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Optical sensitisation of energetic crystals with gold nanoparticles for laser ignition

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ABSTRACT

The laser ignition of explosives is safer and more environmentally beneficial than electric ignition systems, but optical sensitisers must be present to facilitate heating by optical absorption. We investigated, for the first time, the optical sensitisation of cyclotrimethylenetrinitramine (RDX) crystals by doping them with gold nanoparticles to enhance laser ignitibility using a near-infrared diode laser. RDX crystals physically coated with gold nanoparticles or recrystallised from a solution containing gold nanoparticles were tested for optical sensitisation by micro-imaging with a scanning electron microscope, and high-speed video was used to experimentally observe the enhanced laser ignitibility. The gold nanoparticles achieved effective optical sensitisation and significantly enhanced the laser ignitibility of RDX, reducing the laser ignition threshold power from more than 45 W to as little as 1 W. Our results show that gold nanoparticles are effective as optical sensitisers for the ignition of energetic materials using a small, low-power diode laser.

1. Introduction

Explosive ignition by laser irradiation has been investigated for different types of primary and secondary explosives using different wavelengths and types of laser [1–8]. Laser ignition offers the prospect of safer, cleaner and more environmentally friendly ignition systems by replacing current electric ignitors that rely on toxic chemicals (e.g. lead azide) and/or sensitive primary explosives. Reliable ignition has been achieved with low-power lasers, enabling miniaturisation and cost reductions. The laser power required to ignite energetic materials was reduced by mixing energetic materials with optical sensitisers such as carbon black [1,2,9–13]. The addition of ~3% (w/w) carbon black powder significantly increases the optical absorption and thus the laser ignitibility of the energetic materials. For example, mixing FOX-7 and hexanitrostilbene with carbon black for optical sensitisation greatly improved their near-infrared (NIR) absorption characteristics [1,2].

The laser irradiation of explosives causes heating by optical absorption, resulting in the formation of hotspots at discontinuities and inclusions present in the explosive material. This is considered the dominant mechanism responsible for laser ignition as indicated by the ignition of high-explosive nitrogen materials using xenon flash and CO_2 lasers [3,4,14,15]. The increase in temperature of explosive materials accelerates exothermic decomposition, eventually achieving a sufficiently high temperature to ignite the explosive. Optical sensitisation has made explosives ignitable at various laser wavelengths, even within the NIR region where explosive materials have little optical absorption. Therefore, small and inexpensive infrared diode lasers could become the most suitable power sources for miniature laser ignition devices.

In addition to common optical sensitisers such as carbon black, nanoparticles have been used as additives in energetic materials to enhance their optical and thermal properties and thus their ignition performance [3,6,16,17]. Carbon nanotubes are promising optical sensitisers because of their strong optical absorptivity and unique optical behaviour [3]. Pentaerythritol tetranitrate (PETN) sensitised with nickel nanoparticles can be ignited using a pulsed YAG laser, and it may be possible to modify the sensitivity of PETN by controlling the addition of such particles [6].

The phenomenon of surface plasmon resonance (SPR) allows metallic nanoparticles to be used as effective optical sensitisers, e.g. aluminium nanoparticles can enhance localised heating due to SPR [17]. Nanoparticles exposed to electromagnetic (EM) radiation with a wavelength longer than the particle diameter demonstrate an SPR phenomenon in which conduction-band electrons oscillate coherently, leading to strong EM waves on the particle surfaces and enhanced optical absorption and scattering. The strongly absorbed optical energy at a specific wavelength band is quickly converted to heat via a series of non-radiative processes over the particle surfaces [17,18]. The enhanced ability to absorb and quickly

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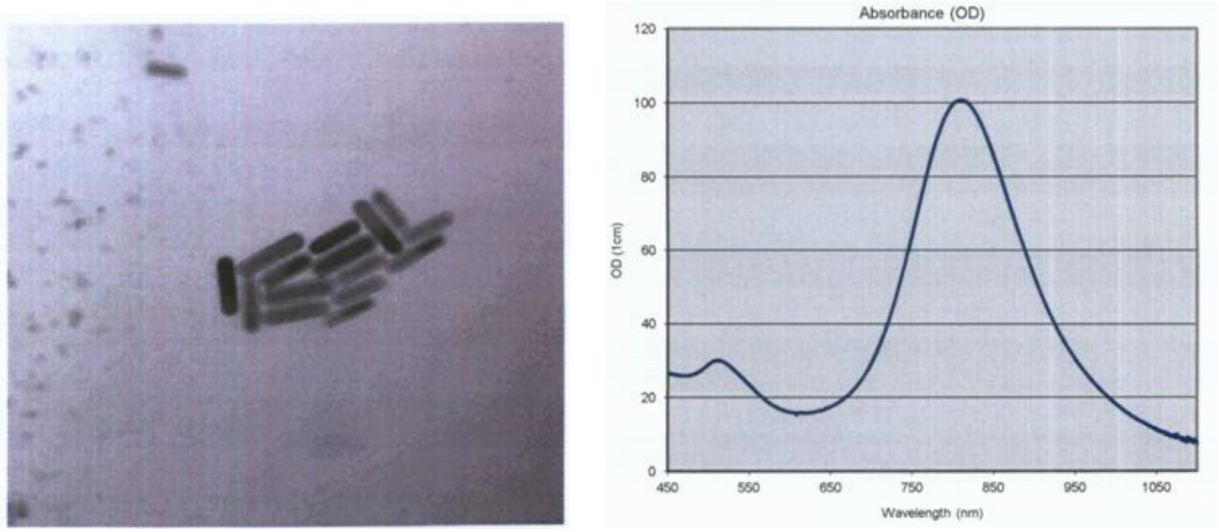

