

PREPARATION OF GOLD NANOPARTICLES USING POLYSACCHARIDE DIALDEHYDES AND STUDY OF THEIR CATALYTIC ACTIVITY

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<https://doi.org/10.37904/nanocon.2023.4777>

Abstract

Gold nanoparticles (AuNPs) find application in various areas depending on their properties, shape and size distribution, which are mainly influenced by the preparation conditions. Moreover, due to the trend in recent years, toxic reducing and stabilizing agents are being abandoned during the synthesis of AuNPs, and alternative substances for one-pot green synthesis are being sought. Examples of such substances are polysaccharides, which are non-toxic, biocompatible, and biodegradable. In addition, they have the advantage that they can serve as reducing and stabilizing agents simultaneously during the reaction. Nevertheless, polysaccharides are structurally highly diverse compounds with a wide range of molecular weights and often non-stoichiometric composition. By selective oxidation of polysaccharides, these problems can be at least partially eliminated, and we can control the molecular weight, degree of oxidation and overall resulting properties of polysaccharides. Therefore, our work focused on preparing gold nanoparticles using the dialdehyde polysaccharides, specifically dialdehyde dextran (DADXA), dialdehyde hyaluronan (DAH), dialdehyde cellulose (DAC) and dialdehyde alginate (DAAL). After synthesis, the AuNPs were characterized, and their catalytic efficiency was tested on the reduction of 4-nitrophenol to 4-aminophenol. According to the study, all samples were found to be suitable catalysts for this reaction, with the best results obtained for AuDADXA, with initial TOF 37.1 min⁻¹ and $k = 0.78 \text{ min}^{-1}$.

Keywords: Dialdehyde cellulose, dialdehyde alginate, dialdehyde hyaluronan, dialdehyde dextran, catalysis

1. INTRODUCTION

In recent years, gold nanoparticles (AuNPs) have been intensively studied not only in terms of their synthesis but also in terms of possible applications. That is because AuNPs have gained popularity due to their excellent electrical and optical properties and the possibility of modifying their surface, thus targeting their use in a specific field [1]. Their electrical and optical properties are closely related to the size and shape of the nanoparticles, and these parameters can be optimised by the conditions in the synthesis of AuNPs [2, 3]. For example, nanoparticles with irregular surfaces and larger sizes are suitable for Surface Enhanced Raman Scattering improvement. Whereas for catalytic effects, a high surface-to-volume ratio of nanoparticles is essential, i.e. the smaller the nanoparticles, the greater the catalytic efficiency [4, 5]. AuNPs are suitable for various catalytic reactions such as oxidation of alcohols and aldehydes, reduction of nitro groups or low-temperature oxidation of carbon monoxide [5, 6]. One particular type of reaction that can be catalysed by AuNPs is the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). 4-NP is a toxic pollutant produced in the manufacture of explosives, plasticisers, herbicides and pesticides. Its removal from the environment is difficult due to its thermal stability, photostability and high resistance to biodegradation. 4-AP is a substance with lower toxicity, which can be used, for example, in the production of drugs such as phenacetin or paracetamol [7, 8]. The advantage of this catalytic reduction is the ease of monitoring it using UV-Vis spectrometry. The decrease in absorbance at 400 nm, a region characteristic of 4-NP, is observed during the

reaction [9]. Besides developments in the applications of AuNPs, there have also been advances in their synthesis [10].

The preparation has evolved since Michael Faraday first described the synthesis of AuNPs. Still, the essence has remained the same – the reduction of gold salts in the presence of reducing and stabilising agents [11]. However, a trend to develop a one-step, so-called green synthesis method has emerged in recent years. This is also one of the reasons why the use of polysaccharides for the synthesis of AuNPs has been investigated. Besides their biocompatibility, biodegradability and renewability, their advantage is their ability to act as reducing and stabilising agents simultaneously [12]. Different polysaccharides such as cellulose, dextran, hyaluronic acid or alginate can be used for synthesis, each having its characteristics and uses in science and industry [13–15]. However, the limiting variables in using natural polysaccharides are their molecular weight and composition diversity, which both depend on their source of origin. These limitations led us to the idea of using selective oxidation of polysaccharides, which would make it possible to at least partially eliminate the effect of different molecular weights and degrees of oxidation [16].

Therefore, our study deals with the preparation of periodate oxidised polysaccharides, namely dialdehyde cellulose (DAC), dialdehyde dextran (DADXA), dialdehyde hyaluronan (DAH) and dialdehyde alginate (DAAL) and their use for the preparation of AuNPs. Furthermore, the catalytic activity of different AuNPs for reducing 4-NP to 4-AP was investigated, and their efficiency for this application was compared.

