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Preparation, aging and temperature stability of PEGylated gold nanoparticles

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ABSTRACT

This work is aimed on preparation and characterization of gold nanoparticles (AuNPs) by direct deposition into polyethylene glycol (PEG) and thiolated polyethylene glycols (PEG-SH; PEG-S_2H_2). Furthermore, this work investigates temperature stability and aging of the prepared PEGylated AuNPs. The prepared colloidal nanoparticles were characterized by several analytical techniques. Transmission electron microscopy and UV–vis spectroscopy revealed the shape of AuNPs is spherical in all PEG solutions. The size of the prepared AuNPs was between 2.1 and 5.9 nm, depending on the capturing medium. The particle size was confirmed by dynamic light scattering measurement, which provided additional information on monodispersity of the samples. Atomic absorption spectroscopy showed the concentration of AuNPs increases linearly with deposition time which also corresponds with the optical absorption and color of the prepared PEGylated AuNPs. For AuNPs smaller than 3 nm the absence of surface plasmon resonance peak was observed, which is caused by both the small size of the nanoparticles and/or attachment of thiolated PEG to the surface of the AuNPs. AuNPs stabilized by PEG-SH were more stable and resistant to increased temperature than AuNPs stabilized by PEG-S_2H_2. These AuNPs subjected more easily to aggregation which resulted in decrease of absorption in the UV–vis spectra. The highest stability was observed for the Au core of 2.9 nm in size protected by PEG-SH. The prepared materials can find applications in medicine and catalysis.

1. Introduction

Gold nanoparticles (AuNPs) have attracted significant attention in the past decade as a multifunctional platform for various bioapplications, including drug and gene delivery, photothermal therapy, biosensing, antibacterial activity, cytocompatibility and radio sensitization, owing to their tunable size, morphology, adjustable surface chemistry, and low toxicity [1–3]. However, non-functionalized AuNPs are not stable under normal physiological conditions. The high ionicity in blood can trigger NP agglomeration [4–6]. Therefore, careful selection of preparation conditions aims to control the size of the AuNPs making the resultant AuNPs to be stable and of a uniform size. These attributes are due to the fact the AuNPs can be protected by stabilizers, which prevent both direct collisions of AuNPs and their further growth [7].

Food and Drug Administration approved polyethylene glycol (PEG) was most commonly introduced agent to modify the NP surface. Due to its excellent hydrophilicity, biocompatibility, and nonfouling ability, PEGylation of NPs can effectively prevent their aggregation and non-specific protein adsorption in biological environment, resulting in a “stealth” behavior and therefore reduce the reticuloendothelial system uptake and enhance circulation time [4,8,9]. The PEGylation of AuNPs is generally realized by covalent coating of thiolated PEG ligands, because thiols can be anchored onto the gold surface via chemisorption [10]. Recently, multidentate PEG ligands have attracted more attention due to their ability for enhancing the affinity to gold surface and improving the performance of AuNPs in biological application [4,5,11–13].

In many studies, NPs preparation is a multistep process with quite complex purification procedures: the NPs are first synthesized using a small molecule surfactant (e.g. citrate) as a capping agent, and then subsequently the capping agent is exchanged with PEG ligands in a second step [14–19].

In our study we present a simple, reproducible, environmentally friendly, low cost and easily applicable approach of AuNPs preparation by direct deposition of Au into mixture of polyethylene glycol (PEG) and thiolated PEG. For stabilizing of AuNPs we have chosen PEG, methoxy PEG thiol (PEG-SH), and PEG dithiol (PEG-S_2H_2). The −OH groups of PEG create hydrogen bridges with water which leads to formation of a solvatation shell and stabilization of the NPs preventing aggregation during dissolution. A stronger stabilization is achieved with

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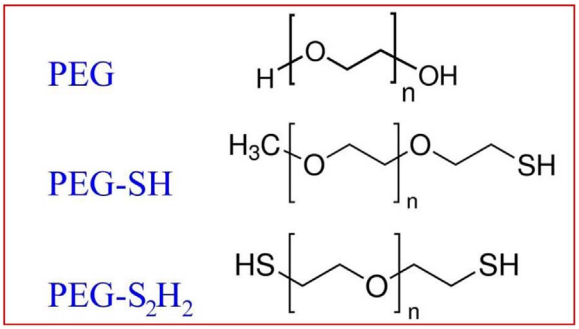

Fig. 1. Structural formula of polyethylene glycol (PEG), polyethylene glycol methyletherthiol (PEG-SH) and polyethylene glycol dithiol (PEG-S_2H_2).

Table 1
Designation and preparation details of three types of PEGylated AuNPs.

