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Copper nanoparticles in glycerol-polyvinyl alcohol matrix: In situ preparation, stabilisation and antimicrobial activity

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ABSTRACT

Herein, we present a simple and affordable green synthesis of a nanocomposite material consisting of copper nanoparticles stabilized in a polyvinyl alcohol-glycerol matrix. TEM, UV-Vis and XRPD (X-ray Powder Diffraction) techniques were used to characterize the nanoparticles; properties of the polymer matrix were studied by NMR, IR and Raman spectroscopy as well as DSC measurements. The nanocomposite can be produced in two forms: gel and moldable plastic. Both the forms can be easily shaped at elevated temperature. The materials show very good long-term stability in air, protecting the produced copper nanoparticles from oxidation.

Furthermore, we proved the application potential of the new nanocomposite as catalyst in copper catalyzed Huisgen 1,3-dipolar cycloaddition of azide and alkyne (frequently used in *click-chemistry*). In addition, antibacterial tests have proven inhibition of bacterial growth of both Gram-negative (*Escherichia coli*) and Gram-positive (*Enterococcus faecalis*) bacteria in the presence of the nanocomposite.

1. Introduction

Copper and its alloys have been utilized for their antibacterial properties almost since their discovery, even long before the microbial nature of diseases was revealed. Compared with lead used in the past for similar purposes, copper is an essential trace element for flora and fauna; however, it is toxic for some microorganisms. Therefore, copper nanoparticles (NPs) are currently an object of intensive research, owing to their interesting bactericidal properties [1–6]. These results open gates to promising applications, especially in the field of fight with antibiotic-resistant bacteria [7]. On the other hand, copper NPs exhibit potential cytotoxic effect [8,9], which raises some uncertainties since the oxidative stress causes drop in cell viability [1]. Free copper enables catalysis of reactive oxygen and the ability to reach various organs in human body is quite natural for nanoobjects. This can possibly cause DNA damage and lead to serious diseases such as cancer. Apart from the application in biology, copper NPs possess interesting catalytical properties. Recently, researchers have focused on catalytic properties of Cu nanosystems, which have been used for cross-coupling reactions performed at room temperature [10], Huisgen 1,3-dipolar cycloaddition [11,12], or in sensors for glucose detection [13].

In general, copper NPs can be synthesized by various methods: thermal decomposition of precursors [3]; reduction from a solution by mild reducing agents, e.g. ascorbic acid [2] or polyols [14]; electrochemical methods, for example liquid phase plasma reduction process [15]. Other, rather miscellaneous, methods for copper NPs preparation include photoreduction [16], microwave-assisted

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syntheses [17], microemulsion techniques [18], laser ablation [19] or even synthesis taking the advantage of Co-60 gamma radiation [20]. The main drawback of most of the aforementioned methods is that they require rather expensive and complicated equipment and powerful energy supply; the only exception is the direct reduction method. However, during the reduction process, toxic solvents (e.g. ethylene glycol) are usually used to stabilize the NPs. The resulting mixture has an unpredictable impact on environment. Fortunately, environmentally friendly precursors can be also used in this approach [2]. Therefore, modified direct reduction seems to be the method of choice for copper NPs synthesis.

As an affordable and environmentally friendly solvent and reduction agent, glycerol can be used for various syntheses of heavy metals compounds [21,22] and their respective nanoparticle systems [14,23–26]. This alcohol has many interesting properties such as high boiling temperature, low toxicity and very favourable price. As a reducing agent, it is used for various large scale reduction reactions, because it allows controlling their kinetics by temperature elevation up to 563.15 K (290 °C). The interaction of hydroxyl groups in glycerol with the surface of NPs leads to significant metal NPs stabilisation [27]. Viscosity of glycerol can be easily adjusted by either change of temperature or by addition of water, which is helpful during NPs preparation. Due to its properties, glycerol is often used as a plasticizer in some polymers [28–30].

Polyvinyl alcohol (PVA) has found various industrial applications – for example as a textile sizing agent, an adhesive for wood, textile and leather and a glue thickener. PVA is also a component of medical products such as artificial tears. Last but not least, it can be used as a NPs stabilizer [31–33]. Its affordability, low ecotoxicity, biodegradability (albeit slow) and sustainable production are the main factors that mark it as a reasonable precursor for large scale NPs production.

Copper NPs-polymer composites have recently been in the centre of attention for various reasons, be it their potential biocompatibility and antimicrobial activity [5,6] or experiments seeking to enhance thermal conductivity of polymer materials [34]. However, a copper NPs-containing composite based on PVA has not been reported to this date.