2. EXPERIMENTAL SECTION

2.1 Materials

Polysaccharide dialdehydes were prepared from cellulose (Sigmacell Type 20, Sigma Aldrich), sodium hyaluronate (HA, $M_w = 1500$ kDa, Contipro, Czech Republic), dextran ($M_r = 100\ 000$, Sigma Aldrich) and sodium alginate (LF200S, FG = 0.68, FGG = 0.57, $M_w = 250$ kDa, FMC Biopolymer AS) by oxidation using sodium periodate (NaIO_4 ; VWR, Czech Republic) and ethylene glycol (Penta, Czech Republic). The precursor Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$; Sigma Aldrich) and also sodium hydroxide (NaOH; Lachner, Czech Republic) were used for the preparation of gold nanoparticles. Sodium borohydride (NaBH_4 , Sigma Aldrich) and 4-nitrophenol (4-NP, Sigma Aldrich) were used to perform the catalytic reaction. All chemicals were of analytical purity and demineralized water was used throughout the experiment.

2.2 Preparation of polysaccharide dialdehydes

DAAL, DADXA and DAH were prepared by periodate oxidation of natural polysaccharides in a polysaccharide : NaIO_4 ratio 1 : 1.25 at laboratory temperature for 24 h without light. Subsequently, the samples were dialyzed for 96 h in demineralized water (14 kDa MWCO membrane), filtered and lyophilized. DAC was prepared similarly, at the same ratio, but the reaction was run at 30 °C for 72 h. Oxidation was terminated by adding excess ethylene glycol, and the solution was purified by centrifugation (9000 rpm, 15 min, 3 times) and homogenization (1000 rpm, 10 min). The purified DAC was then solubilized (80 °C, 2 h), centrifuged again (10 000 rpm, 15 min), filtered and lyophilized.

2.3 Preparation of gold nanoparticles

Preparation of 0.6 wt.% solutions of polysaccharide dialdehydes started the day before (40 °C, incubated orbital shaker). On the second day, the pH of the solutions was adjusted to 7 using NaOH solution. The samples were then placed in a 90 °C oil bath for 15 min. An appropriate amount of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution was added to give a sample a 0.5 mg/mL final concentration. This step was followed by adding NaOH solution to provide a 200 $\mu\text{g}/\text{mL}$ final concentration in a sample. The gold precursor and NaOH solution additions were chosen based on studies previously performed for dialdehyde cellulose [17]. The reaction was instant for AuDADXA, AuDAH and AuDAC samples, which were subsequently cooled in the refrigerator, and acid dialysis

(5 L HCl solution of pH 3.5 and 50 kDa membrane) followed. The AuDAAL synthesis was similar, except that the formation of nanoparticles did not occur immediately, so it was kept in the 90 °C oil bath for 20 min.

2.4 Catalysis

The catalytic activity of the prepared gold nanoparticles was investigated in a model reaction, following previous study for gold nanoparticles prepared using dicarboxy polysaccharides [18]. The catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) was investigated using a UV-Vis spectrometer by recording the time-dependent decrease in absorbance at 400 nm. The baseline was measured on a solution consisting of 2 mL of demineralized water and 1 mL of NaBH₄ solution (7.5 mg/mL). Catalytic efficiency measurements were then performed on solutions that contained 1 mL of NaBH₄ (7.5 mg/mL), 1.7 mL of demineralized water, 0.1 mL of 4-NP (0.71 mg/mL), and 0.2 mL of AuNPs solution (0.01 mg/mL), which was added as the last component. Since the reaction follows pseudo-first-order kinetics, plots of the dependence of $\ln(c_t/c_0)$ on time (t) were created, from which the rate constant (k) can then be determined. The turnover frequency (TOF), which indicates the moles of reactant converted by a given amount of catalyst per minute, was also calculated and expressed for the initial 4-NP concentration [19].

2.5 Characterization of AuNPs and polysaccharide dialdehydes

Infrared spectroscopy (FT-IR)

A Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific, USA) was used for qualitative spectral analysis of prepared dialdehyde polysaccharides using a diamond crystal with ATR mode. Spectra were taken in the wavenumber range from 500 to 4000 cm⁻¹.

Dynamic light scattering (DLS)

The Zetasizer Nano ZS90 instrument (Malvern Instruments, UK) was used to measure the hydrodynamic radius (r_h) of individual AuNP solutions, given the chosen parameters: temperature 25 °C, Smoluchowski model and DTS0012 cell.

