Silver Azide Nanoparticles Embedded into Silica as Energetic Nano-materials

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Silver azide is a primary high explosive that can be initiated by different means. In this work, silver azide nanoparticles were obtained, embedded into silica, and further derivatized with biotin. TEM, DLS, and IR measurements were used to characterize the hybrid energetic nanoparticles. The hybrid nanoparticles are made from an explosive core (silver azide) and a shell (silica), to which has been attached through an organic linker a biological target vectot (biotin).These hybrid nanoparticles can be used as models to study smart energetic nano-materials
Keywords: silver azide; silica; nanoparticles; biotin.

1. INTRODUCTION

Silver azide is a simple chemical that can be used as a vigorous primary explosive (initiating the explosion of more stable compounds). The explosion of this energetic material can be triggered by heat, impact, friction, or even ultraviolet light [1].

Inspired by the literature data that showed the use of single carbon nanotubes as 'smart bombs' in a photo-acoustic therapy procedure that targets cancer cells [2 – 4], we have developed a different system that can fulfill a similar function. Briefly, the idea was to use silver azide nanoparticles (the energetic material) in conjunction with a target vector, such as biotin. Biotin (also known as vitamin H, B_7, or coenzyme R) can bind very strongly to avidin-type proteins with a high degree of affinity and specificity [5, 6].

Information in the literature regarding silver azide nanoparticles is extremely scarce. Silver azide (AgN_3) has been used to obtain silver nanoparticles (Ag NPs) by a solvo-thermal decomposition [7]. Conversely, there is a tremendous amount of data on biotinylation, the procedure in which biotin is covalently attached to a protein or any other molecule [8 – 10].

Our model of smart energetic material consists of an explosive core of AgN_3 NPs, embedded into silica containing free amino groups, to which biotin was covalently attached (Fig. 1).

2. EXPERIMENTAL

All chemicals and solvent were supplied by Sigma-Aldrich. TEM picture were recorded with a Jeol 200CX microscope operated at 200 kV, with a carbon copper grid on which a drop of the diluted nanoparticles solution was deposited and allowed to dry at room temperature. DLS measurements were made using a Beckman-Coulter Delsa

Nano C Submicron Particle Size Analyzer for the hydrodynamic diameter measurement. The scattered light was measured at 165° from the incident beam. The CONTIN method was used to resolve particle size distributions.

Caution! Silver azide is a very powerful and hazardous material. Do not synthesize large quantities. Impact, friction, static electricity, temperature, and pressure may induce the detonation. A special awareness must be taken on the proper and safe storage and disposal.

Synthesis of AgN_3 NPs. Typical procedure uses two equal volumes of solvent (water, methanol or water-methanol mixture, between 10 – 50 mL), one containing 17 mg of silver nitrate and the other one containing 6.5 mg sodium azide. The two solutions are mixed under stirring, and after 5 min decanted and used further. For the synthesis of PVP protected AgN_3 NPs, the mixture contained 40 mg PVP.

Coverage of AgN_3 NPs with silica. To the previous solution of AgN_3 NPs was added under stirring 0.02 mL 3-aminopropyl-trimethoxysilane and 0.03 mL tetramethyl-orthosilicate, and the mixture stirred for about 1h.

Labeling of hybrid NPs with biotin. Solid hybrid NPs were obtained by centrifugation, washed several times with methanol, then with DCM, and dried. The resulting solid was suspended into DCM, to which biotin (25 mg) and EEDQ (20 mg) were added, and the mixture stirred over night. The next day the solution was centrifuged, and the solid washed for about 10 times with methanol, until no trace of organic compound can be found in methanol.

3. RESULTS AND DISCUSSION

To achieve our goal, we first obtained the required AgN_3 NPs starting from silver nitrate and sodium azide. Several parameters (the concentration of the reactants, solvent, and the presence (or absence) of polyvinylpyrrolidone (PVP) as a stabilizing ligand) were varied, and the change in the size and shape of the resulting AgN_3 NPs was observed.

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First, it was found that the concentrations of the starting materials (silver nitrate and sodium azide) must be carefully chosen to obtain a good colloidal solution of AgN_3 NPs (higher concentrations led to higher agglomeration, while lower concentration might lead to dissolution of the AgN_3 NPs in the next synthesis step).
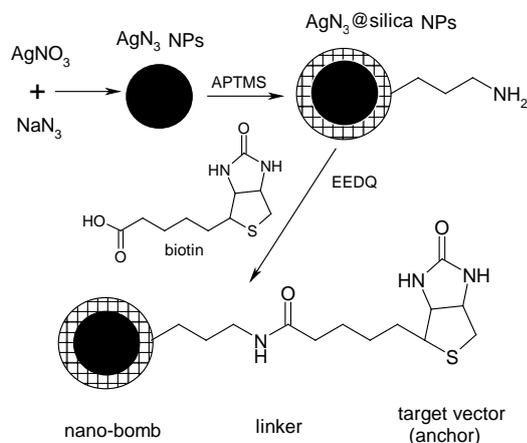
**Fig. 1.** Synthetic procedure of a smart energetic nano-material

For the solvent, water and methanol were used, as well as their 1/1 mixture. It was noticed that in pure methanol, most of the silver azide precipitates, although some AgN_3 NPs can be found in the solution (see supplementary data S1). However, in water or in the water-methanol mixture, AgN_3 NPs are formed in good yields. Their size varies from 50 to 500 nm, and they show a wide size distribution. In the end, the synthesis in water was chosen, as it seems to be the most appropriate for the final purpose.

