Cellulose Acetate and Silver Nanoparticles

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Contributor: Klaudia Hurtuková

Natural patterns and structures provide inspiration for scientists of diverse technological backgrounds to create artificial products (from different materials) with similar properties as naturally occurring products. One such pattern is the naturally occurring honeycomb-like pattern (HCP). The surfaces of products with this pattern consists of thousands of interconnected hexagonally formed cells that create an efficient structure with a large surface area. The HCP, due to its excellent properties, such as structural and mechanical strength, low density, and porosity, has found applications in several areas, including architecture, chemical engineering, mechanical engineering, and biomedicine. HCP-like structures have also been widely used as carriers in tissue engineering (TE).

biopolymers | honeycomb-like pattern | surface nanostructures | silver nanoparticles | antimicrobial activity | surface morphology | antibacterial properties | silver sputtering | active materials

1. Overview

Fluorinated ethylene propylene modified by plasma treatment was used as a suitable substrate for the formation of the HCP structures. Further, we modified the HCP structures using silver sputtering (discontinuous Ag nanoparticles) or by adding Ag nanoparticles in PEG into the cellulose acetate solution. The material morphology was then determined using atomic force microscopy (AFM) and scanning electron microscopy (SEM), while the material surface chemistry was studied using energy dispersive spectroscopy (EDS) and wettability was analyzed with goniometry. The AFM and SEM results revealed that the surface morphology of pristine HCP with hexagonal pores changed after additional sample modification with Ag, both via the addition of nanoparticles and sputtering, accompanied with an increase in the roughness of the PEG-doped samples, which was caused by the high molecular weight of PEG and its gel-like structure. The highest amount (approx. 25 at %) of fluorine was detected using the EDS method on the sample with an HCP-like structure, while the lowest amount (0.08%) was measured on the PEG + Ag sample, which revealed the covering of the substrate with biopolymer (the greater fluorine extent means more of the fluorinated substrate is exposed). As expected, the thickness of the Ag layer on the HCP surface depended on the length of sputtering (either 150 s or 500 s). The sputtering times for Ag (150 s and 500 s) corresponded to layers with heights of about 8 nm (3.9 at % of Ag) and 22 nm (10.8 at % of Ag), respectively. In addition, we evaluated the antibacterial potential of the prepared substrate using two bacterial strains, one Gram-positive of *S. epidermidis* and one Gram-negative of *E. coli*. The most effective method for the construction of antibacterial surfaces was determined to be sputtering (150 s) of a silver nanolayer onto a HCP-like cellulose structure, which proved to have excellent antibacterial properties against both G+ and G− bacterial strains.

2. HCP-Like Films

Natural patterns and structures provide inspiration for scientists of diverse technological backgrounds to create artificial products (from different materials) with similar properties as naturally occurring products [1][2]. One such pattern is the naturally occurring honeycomb-like pattern (HCP) [2][3]. The surfaces of products with this pattern consists of thousands of interconnected hexagonally formed cells that create an efficient structure with a large surface area. The HCP, due to its excellent properties, such as structural and mechanical strength, low density, and porosity, has found applications in several areas, including architecture, chemical engineering, mechanical engineering, and biomedicine [1][2][4]. HCP-like structures have also been widely used as carriers in tissue engineering (TE) [5].

Carriers that are mainly used in TE should mimic their extracellular matrix (ECM) morphology to ensure compatibility with living organisms and a three-dimensional (3D) structure. The ECM provides a natural environment for cultured cells, improving their adhesion, proliferation, and differentiation [6][7][8]. The surface morphology and porous nature of HCP-like structures make them irreplaceable substrates that are useful for cell differentiation and proliferation and the creation of functional and protective sites for the adhesion of biomolecules and growth factors and the production of specific drug delivery spaces [9]. A suitable alternative to carriers for different 3D cell cultures appears to be HCP-like film structures due to their geometric regularity, which can provide mechanical and biochemical advantages in the ECM, as in living organisms [10].

The HCP-like films can be prepared in two ways, namely the (i) breath figure (BF) and (ii) improved phase separation (IPS) approaches. In 1994, Widawski et al. first prepared HCP-like films [9][11] and found that factors such as the wet conditions, solvent type, polymer structure, and molecular weight affect the spontaneous organization of pores in periodic hexagonal fields [9]. This method was named the BF approach and has undergone substantial evolution in recent decades [12]. This method has attracted that attention of scientists, mainly due to its simplicity (few steps and low complexity of preparation), economic feasibility, use of harmless and affordable media (water), fast preparation times for many porous films with large surface areas, and applicability to various polymers, as well as this method allowing the tailoring of the size and shape of the pores by changing the process parameters, such as the air humidity and polymer concentration [9]. Although the BF method has many of the mentioned positive properties in terms of versatility and cost-effectiveness, it may have applicability for commercial polymers and in very humid process conditions [13].