Ultraviolet-visible spectroscopy (UV-Vis)

The double-beam UV-Vis spectrometer Lambda 1050 (PerkinElmer, USA) was used to determine the LSPR values of individual AuNP solutions measured in the wavelength range of 250 to 800 nm.

Transmission electron microscopy (TEM)

A JEM-2100 transmission electron microscope from JEOL company in Japan was used to take gold nanoparticle images. Diluted AuNP samples were deposited on a 300 mesh copper grid coated with a Formvar membrane and dried; the acceleration voltage used for the measurement was 160 keV.

3. RESULTS AND DISCUSSION

First, polysaccharide dialdehydes were prepared by oxidation of the vicinal -OH groups of the polysaccharide to -CHO with simultaneous cleavage of the carbon-carbon bond. This conversion was confirmed by FTIR analysis (**Figure 1**, left side). All polysaccharide derivatives showed characteristic absorption bands at 1735 cm⁻¹ and 885 cm⁻¹, indicating the formation of carbonyl groups and hemiacetals after oxidation. Also, the absorption band of the -C=O group vibration of -COOH was present for the DAAL and DAH samples around 1600 cm⁻¹ as they contained it in their structure.

Subsequently, AuNPs were prepared using polysaccharide dialdehydes, and UV-Vis spectra were measured on the resulting solutions, see **Figure 2** left side. According to LSPR wavelength values, AuDAC and AuDAH nanoparticles seem to be larger and AuDADXA, AuDAAL smaller. These results also correspond to the solution's colour because solutions containing larger particles, i.e. AuDAH and AuDAC, were coloured purple

and those containing smaller particles, AuDAAL and AuDADXA, were reddish. However, the color can also be influenced by the shape, homogeneity of AuNPs and the thickness of the stabilizing shell around the AuNPs.

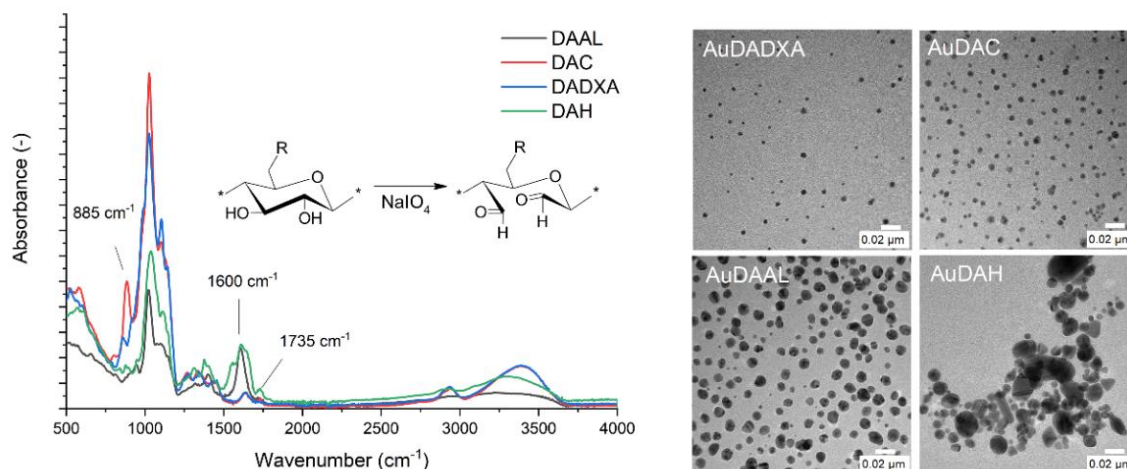


Figure 1 FTIR spectra for DAAL, DAC, DADXA and DAH with a general scheme for the periodate oxidation of polysaccharides (on the left) and TEM images of prepared AuNPs (on the right)

