Novel explosive method for the synthesis of silver nanoparticles

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Abstract

The detonation of explosive materials creates unique and extreme conditions, which typically require expensive, specialised equipment to replicate and are far more time-consuming than simple detonation processes.[1] These extreme conditions, however, can be harnessed for the synthesis of functional inorganic materials. Recent investigations into silver-based explosives have demonstrated the generation of silver nanoparticles during detonation, marking an advancement in the BANG (Bristol Accelerated Nanoparticle Generation) method, previously limited to gold.[2] This solvent-free synthesis enables the creation of uncapped, heterogeneous nanoparticles, offering enhanced versatility for subsequent functionalization or application. Nanoparticle formation was verified using transmission electron microscopy (TEM), while their composition was confirmed through electron and X-ray diffraction (XRD) techniques.

Keyword: nanoparticles; silver azide; silver fulminate; BANG

1 Introduction

Published in 2024, the paper by Uszko *et al.* proved a long-assumed stipulation that fulminating gold detonation produces gold nanoparticles.[2] It was the first example of the BANG (Bristol Accelerated Nanoparticle Generation) method, and it opens up a question of whether this method can be applied to other materials.

Unlike metals such as iron and cobalt, silver is said to only have a face-centred cubic (FCC) structure.[3,4] However, reports by Novogrodova *et al.* from the late 1970s on geological samples of native silver confirm the presence of hexagonal close-packed (HCP) silver polytypes 4H and 2H.[5,6] The elusive hexagonal phase was later reported to be size-stabilised in nanocrystalline silver.[7] Cao *et al.* provide a deeper investigation into hexagonal silver, not only confirming its presence but also identifying the conditions required for its creation. The transition between FCC and HCP phases took place between 400 and 500 °C on rapid cooling, in the case of Cao *et al.* using liquid nitrogen, which allowed the preservation of the HCP phase.[4] Rapid cooling from high temperatures in this way is analogous to the conditions present during detonation.

In this paper, we investigate selected silver explosives and determine whether the BANG method can be applied to silver and if it can be used to achieve the elusive HCP phase.

2 Results & discussion

All three tested materials i.e. silver azide, silver fulminate and silver acetylide produced nanoparticles on detonation, an example of them at low magnification can be seen in Figure 1.