To avoid high humidity, low volatility solvents can be added to the polymer solution. The IPS method uses a two-step film-forming process that can be used on many commercially available polymers. In this procedure, methanol (MeOH) is added directly to the polymer solution in the chloroform ($CHCl_3$) to form a tertiary polymer–good solvent–bad solvent system [13][14]. The ordered HCP-like structures on the surfaces of the substrates are formed after immersion of the sample into the polymer solution and subsequent drying in normal ambient air without adding additional moisture. The surface morphology of the structures depends mainly on the amount of MeOH added, but also on the concentration of the prepared solution and the ambient humidity; however, with the IPS method, the key factor affecting the pore shape, size, number, and density is the volume of MeOH in the solution. With a low MeOH content in the solution (below 10%, *v*/*v*), small round pores can be detected on the surface of the polymer. At the concentration of 15% (*v*/*v*), the pores have a hexagonal shape and are close to each other. In the case of a surplus or without the addition of methanol, the HCP-like structures are disrupted [13][14].

The cellulose acetate polymer is the most interesting of the cellulose derivatives for a wide variety of applications [15][16]. Due to its properties, including its relatively low cost, biocompatibility, biodegradation in human and animals [16][17], nonpoisonousness, mechanical strength, and dissolution in water, cellulose acetate has mainly been utilized in the field of TE [15][17][18]. It has also found use in bioapplications, drug delivery, antibacterial applications, and wound dressings [16][18][19]. Acetylation of cellulose reduces its crystallinity, providing improved biodegradability in vivo compared to plant cellulose and some of its derivatives. Ester and aerobic conditions also promote degradation [18][20][21]. IPS methods can be used with cellulose acetate to form regular hexagonal HCP-like structures.

In the search for a polymer with CA-like properties, the non-biodegradable polyethylene glycol (PEG) polymer has proven to be a suitable candidate. Comparable to CA, PEG is used mainly as a carrier, including for drug delivery or for applications involving organs and tissues [22][23]. Additionally, it is resistant to protein absorption, making it suitable for in vivo and in vitro studies [24]. PEG is mostly used in the form of hydrogels. Its properties imitate a three-dimensional environment similar to soft tissues and enable the diffusion of nutrients and cell waste [25][26]. PEG is a biodegradable polymer only when copolymerized with other biodegradable polymers, such as polyglycolic acid (PGA) and poly-L-lactide acid (PLA) [27]. Many scientists have reported that PEG-based surfaces offer protection from external contamination; however, the protection level is not very high and a certain number of bacteria can get onto the polymer [28][29][30][31]. This is why the main goal is to find an antibacterial agent that can efficiently eliminate bacterial contamination, while at the same time being biocompatible with the human body [32]. One such effective option is silver nanoparticles (AgNPs), since they have good antibacterial, antiviral, and antifungal activity [33][34][35][36]. Ag acts as an antibacterial agent in its ionic form at low concentrations, although no significant antibacterial effect was found in the Ag^0 form. The deposition of an Ag layer on a substrate’s surface is mostly achieved by sputtering in a vacuum environment [37].

3. Conclusions

The Ag nanostructure was prepared in two forms—as a thin layer on the HCP-like surface or sputtered into PEG, which was used for HCP preparation itself. Through combinations of the proposed modification methods (plasma exposure, addition of AgNPs into the source solution, direct Ag deposition, and isolated cluster formation), we managed to prepare HCP-like structures with differences in morphology, surface chemistry, wettability, and antibacterial properties. The plasma deposition process created an optimal surface for the formation of an HCP-like cellulose acetate structure. The HCP samples also had good surface wettability, and surprisingly the HCP-like pattern from cellulose acetate significantly suppressed the colonization of both *S. epidermidis* and *E. coli*.

Sputtering of thin Ag layers increased the contact angle of the pattern, causing particular disruption but combined with remarkable effects against both evaluated bacterial strains. The greatest decreases of CFU for both bacterial strains were determined for HCP-like units sputtered with Ag for only 150 s. The incorporation of AgNPs into the polymer solution with PEG also decreased the uniformity of the HCP pattern. The selected samples are good candidates for testing in vitro for scaffold applications in tissue engineering.

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