Regarding the use of a stabilizing ligand, it was noticed that the AgN_3 NPs that were synthesized in the presence of PVP formed a more stable suspension, with a narrower size distribution. Fig. 2 a shows the AgN_3 NPs obtained in the absence of PVP, while Fig. 2 b shows the AgN_3 NPs obtained in the presence of PVP. The results are unsurprising, as PVP is known to be a good stabilizing ligand for the synthesis of NPs [11, 12].

However, our previous experience and the available literature [13] showed that PVP-protected Ag NPs are difficult to be embedded into a silica layer. This is due to the protective layer of ligand (PVP) that prevents good contact between the metal surface and the silica precursor, eventually leading to a mixture of free Ag NPs and covered ones.

To obtain a full coverage (although not necessary) of AgN_3 NPs with silica, many experiments were performed, varying the concentration of the reactants, the duration of the reaction, and the solvent. Fig. 2 c shows the TEM image obtained for plain AgN_3 NPs covered with aminopropylsilica, while Fig. 2 d shows the TEM image obtained for the AgN_3 NPs synthesized in the presence of PVP and covered with aminopropylsilica. It can be seen that in the first case, all of the AgN_3 NPs are covered with silica, while in the second case, the silica NPs may embed more than one Ag NP. For the AgN_3 NPs obtained either in a mixture of methanol-water or in the presence of PVP, the coverage procedure usually affords a mixture of free and embedded NPs (for details see Fig. 3 a – c); when using

low concentrations of AgN_3 NPs, only silica NPs are observed (Fig. 3 d).
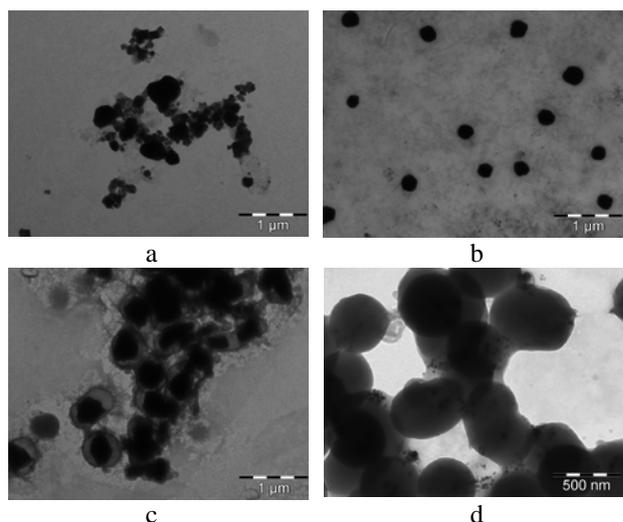
Fig. 2. TEM pictures of AgN_3 NPs obtained in the absence (a) and presence (b) of PVP; (c) and (d) are the corresponding hybrid NPs (covered with silica)

DLS analysis can provide similar information as TEM, regarding the mean size and size distribution [14]. Our experiments showed that there is a difference in the size of the hybrid nanoparticles (AgN_3@silica) between those extracted from the TEM pictures and those obtained from the DLS analysis (see supplementary data S2). This result can be explained through the two different techniques employed; a TEM picture always shows a limited sample of all of the NPs, while the DLS measurements acquire data for all of the NPs based on the hydrodynamic size, which is usually larger than the actual size.
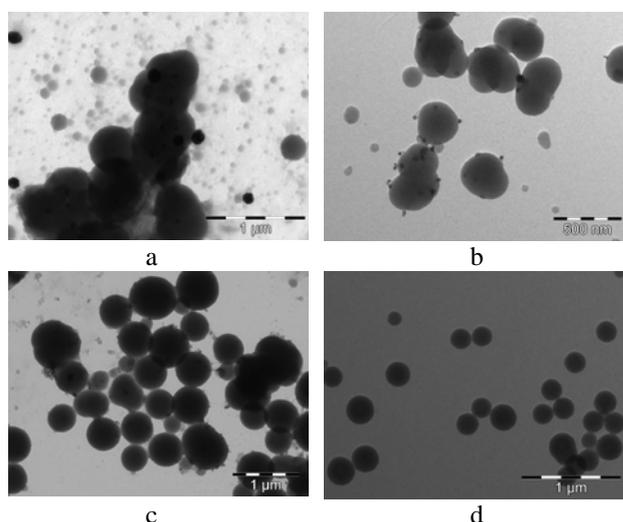
Fig. 3. TEM picture obtained in the attempts to embed AgN_3 NPs into silica: a – for PVP protected AgN_3 NPs; b – for AgN_3 NPs obtained in water-methanol; c – for PVP protected AgN_3 NPs obtained in water-methanol; d – for AgN_3 NPs obtained in methanol

