



Conductive Oxides for Formulating Mitigated-Sensitivity Energetic Composite Materials

Pierre Gibot, Estelle Puel, Bastien Lallemand, Franck Oudot

► To cite this version:

Pierre Gibot, Estelle Puel, Bastien Lallemand, Franck Oudot. Conductive Oxides for Formulating Mitigated-Sensitivity Energetic Composite Materials. *Journal of Composites Science*, 2022, 6 (6), pp.174. 10.3390/jcs6060174 . hal-03797076

HAL Id: hal-03797076

<https://hal.science/hal-03797076>

Submitted on 4 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Conductive Oxides for Formulating the Mitigated Sensitivity of Energetic Composite Materials

Pierre Gibot ^{1,*}, Estelle Puel ², Bastien Lallemand ¹, and Franck Oudot ¹

¹ NS3E laboratory, UMR 3208 ISL/CNRS/UNISTRA, French-German Research Institute of Saint-Louis (ISL), 5 rue du Général Cassagnou, BP70034, 68301 Saint Louis, France; bastien.lallemand@isl.eu (B.L.); franck.oudot@isl.eu (F.O.)

² Faculty of Science and Engineering, University of Toulouse III Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse, France; estelle.puel@cea.fr

* Correspondence: pierre.gibot@cnrs.fr

Abstract: Composite energetic nanomaterials, otherwise known as nanothermites, consist of physical mixtures of fuel and oxidizer nanoparticles. When a combustion reaction takes place between both components, extremely impressive conditions are created, such as high temperatures (>1000 °C), intense heat releases ($>kJ/cm^3$), and sometimes gas generation. These conditions can be adjusted by modifying the chemical nature of both reactants. However, these energetic composites are extremely sensitive to electrostatic discharge. This may lead to accidental ignitions during handling and transportation operations. This study examines the use of a n-type semiconductor ITO material as an alternative oxidizer combined with aluminum fuel. Indium tin oxide (ITO) ceramic is widely used in the elaboration of conducting coatings for antistatic applications because of its ability to conduct electrical charges (n-type semiconductor). The energetic performance of the Al/ITO thermite was determined, i.e., the sensitivity threshold regarding mechanical (impact and friction) and electrostatic discharge (ESD) stresses, as well as the reactive behavior (heat of reaction, combustion front velocity). The results demonstrate insensitivity toward mechanical stresses regardless of the ITO granulometry. As regards the spark sensitivity, using ITO microparticles considerably raises the sensitivity threshold value (<0.21 mJ vs. 13.70 mJ). A combustion velocity of nearly 650 m/sec was also determined.

Keywords: nanothermites; indium tin oxide; combustion reaction; sensitivities properties; spark test

1. Introduction

Energetic materials (EMs) are a large family of materials, including explosives, propellants, and energetic fuel–oxidizer mixtures. EMs store enormous heat energy in their structures (monomolecular and multicomponents) which is released during the decomposition reactions classified as detonation, deflagration, and combustion reactions, respectively [1]. Thermites are an example of energetic fuel–oxidizer mixtures generally made up of a metal fuel (aluminum (Al), boron (B), magnesium (Mg), and zirconium (Zr)) with an oxide ceramic material (ferric oxide (Fe_2O_3), molybdenum oxide (MoO_3), cupric oxide (CuO), tungsten oxide (WO_3), and stannic oxide (SnO_2)), both on a micron scale. After stimuli, a redox reaction takes place, generating high temperatures (2000–3000 K), high energy densities ($>kJ/cm^3$), and gas production, as determined by the choice of the components [2].

Over the past two decades, thermite composite materials have received growing attention in pyrotechnics thanks to nanotechnology. For example, mixing nanopowders of fuel and oxidizer (i.e., nanothermites) greatly improves the ignition and combustion speed because those mixtures are more intimate and homogenous and increase the interfacial contact area between the fuel and the oxidizer. Thus, the ignition duration and the combustion rate can be reduced and increased, respectively, by approximately 2–3 orders

of magnitude for a given composite material [3,4]. However, downsizing components that constitute energetic thermite materials does not only lead to enhanced performance, as the sensitivity properties of such mixtures to certain external stimuli can also increase, for example. This makes their synthesis, handling, and transport hazardous for operators. Stimuli frequently encountered during the characterization of EMs include heat, impact, friction, and spark (or electrostatic discharge) [5]. These tests were established by NATO in standardization agreements [6–8]. Regarding shock and friction tests, minimal threshold values of 2 J and 80 N are thus required to transport EMs on public roads, while the literature mentions a spark sensitivity threshold of 8–20 mJ, corresponding to a discharge capacity of a human body [9–11]. For example, Al/WO₃, Al/SnO₂, Al/Bi₂O₃, Al/MoO₃, and Al/Fe₂O₃ nanothermites present spark sensitivity threshold values of < 0.14 mJ, < 0.21 mJ, 0.125 × 10⁻³ mJ, 0.05 mJ, and 1.25 mJ, respectively [12–14]. To increase these thresholds, some authors work on the desensitization of nanothermites by adding electrical conducting ingredients in the energetic mixtures as carbon particles (nanotubes, fibres, graphene, and carbon black) and conductive polymers (polyaniline and polypyrrole), or not (Viton A) [15–22]. However, the addition of an additive in the traditional energetic fuel–oxidizer mixtures systematically leads to the degradation of reactive properties, i.e., a higher ignition delay and a lower combustion rate [16,18–22].