Designation of sample	Details of Au sputtering (time in s) into
A	300 s into PEG
B	900 s into PEG
C	1800 s into PEG:PEG-SH (20:1)
D	900 s into PEG:PEG-S_2H_2 (20:1)
E	300 s into PEG:PEG-S_2H_2 (20:1)
F	300 s into PEG and subsequent admixing of 2 ml PEG-SH (the weight ratio of PEG:PEG-SH (20:1))
G	900 s into PEG and subsequent admixing of 2 ml PEG-SH (the weight ratio of PEG:PEG-SH (20:1))
H	300 s into PEG and subsequent admixing of 2 ml PEG-S_2H_2 (the weight ratio of PEG:PEG-S_2H_2 (20:1))
I	900 s into PEG and subsequent admixing of 2 ml PEG-S_2H_2 (the weight ratio of PEG:PEG-S_2H_2 (20:1))

thiol groups that have good affinity to Au. Thiolated PEGs enable a strong Au−thiol bond (197.4 kJ/mol), [20] which provides a strong anchoring that minimizes desorption of PEG. The preferred strategy of PEG modification (PEGylation) is to covalently attach PEG chains directly to the surface of gold nanoparticles through the use of thiol-terminated PEG [18,21–23]. In addition, we have compared the effect of direct deposition of Au into thiolated PEG and post-deposition addition of thiolated PEG on their size, shape, and distribution. Furthermore, the temperature stability and aging was estimated for all prepared colloidal solutions of the AuNPs. The size, morphology and distribution of the prepared AuNPs were determined by transmission electron microscopy (TEM) and dynamic light scattering (DLS) analyses. The AuNP concentrations in the solutions were determined by atomic absorption spectrometry (AAS) analysis. The optical properties, aging and thermal stability of the colloidal solutions were studied by UV–vis spectroscopy.

2. Experimental

2.1. Materials and chemicals

Gold deposition was performed by Sputter Coater SCD 050 (BALTEC, Pfaeffikon Balzers, Liechtenstein) using Au target (purity 99.99%, provided by Safina Ltd., CZ). Sputtering was accomplished at room temperature (25 °C), sputtering time of 300–1800 s, current of 30 mA, voltage of 420–430 V, total argon pressure of 10 Pa (gas purity 99.996%, supplied by Siad Ltd., Czech Republic), an electrode distance of 5 cm. As a capturing media for preparation of metal NPs we used polyethyleneglycol (PEG, M_w = 400 g mol^{-1}, ρ = 1.128 g cm^{-3}), polyethyleneglycol methyl ether thiol (PEG-SH, M_w = 800 g mol^{-1}) and polyethyleneglycol dithiol (PEG-S_2H_2, M_w = 1500 g mol^{-1}) supplied by Sigma–Aldrich Corp., US (see Fig. 1).

2.2. Preparation of gold nanoparticles

The Petri dish of inner diameter of 4 cm was filled with 2 ml of polyethyleneglycol. Direct Au sputtering into thiolated PEGs is not possible because the pure substances are solid. Therefore, we have modified the deposition procedure: Au was sputtered directly into (i) pure PEG, (ii) mixture of PEG with PEG-SH or PEG-S_2H_2 in a weight ratio 20:1 and (iii) into pure PEG which was subsequently mixed with 2 ml of PEG-SH or PEG-S_2H_2 (the weight ratio of PEG:PEG-SH or PEG-S_2H_2 was 20:1). We have summarized the experimental procedure and designation of particular samples in Table 1. The schema of NP preparation by direct sputtering of Au into pure PEG or thiolated PEGs mixture is presented in Fig. 2. After the Au sputtering the PEG with AuNPs was transferred into 25 ml vials and mixed with distilled water in the volume ratio of 1:9 (PEG:water) [24]. Immediately after the sputtering selected samples were heated up to 35, 60, 70 and 100 °C (performed on heating device IKA-c-MAG HS7, supplied by MANEKO Ltd. CZ) for 1 h. The aging tests were performed on samples stored at room temperature (RT).

2.3. Analytical methods

UV–vis spectroscopy was used to characterize the optical properties, aging and thermal stability of the samples. Absorbance was measured in a 10-mm cell (Hellma Analytics cell, Quartz SUPRASIL, Type No. 100-QS) using Perkin-Elmer Lambda 25 spectrophotometer (Perkin Elmer Inc., Waltham, Massachusetts, US). Spectra were acquired before and after thermal treatment (35, 60, 75 and 100 °C) in the range of 300–800 nm.

DLS was employed for determination of the hydrodynamic size and size distribution of the nanoparticle colloids. The analysis of the samples was performed by Zetasizer ZS90 (Malvern Instruments Ltd.,

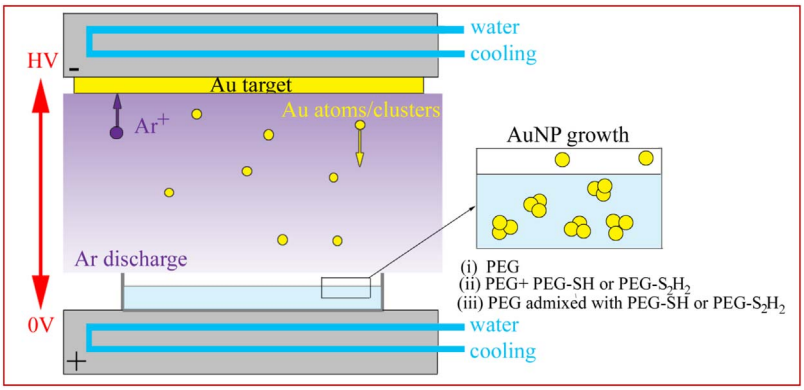

Fig. 2. Schema of preparation of PEGylated AuNPs by direct sputtering into liquid media of (i) PEG; (ii) PEG + PEG-SH or PEG + PEG-S_2H_2 (see experimental).