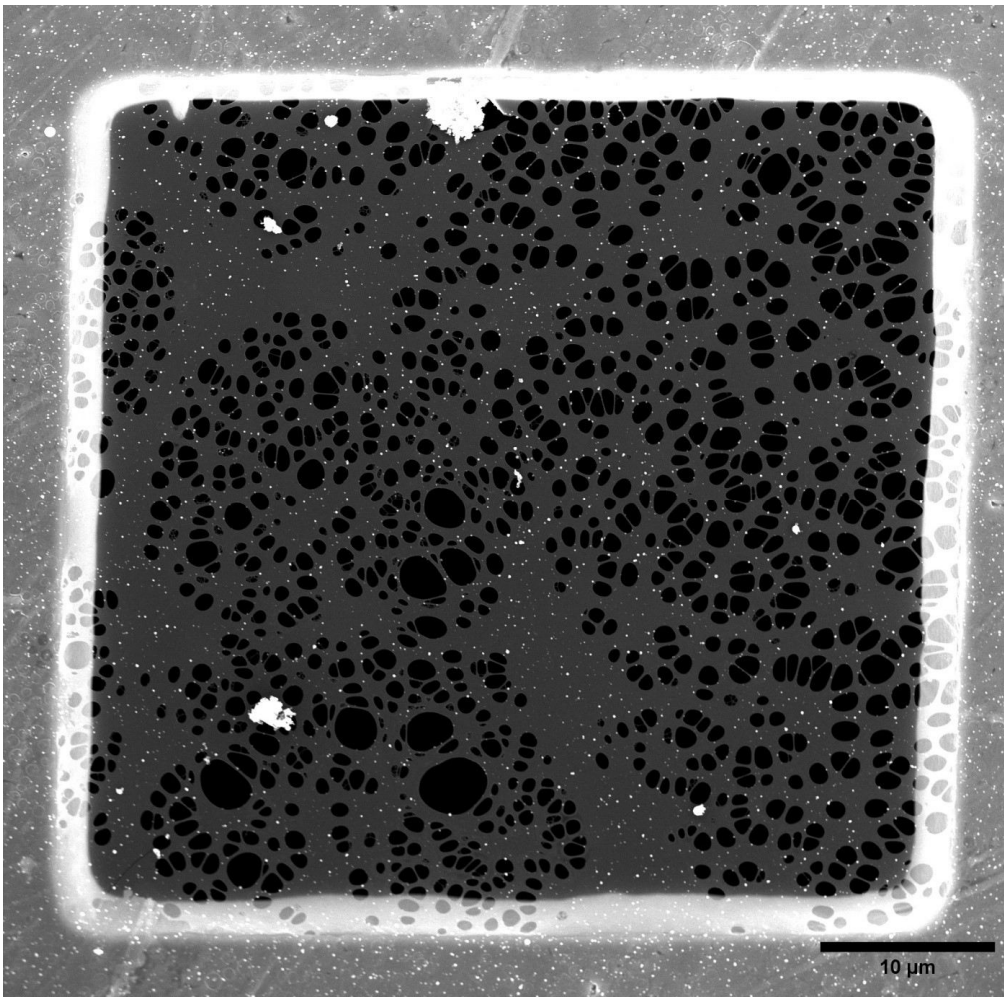

Figure 1. A scanning electron microscope micrograph showing a group of heterogenous silver nanoparticle clusters (white) dispersed on a holey carbon film (grey) on a copper grid (frame). Particles were created in the detonation of silver fulminate.

The composition of particles was confirmed to be silver, for all tested materials, by energy dispersive x-ray spectroscopy (EDS). Typical EDS plots of singular particles are shown in Figures 2,3 and 4.

Besides silver, Figures 3 and 4 show the presence of copper and carbon; these are from the grids used for particle collection, as well as aluminium, which was used to hold the grids in the detector.

The *d*-spacing of lattice fringes in Figure 5 is 1.169 Å when measured in the red box and 1.358 Å when measured within the white box. The red box measurement corresponds to the Silver FCC (222) plane, according to the Inorganic Crystal Structure Database (ICSD) structure collection code #22434. While the white box corresponds to the Silver HCP ($10\bar{1}3$) plane, according to ICSD structure collection code #56269.

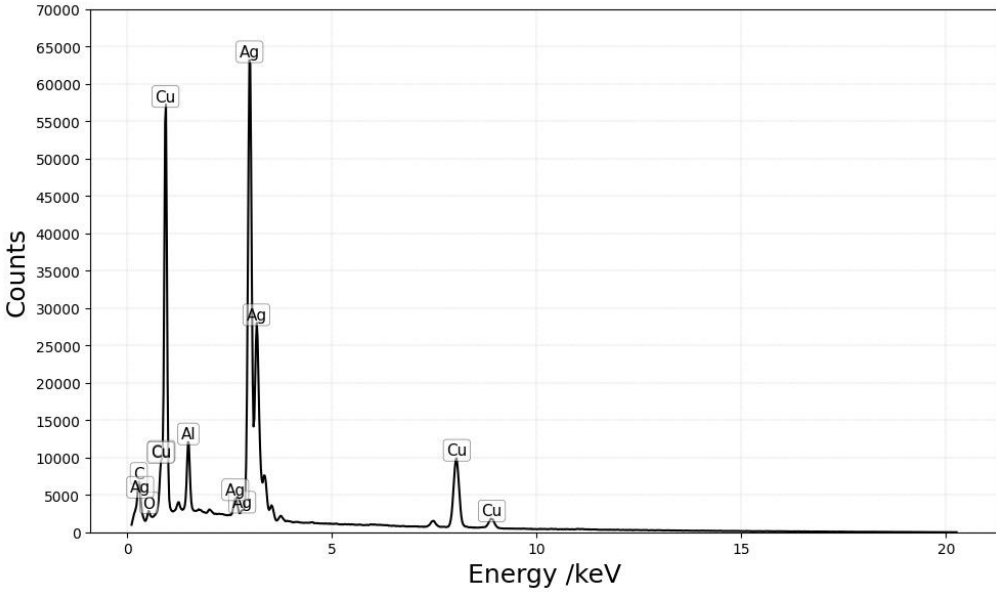

Figure 2. Typical EDS spectrum of nanoparticle created in a detonation of silver fulminate.