Moreover, with respect to the TEM measurements, some reports have shown that the electron-beam might induce decomposition of the AgN_3 NPs [15]; this phenomenon is observed in our TEM images using energy
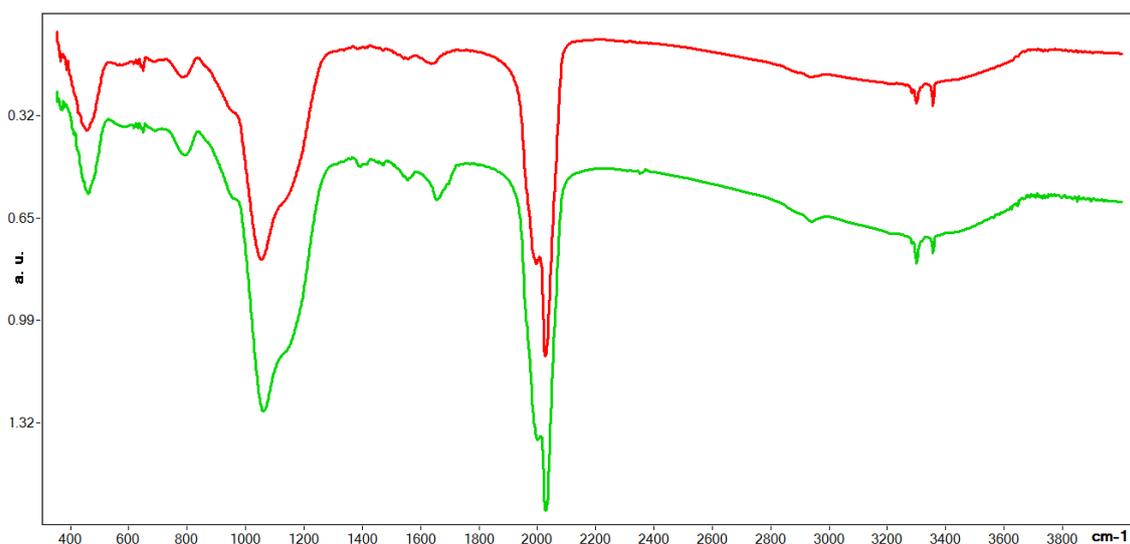
Fig. 4. IR spectra of the hybrid AgN_3@silica NPs (red) and the hybrid biotin-derivatized AgN_3@silica NPs (green)

dispersive spectroscopy (EDS), which showed that the sample contained more silver than expected (see supplementary data S3).

The last step of the synthetic route was to covalently bond biotin to the hybrid NPs (as shown in Fig. 1). Biotin cannot be directly attached to AgN_3 NPs; therefore, the next step in our procedure was to cover these nanoparticles with a layer of silica, specifically aminopropylsilica, which contains free amino groups (as shown in Fig. 1). These free amino groups easily react with carboxylic acids with the aid of a coupling agent such as dicyclohexylcarbodiimide (DCC) or 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ) [12]. EEDQ was used, due to our previous success with this coupling agent compared with DCC [16]. Fig. 4 shows the recorded IR spectrum of the AgN_3@silica NPs (red), superimposed with the IR spectrum of the hybrid NPs functionalized with biotin (green).

Although the spectra look very similar (Si-O-Si, -N_3, -CH_2-, and Si-OH groups appear at approximately 1050, 2030, 2930, and 3300 cm^{-1}), a more intense band corresponding to the newly formed amide (-CO-NH-) groups can be seen at 1650 cm^{-1}.

Regarding the known behavior of AgN_3, literature data showed that the explosion temperature can reach 3500 K [17], and the mechanism of decomposition is quite complicated, following a peculiar kinetics [18].

However, AgN_3 can be regarded as an unstable material, as day light can induce decomposition; as well, heat works in the same manner, and if these processes are controlled, the results of decomposition can be silver nanoparticles [7]. It was also shown that the thermal decomposition starts at 523K, the initial mechanistic step being the scission of a N-N bond [19].

Our simple heating tests on the AgN_3 NPs showed that whether they were embedded in the silica layer or not, or further derivatized with biotin, they all retained their explosive properties.

4. CONCLUSIONS

In conclusion, it was shown that by following simple procedures, AgN_3 NPs can be embedded into a silica layer,

which can be further derivatized with organic compounds of interest (biotin in our case). These hybrid nanoparticles can be used to study energetic nano-materials, with their explosion being trigged simply by heating.

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