For the massive application of nanomaterials as antimicrobial agents, their health and environmental safety are of great importance. Similarly, industrial safety of the very process of fabrication is required. Therefore, the development of new and safe large scale preparations of these materials is desired. In this contribution, we present a new method for the preparation of copper NPs, which are directly in-situ stabilized by the present polymer matrix. We show that although the Cu NPs are embedded in the glycerol-PVA matrix forming a nanocomposite, they retain their bactericidal as well as catalytic activity.

2. Experimental

Polyvinyl alcohol (PVA; avg. mol. wt 72000 g/mol) was purchased from Sigma-Aldrich (Czech Republic), glycerol was achieved from Penta (Czech Republic). Sodium carbonate was obtained from Lach-Ner (Czech Republic) and copper nitrate trihydrate was purchased from Lachema (Czech Republic).

Experiments were carried out under various experimental configurations and in various volumes.

To increase clarity, we divided the experiments to two general groups: the first group contains “gel experiments” during which the gel polymer was formed; the second group is “moldable plastic experiments”.

In the typical gel experiment, sodium carbonate (0.5 g) and PVA (1.0 g) were put into a glass container, followed by glycerol (35 mL) and aqueous copper nitrate (1 mL, 50 g/L). The glass container was then placed into an oil bath and remained open to atmosphere. A control experiment in a drying kiln was performed as well, however, there was no difference in comparison to the oil bath approach. Either way, the whole experiment was carried out without a condenser. The solution was stirred and heated from room temperature up to 423.15 K (150 °C), it was kept at this temperature for 40 min, and then the container was quickly cooled with water to room temperature.

In the typical moldable plastic experiment, the amount of sodium carbonate and copper nitrate was the same (0.5 g and 1 mL of 50 g/L solution, respectively) but more PVA (4 g) was added. The volume of glycerol was again 35 mL. After the reduction, the mixture was cooled down to room temperature. It could be afterwards heated above its melting temperature (543.15 K/270 °C) to approximately 573.15 K (300 °C) for 5 min to achieve low viscosity which allowed casting of the material. Also blank experiments have been carried out for studying the nature of the polymer. Further, the solubility of the prepared polymer in various solvents was examined (*vide infra*).

X-ray powder diffraction (XRPD) data were collected at room temperature with X'Pert PRO θ-θ powder diffractometer with parafocusing Bragg-Brentano geometry using CuKα radiation (λ = 0.15418 nm, U = 40 kV, I = 30 mA). X'Pert HighScore Plus program was used for processing of data from X-ray Powder Diffraction analysis. Sizes of nanocrystals were calculated using the Scherrer formula.

The samples for transmission electron microscopy (TEM) were prepared by the deposition of the studied sample onto a carbon coated copper grid, the excessive solution was removed and the grid was dried by Whatman filtration paper. The samples were observed by transmission electron microscope JEOL JEM-1010 at the accelerating voltage of 80 kV. TEM images were taken by a SIS MegaView III digital camera (Soft Imaging Systems) and analysed by AnalySIS v. 2.0 software.

Differential scanning calorimetry (DSC) measurements were carried out in platinum containers using calorimeter Setaram DSC 131. Temperature increment was 10 K/min, from 323.15 K (50 °C) to 673.15 K (400 °C).

Light absorption data were collected using UV-Vis spectrophotometer CARY 300 and processed by CARY win UV software. The measurements of thin (<100 μm) layer of the material were performed, since the samples were opaque in thick layers.

The structures of the starting material and products were studied by ^{1}H NMR spectroscopy (Varian Gemini 300 HC instrument), dimethyl sulfoxide-d6 was used as a solvent and the signals of the solvent served as an internal standard.

Infrared spectra were recorded using the FT-IR spectrometer Nicolet 6700 (Thermo Fisher Scientist, USA) equipped with single ATR attachment (ZnSe crystal) with the resolution of 4 cm^{-1} and 256 scans per spectrum. Raman spectra were collected on the FT-spectrometer EQUINOX 55 equipped with Raman module FRA 106/S, Nd:YAG laser (excitation line 1064 nm, laser power was set to 150 or 200 mW depending on the type of a sample measured and Ge diode detector was cooled with liquid nitrogen (Bruker Optics, Germany). The spectral resolution of 4 cm^{-1} and accumulation of 1024 scans for each spectrum were used. The resulting spectrum is the average of 12 spectra. Spectra were processed by Omnic 8 (Thermo Fisher Scientist, USA). In case of the dark samples the baselines of spectra were corrected using a filter [35].

Substances for testing the catalytic activity of the nanocomposite were either commercially available or prepared as follows. Benzyl azide was prepared by stirring a solution of sodium azide (1.46 g; 22.5 mmol) and benzyl bromide (2.57 g; 15 mmol) in an acetone/water (20 mL/5 mL) mixture. The reaction mixture was stirred at room temperature for 30 h, diluted with water (20 mL)