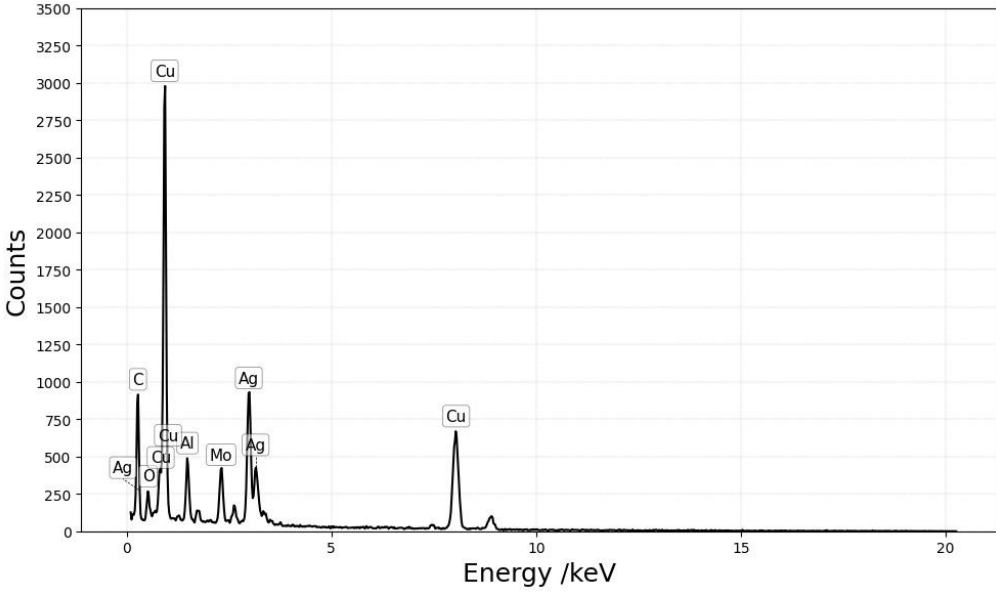

Figure 3. Typical EDS spectrum of nanoparticle created in a detonation of silver azide.

Similar results were obtained for particles created in the detonation of silver fulminate shown in Figure 4. The *d*-spacing in the red box of 2.312 Å corresponds to the Silver FCC (111) plane, according to the ICSD structure collection code #22434. While the white box and 1.243 Å corresponds to the Silver HCP ($11\bar{2}1$) plane, according to the ICSD structure collection code #56269.

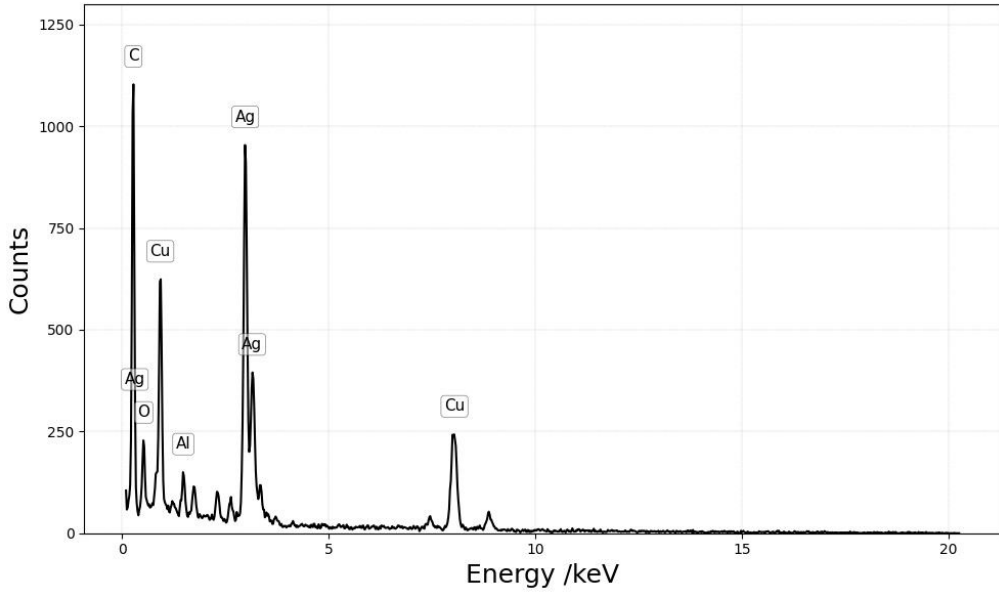

Figure 4. Typical EDS spectrum of a nanoparticle created in a detonation of silver acetylide.

