can be used as a carrier for drug delivery, as well as a component of biomedical materials [11–14]. PVA hydrogels have attracted great interest in the fields of tissue engineering and regenerative medicine as matrices for repairing and regenerating a wide variety of tissues and organs [12]. There is growing interest in incorporating nanomaterials into polymer matrices to create antibacterial and biocompatible polymer nanocomposites for a wide range of applications, such as thin films for biosensors and biomedical devices, fibers for wound dressing, and dispersions with antimicrobial properties [15,16]. The addition of graphene, even at a very low concentration (usually less than 5%), into a polymer matrix can significantly improve the mechanical, thermal, electrical, and gas barrier properties of the polymer [17–22].

Among noble-metal nanoparticles, silver (Ag) has been used most extensively as an antibacterial agent. At the nanoscale, Ag exhibits remarkable physical, chemical, and biological properties [23,24]. Ag ions and Ag-based compounds exhibited strong biocidal effects on many species of bacteria [25]. The use of Ag/polymer nanocomposites as antibacterial agents, however, is relatively new.

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Because of their high reactivity due to a large surface to volume ratio, nanoparticles have a crucial role in inhibiting bacterial growth [23,26–30]. Highly pure metal nanoparticles as well as the possibility of precise control of particle size can be achieved by electrochemical synthesis by adjusting the current density or applied potential [28,31]. This procedure is therefore highly attractive for creating nanocomposites for biomedical applications.

In this work, silver nanoparticles (AgNPs) were electrochemically synthesized in colloid dispersion by reduction of silver ions, using PVA as a capping agent, with and without graphene. The effect of the graphene on the amount and size of AgNPs was investigated, as well as the interaction between AgNPs, graphene, and PVA. An additional aim was to prepare Ag/PVA and Ag/PVA/Gr thin films and hydrogel discs from synthesized colloid dispersions and to investigate their physico–chemical and mechanical characteristics, thermal stability, silver release, and antibacterial activity. These materials have potential for use in wound dressings, soft tissue implants, and drug carriers.

2. Experimental

2.1. Materials and methods

The following chemicals were utilized in this work: fully hydrolyzed PVA powder ("hot soluble", Mw = 70,000–10,0000 g mol^{-1} Sigma, St. Louis, MO, USA), $AgNO_3$ (M. P. Hemija, Belgrade, Serbia), KNO_3 (Centrohem, Stara Pazova, Serbia), and graphene powders (Graphene Supermarket, Calverton, NY, USA). In all experiments, ultra-pure water from a Milli-Q system (Millipore, Billerica, MA, USA) was used as well as N_2 gas of high purity (99.5%, Messer Tehnogas a.d., Belgrade, Serbia).

2.2. Preparation of Ag/PVA and Ag/PVA/Gr colloid dispersions

To prepare Ag/PVA, PVA powder was first dissolved in hot water (90 °C), and after cooling of the solution at room temperature, it was mixed with KNO_3 and $AgNO_3$ to obtain a solution with a final concentration of 10 wt. % PVA, 0.1 M KNO_3, and 3.9 mM $AgNO_3$. To prepare Ag/PVA/Gr, graphene was added to dissolved PVA under vigorous stirring. After the solution was cooled to room temperature and sonicated, KNO_3 and $AgNO_3$ were added to obtain a final concentration of 10 wt. % PVA, 0.01 wt.% Gr, 0.1 M KNO_3, and 3.9 mM $AgNO_3$.

Electrochemical reduction of silver ions was performed galvanostatically using a Reference 600 potentiostat/galvanostat/ZRA (Gamry Instruments, Warminster, PA, USA) in an electrochemical cell containing 50 cm^3 of PVA solution or PVA/Gr dispersion. Two platinum electrodes were employed as working and counter electrodes, and a saturated calomel electrode (SCE) was used as a reference electrode. The applied current density was 40 mA cm^{-2} and the reaction time was 30 min. Synthesis was performed under continuous stirring; N_2 was introduced in the solution 20 min prior to synthesis, followed by continuous N_2 flow over the solution during synthesis.