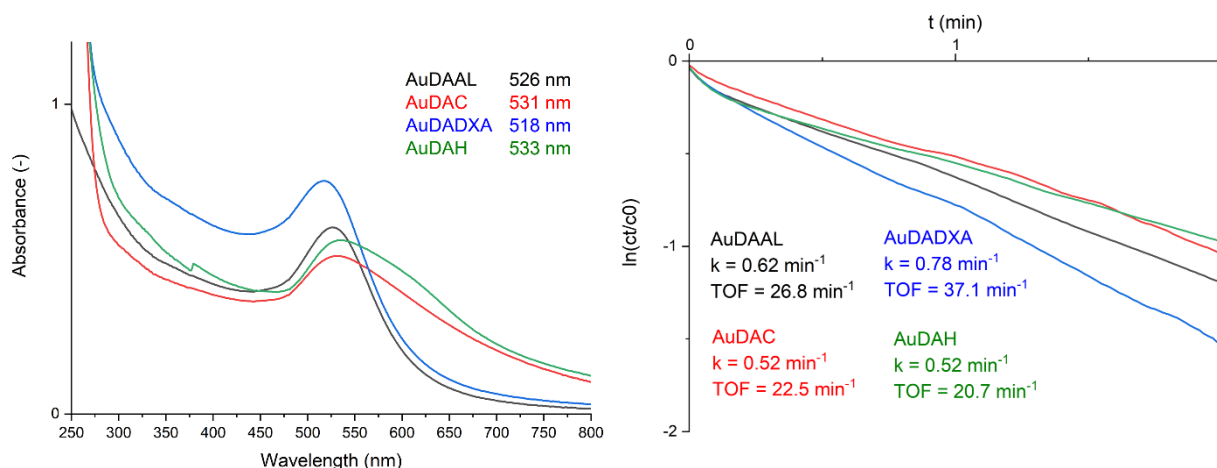


Figure 2 UV-Vis spectra with LSPR values for AuDAAL, AuDAC, AuDADXA and AuDAH (left side), time-sweep experiment showing a decrease of intensity of 400 nm band characteristic for the 4-NP reduction for individual AuNPs samples with TOF and k values (right side)

Next, the hydrodynamic radius of the stable (non-sedimenting) AuNPs was measured using DLS analysis, see **Table 1**. The obtained results corresponded with the ones from UV-Vis analysis. The largest nanoparticles were formed using the DAH derivative, having 109 ± 5 nm in size. Regarding size, AuNPs synthesized using DAC derivative were next, followed by DAAL. The smallest nanoparticles were obtained using DADXA, 18 ± 1 nm. The higher polydispersity value for the AuDAH and AuDAC samples is because, in addition to the fraction of the remaining polysaccharide, these samples contained a small fraction of smaller nanoparticles.

According to TEM images, see **Figure 1** (right side), the smallest nanoparticles were indeed observed with AuDADXA, but the second smallest were AuDAC, which contradicts the DLS and other measurements. However, this can be explained by the presence of a polymer shell around the AuDAC nanoparticles formed by DAC macromolecules. For other samples observed by TEM, a smaller size was observed than by DLS, however, AuDAAL particles are visibly larger than AuDADXA. A relatively high nanoparticle size distribution was observed for the AuDAH sample.

Table 1 Hydrodynamic radius (r_h) values for individual AuNPs and their polydispersity index (PDI)

Sample	r_h (nm)	PDI
AuDADXA	18 ± 1	0.315 ± 0.005
AuDAH	109 ± 5	0.561 ± 0.003
AuDAAL	33 ± 1	0.250 ± 0.004
AuDAC	78 ± 1	0.573 ± 0.004

The catalytic reduction of 4-NP to 4-AP in the presence of sodium borohydride was tested on the prepared AuNPs samples. A time-dependent decrease in absorbance at 400 nm was observed. The time dependence of the basic logarithm of the ratio of the concentration of 4-NP over time to the concentration of 4-NP at the beginning of the reaction was then plotted on a graph, see **Figure 2** (right side). From the slope of the linear regression of these dependencies, the reaction rate constant k could then be obtained, and the TOF value relative to the initial 4-NP concentration was also calculated. The reaction was fastest in the presence of the AuDADXA sample, which had the highest rate constant and TOF value. These results are consistent with the fact that this was the sample with the smallest particles and, hence, the largest surface area of nanoparticles, enabling catalytic reduction. The reaction rate then decreased with increasing nanoparticle size and was slowest for the AuDAH sample. Similarly, the rate of the catalysis using AuDAC was less effective and somewhat slower presumably because the larger polymer shell formed around the AuDAC sample.

4. CONCLUSION

Dialdehydes of cellulose, dextran, alginate and hyaluronan were prepared by periodate oxidation of polysaccharides. AuNPs solutions were subsequently synthesized from these derivatives. All of them showed catalytic activity for the reduction of 4-NP to 4-AP. The most effective were AuNPs formed using DADXA. The reduction reaction then slowed down with increasing size of the prepared AuNPs using dialdehyde derivatives. Thus, it has been shown that significantly better catalytic activity can be achieved under the same conditions by simply changing the polysaccharide. Moreover, these samples are of future interest regarding their possible anchoring to other materials.

ACKNOWLEDGEMENTS

Alžběta Důbravová, Lukáš Münster and Jan Vícha would like to acknowledge the Czech Science Foundation grant 23-07361S and Monika Muchová would like to also acknowledge the Internal Grant Agency of TBU project no. IGA/CPS/2023/006.

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