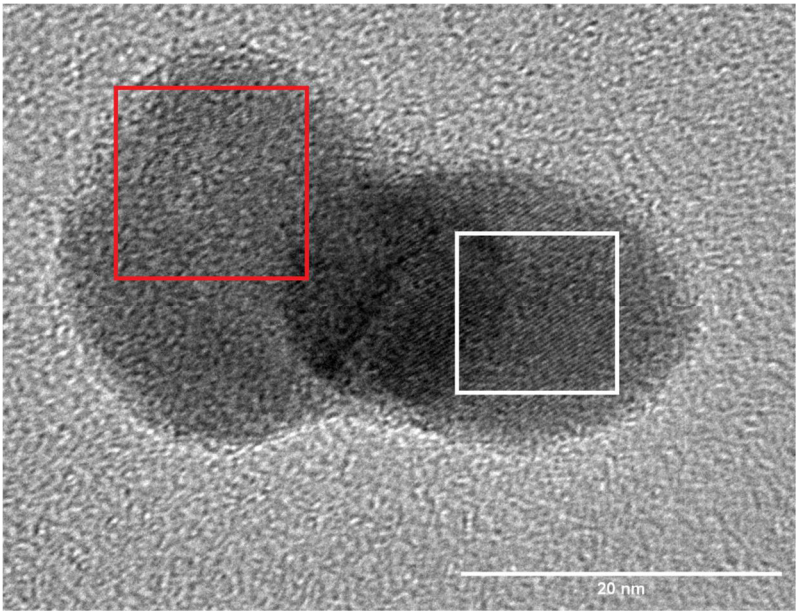

Figure 5. TEM micrograph showing two overlapping nanoparticles with clearly visible lattice fringes. The particles were made in the detonation of silver azide.

X-ray diffraction analysis in Figure 6 was performed on a sample coated from the detonation of silver fulminate. The characteristic peaks corresponding to planes (111), (200), (220) and (311) confirm that the bulk film consists of silver FCC, according to the ICSD structure collection code #22434.

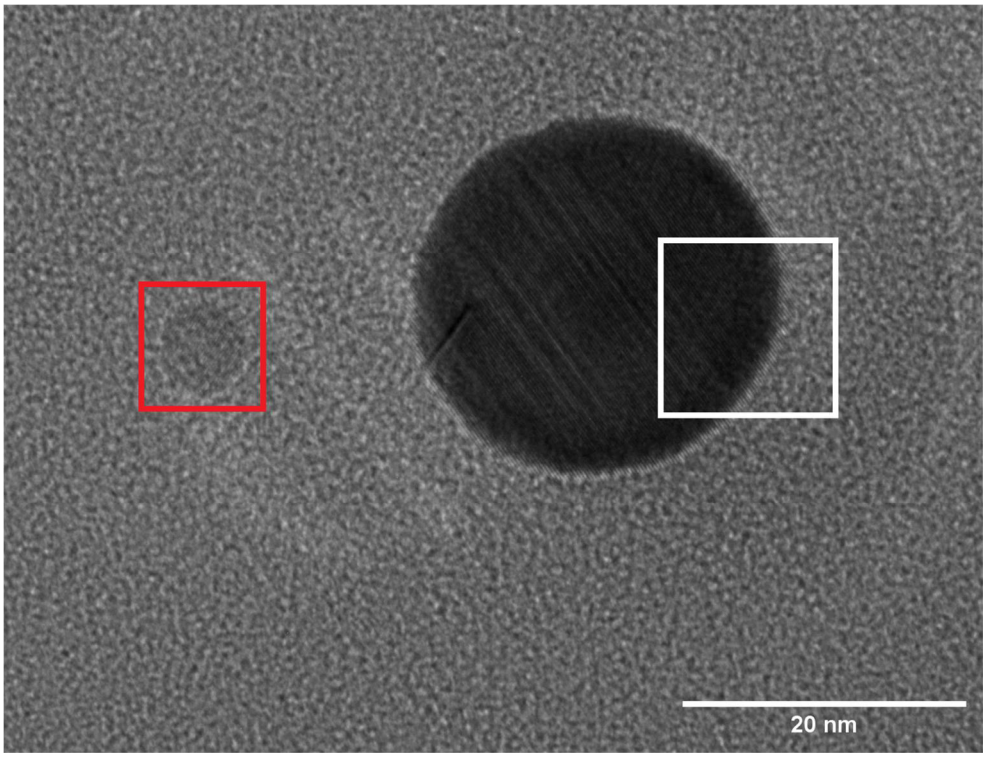

Figure 6. TEM micrograph showing two nanoparticles created in the detonation of silver fulminate. With distinct lattice fringes visible. There is a faint layer of amorphous carbon visible that has been deposited on the larger particle during imaging.