2.3. Preparation of Ag/PVA and Ag/PVA/Gr films

Synthesized Ag/PVA and Ag/PVA/Gr colloid dispersions were poured slowly into a Teflon dish. The solvent was then allowed to evaporate at room temperature for 3 days, and the samples were further dried at 60 °C for 2 days to completely remove the remaining water to yield Ag/PVA and Ag/PVA/Gr composite films by casting. Films with an average thickness of approximately 70 μm were peeled off the substrate for testing.

2.4. Preparation of Ag/PVA and Ag/PVA/Gr hydrogel discs

Synthesized Ag/PVA and Ag/PVA/Gr colloid dispersions were poured slowly into a Petri dish, and subjected to five cycles of successive freezing and thawing (one cycle involved freezing for 16 h at −18 °C and thawing for 8 h at 4 °C). The obtained hydrogels were cut into small discs (d = 10 mm).

2.5. Methods of characterization

2.5.1. UV–visible spectroscopy (UV–Vis)

UV–Vis spectra of Ag/PVA and Ag/PVA/Gr colloid dispersions were recorded by a UV-3100 spectrophotometer (MAPADA, Japan) in the wavelength range between 200 and 1000 nm.

2.5.2. Transmission electron microscopy (TEM)

TEM of the Ag/PVA and Ag/PVA/Gr colloid dispersions was performed using a100 CX electron microscope (JEOL Ltd., Tokyo, Japan) operated at 100 kV.

2.5.3. Cyclic voltammetry (CV)

CV measurements of the Pt electrode in Ag/PVA and Ag/PVA/Gr colloid dispersions were performed using two platinum electrodes as working and counter electrodes, and saturated calomel electrode (SCE) as a reference electrode, using a Reference 600 potentiostat/galvanostat/ZRA (Gamry Instruments) at a scan rate of 50 mV s^{-1}, in the potential region from −1 to 1 V vs. SCE, starting from the open circuit potential, Eocp. All potentials are reported versus the SCE, and stationary voltammograms are shown.

2.5.4. Field emission scanning electron microscopy (FE-SEM)

Surface morphology of Ag/PVA and Ag/PVA/Gr films was analyzed by FE-SEM (LEO SUPRA 55, Carl Zeiss, Germany) used a TESCAN MIRA 3 XMU operated at an acceleration voltage of 200 kV.

2.5.5. Raman spectroscopy

HR-Raman analysis of Ag/PVA and Ag/PVA/Gr films was carried out using a Renishaw Invia Raman spectrophotometer equipped with a 514 nm argon laser. The intensity used was 10% of the total power (50 mW). The spectral range of the analysis was 3500–100 cm^{-1}.

2.5.6. Fourier transform infrared spectroscopy (FT-IR)

FT-IR analysis of Ag/PVA and Ag/PVA/Gr films was carried out using KBr pellets in a Perkin Elmer (Spectrum One system) spectrophotometer. The scan was carried out in the range of 450–4000 cm^{-1} with a spectral resolution of 0.5 cm^{-1}.

2.5.7. X-ray diffraction (XRD)

Philips PW 1051 powder diffractometer with Ni filtered Cu Kα radiation (λ = 1.5418 Å) was employed for Ag/PVA and Ag/PVA/Gr films using a scan-step technique (2θ = 8–80°). Scanning step width was 0.05° with an exposure time of 50 s per step. Phase analysis was performed using the commercially available computer program EVA V.9.0 implemented in the PDF-2 database.

2.5.8. X-ray photoelectron spectroscopy (XPS)

XPS measurements of Ag/PVA and Ag/PVA/Gr thin films were carried out using a K-Alpha System (Thermo Electron) equipped with Al Kα X-ray radiation (1486.6 eV) and a micro-focused monochromator. Elemental profiling was carried out using Ar-ion sputtering.