Fig. 1. Scanning electron micrograph and absorption spectrum of the GNPs used in this study, which were provided by the manufacturer (Nanopartz, USA).

convert EM energy into heat makes plasmonic nanoparticles suitable as optical sensitisers. Gold is ideal as an additive in energetic materials because it is chemically stable and therefore more compatible and less toxic than other metals. During the laser ignition of explosives doped with gold nanoparticles (GNPs), the incident laser radiation induces a large local EM field around the GNPs in contact with the explosives [19–21] due to the coupling of laser radiation into an SPR, or a collective oscillation of the conduction-band electrons [22,23]. When the SPR frequency band is comparable to that of the igniting laser, the GNPs strongly absorb at the laser wavelength and efficiently convert the absorbed energy into heat, producing dense nano-hotspots. Therefore, the ignitibility of explosives is expected to reach an optimum at the specific laser wavelength. The optimisation of SPR absorbance mainly depends on the size and density of the nanoparticles [24,25], and can be tuned to a desirable laser wavelength to enhance laser ignitibility and wavelength selectivity.

Here we experimentally investigated the laser ignition of micro-energetic cyclotrimethylenetrinitramine (RDX) crystals doped with GNPs, aiming to greatly enhance their laser ignitibility. An 808-nm diode laser was used as the igniting power source, and the GNPs demonstrated maximum SPR and thus an optimal optical absorption band at this wavelength. RDX was chosen because it is widely used in explosive products such as propellants, boosters, detonators and the main charge filling compositions of warheads.

2. Method and experimental

2.1. Sample materials

RDX type 1 was used as the high explosive for optical sensitisation. Analytical grade acetone (Sigma-Aldrich Ltd., UK) was used as the solvent to recrystallise the RDX. Rod-shaped GNPs, 10 nm in diameter and 41 nm in length (Nanopartz, USA), achieve strong optical absorption at 808 nm and were chosen as the optical sensitisers (Fig. 1). The citrate-capped GNPs were dispersed in deionised water at a concentration of 3.5 mg/ml. The capping agent was present to prevent nanoparticle aggregation.

2.2. Sample preparation and characterisation

Three types of RDX crystal samples were prepared using different processing methods:

S1 – Pure RDX (Type I) crystals recrystallised from RDX-acetone solution mixed with deionised water.
S2 – 0.5% (w/w) GNP-coated RDX (Type I) obtained by physically mixing pure RDX crystals (S1) with GNPs.
S3 – 0.5% (w/w) GNP-doped RDX (Type I) recrystallised from RDX-acetone solution mixed with GNP dispersions in deionised water.

2.2.1. Re-crystallisation

RDX re-crystallisation was achieved by a crystallisation mechanism based on cooling and evaporation. To obtain S1, 400 mg of RDX powder was weighed in a vial and 4 ml acetone was added. The vial was sealed with a seal cap and heated in an oil bath at ~60 °C until the RDX powder was completely dissolved. Deionised water (1 ml) at room temperature was mixed with the RDX-acetone solution in the vial, which induced a mild crash (or precipitation) into the solution. The vial was sealed with film containing several pinholes and left to cool and evaporate naturally. The sample was nearly dry after 4 days and was placed in a vacuum oven at 100 °C for 1 h to dry completely. Pure RDX crystals (S1) were obtained ready for use. The size of the crystals ranged from sub-millimetre to 1–2 mm (Fig. 2a). RDX doped with GNPs (S3) was prepared in a similar manner to S1, but the deionised water was replaced with 1 ml of the GNP dispersion and 3 ml RDX-acetone solution containing 300 mg RDX was added after mixing (Fig. 2c).

2.2.2. Physical mixing

Pure RDX crystals (~350 mg of S1) were weighed into a glass vial and 0.5 ml of the GNP dispersion was dispensed into the vial. The slurry was mixed to ensure the explosive crystals and the gold particles were dispersed homogeneously. The vial was left in a fume cupboard to allow the water to evaporate. The explosive mix was stirred daily to prevent caking and settlement of the GNPs before they were dry. When the sample was nearly dry it was placed in a vacuum oven at 100 °C to dry completely. This crystal sample (S2) of RDX coated with GNPs had the same doping concentration of 0.5% (w/w) as S3 and was then ready to use, as shown in Fig. 2b.

2.2.3. Sample characterisation

Differential scanning calorimetry (DSC) was carried out using a DSC-30 device (Mettler Toledo) to investigate any potential differences in the thermal properties of the RDX crystal samples.