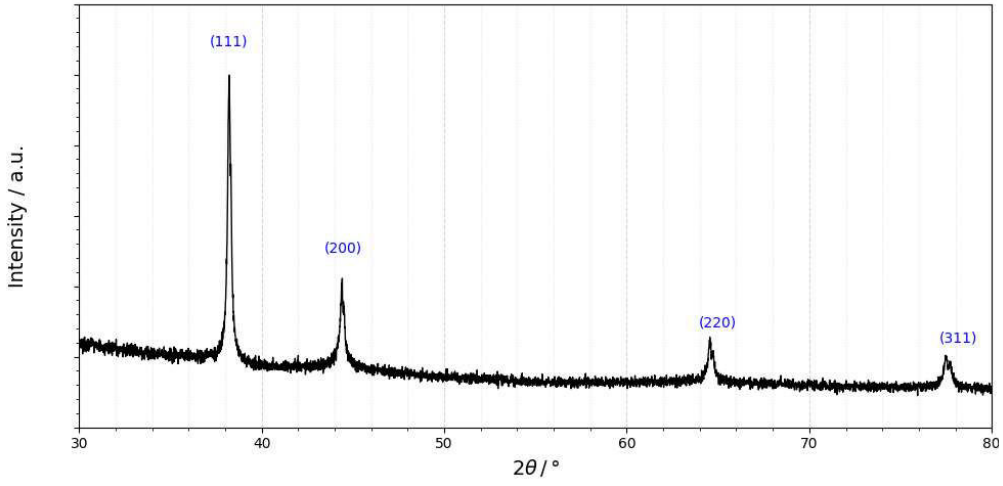

Figure 7. Typical powder X-ray diffraction pattern of a quartz slide coated with silver via the BANG method. The (111), (200), (220) and (311) lattice planes are indicated.

3 Conclusions

The results of EDS, lattice fringe analysis, and X-ray diffraction confirmed the presence of silver nanoparticles produced through the detonation of silver azide, silver fulminate and silver acetylide by the BANG method. Even though the main detectable phase in XRD is FCC, electron microscopy analysis confirmed that the HCP phase was found on both silver fulminate and silver azide samples. The evidence presented in this paper confirmed that the BANG method applies to silver. The unique conditions of the detonation allowed for the creation of the elusive HCP phase, hence the BANG method can provide a new way to synthesize this phase of silver. Follow-up research needs to be conducted to determine what other metals it can be applied to, and if it can be used to create "unusual" crystal phases. This small-scale experiment should stimulate the investigation into its scalability for further applications.

4 Experimental methods

The following sections detail the preparation and characterisation methods employed for the synthesis and analysis of silver-based compounds used in this study.

4.1. Silver fulminate

The procedure for the preparation of silver fulminate was based on those reported in the literature by Taylor *et al.* and Fedoroff et al. Silver nitrate (1.70 g, 10 mmol) was dissolved in 9 ml of 65% nitric acid (9 ml, 130 mmol) and 10 ml of water. After dissolving the silver nitrate, this solution was added to 18.5 ml (300 mmol) of 95% ethanol and the mixture was heated to 80°C, at which point a white precipitate of silver fulminate began to form. After 30 minutes, the silver fulminate was filtered, washed several times with water, and allowed to dry at room temperature for 24 h.[8,9]

4.2. Silver acetylide

Silver acetylide was prepared according to the Stettbacher procedure.[10] Silver nitrate (1.70 g, 10 mmol) was dissolved in 14 ml water; then 15 ml of 25% aqueous ammonia (200 mmol) was added to the silver nitrate solution. After dissolving the temporarily formed white precipitate, with a further addition of ammonia, pure acetylene from a gas cylinder was introduced into the solution. The silver acetylide immediately formed as a white precipitate. This was then isolated by filtration, washed thoroughly with water and allowed to dry for 24 h at room temperature.

4.3. Silver azide

Silver azide was prepared by a precipitation method. A 1 ml aqueous solution of sodium azide (50 mg, 0.76 mmol) was mixed with a solution of silver nitrate (23 mg, 0.13 mmol) in 0.5 ml of deionised water. This resulted in a precipitation of silver azide which was separated using vacuum filtration.[11]

4.4. Particle collection

Particles were collected by detonation of between 10 and 20 mg of silver explosive inside a stainless steel cylinder. A holey carbon film on a 400-mesh copper grid was mounted 10 to 15 cm above the cylinder. The explosive was detonated by heating with a gas torch.

4.5. X-ray diffraction

X-ray Diffraction patterns were acquired on Bruker D8 Advance powder X-ray diffractometer equipped with a PSD LynxEye detector and utilising Cu-Kα radiation (λ = 1.5418 Å). The thin film was prepared similarly to the particle collection described in Section 4.4 with

the mesh grid being substituted with a quartz slide and the distance from the cylinder decreased to 0.5 to 3 cm. The patterns were collected at 0.011° step intervals over a 2 θ range from 30 to 80° at 1 second per step.

4.5.1. Electron microscopy

Particles were analysed using JEOL-2100 TEM, silver acetylide was analysed using JEOL-1400 TEM. SEM was performed on FEI Helios dual beam system with an Oxford Instruments Symmetry S2 EDS detector.

Acknowledgements

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