Transparent conductive oxides (TCOs) are oxide ceramics with unique properties of transparency and electrical conductivity. Among the TCO materials, indium tin oxide (ITO) [23], an n-type semi-conductor material, is the most investigated one compared to other materials, including antimony-doped tin oxide (ATO) and aluminum zinc oxide (AZO). As a result, it is widely used in various fields, such as solar cells [24], liquid crystal and flat-panel displays [25,26], light-emitting diodes [27], electromagnetic shielding [28], infrared reflectors [29], and anti-static coatings [30]. These applications are possible due to the high electrical conductivity of ITO resulting from the presence of oxygen vacancies caused by the insertion of dopant tetravalent tin cations (Sn⁺⁴) into the In₂O₃ indium oxide structure (In³⁺) [23]. Therefore, ITO, an oxygen-containing material with high intrinsic antistatic properties, is used to play a dual role in energetic composites, i.e., acting as an oxidizing component while allowing for the dissipation of electrostatic discharges, thus making the formulation of desensitized reactive binary nanothermites possible.

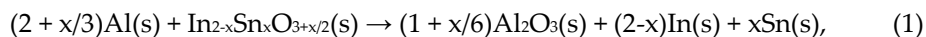
Herein, the mixture of indium tin oxide (ITO) and aluminum (Al) nanoparticles, as oxidizer and fuel, respectively, was studied. The performance of the Al/ITO thermite, i.e., its sensitivity thresholds to spark and mechanical stimuli, as well as the reactive properties (combustion wave velocity) were determined. A comparative study was carried out with different ITO grain sizes to investigate the influence of size effects on the performance. This type of composite material was investigated for the first time.

2. Materials and Methods

Indium tin oxide nanopowder (ITO, In₂O₃:SnO₂ = 90:10 wt. %, Mw = 279.91 g/mol., particle size (PS) < 50 nm) and acetonitrile were purchased from Sigma-Aldrich (Saint-Louis, MO, USA). Aluminum nanopowder (Al, apparent particle size = 50 nm, 65.5 wt. % of active Al) was provided by QNA Intrinsiq Materials Inc. (Rochester, NY, USA). Indium tin oxide raw powder (ITO, In₂O₃:SnO₂ = 90:10 wt. %, 30–44 µm powder, 99.99%) was obtained from Alfa Aesar (Kandel, Germany). Chemical reagents were used as received and without any further purification.

2.1. Preparation of the Al/ITO Energetic Composite

Based on the writing of the traditional aluminothermic reactions, the reaction between aluminum and indium tin oxide (ITO) is given below:



where alumina (Al_2O_3) inorganic specie, indium (In), and tin (Sn) metals are the solid combustion products. ITO is described with an excess of oxygen in order to respect the electrical neutrality.

For the present work, the reactants were mixed according to an equivalence ratio (Φ) of 1.2; i.e., with an excess of fuel to boost the reactivity of the mixture. The formula of the equivalence ratio is described in Equation (2):

$$\Phi = ((\text{F/O})_{\text{exp.}})/((\text{F/O})_{\text{st.}}), \quad (2)$$

where F/O is the mass ratio between the active fuel (Al) and the oxidizer (ITO) components, and the subscripts exp. and st. are the “current” and stoichiometric conditions.

Typically, 133.5 mg of passivated Al (assuming 65.5 wt. % of active Al determined by means of a thermo gravimetric analysis) and 366.5 mg of indium tin oxide powders (μm and nm) were suspended in 100 mL of acetonitrile in a round-bottomed flask. The suspension was stirring during 1 h and punctually interrupted by sonication steps (3×5 min.) to break up agglomerates and optimize the homogeneity of the energetic formulation. The solvent was evaporated at 80°C under 200 mbar until a dried grey mixture was obtained. This mixture was stored in a conducting container for further experiments.

2.2. Characterization Techniques

A Nova Nano-SEM 450 scanning electron microscope (SEM, FEI, Hillsboro, OR, USA) operating at a voltage of 10 kV was used to observe the microstructures of the different (multi)materials. The samples were coated with a thin gold layer before examination. Chemical elemental maps regarding aluminum, indium, and tin metal were obtained from an electron diffusion scattering analysis (EDS). Textural properties of the materials, such as the specific surface area (SSA), were determined by nitrogen physisorption measurements at -196°C performed on an ASAP2020 apparatus (Micromeritics, Norcross, CA, USA). Analyses were achieved on degassed samples (200°C , 6 h, vacuum $< 10 \mu\text{mHg}$) and the SSAs were determined by considering the Brunauer–Emmet–Teller (BET) model applied in the 0.05–0.20 relative pressure domain. A 2010 low-noise multimeter model (Keithley, Solon, Oh., USA) was used to measure the electrical conductivity properties of the samples. The procedure, based on a two-probe method, is described in [20]. Note that the loading densities of the samples were determined and expressed (in %) as a function of their respective theoretical maximum densities (TMD). Similar densities were used, allowing for a direct comparison of the electrical properties between the samples.

The energetic performance of the Al/ITO thermites were investigated through the determination of the sensitivity thresholds toward different external stimuli, their ignition abilities in open environment, the determination of the combustion rate in tube experiments, and the heat of reaction by means of a calorimetry bomb.

The electrostatic discharge (ESD) sensitivity, given in millijoules (mJ), was determined on an OZM ESD 2008A apparatus in an oscillating mode. A few mg of the Al/ITO nanothermite was placed between two electrodes 1 mm apart and submitted to a spark. The energy delivered by the spark is determined from the applied high voltage (4–10 kV) and a condensator capacity. The impact and friction sensitivity thresholds of the energetic mixture, expressed in joules (J) and newtons (N), respectively, were determined by using a fall-hammer and Julius Peter BAM apparatus, respectively. To measure the impact sensitivity threshold, the measurement principle was based on the dropping of weights from a defined height on the sample (40 mm^3) placed between two metallic cylinders. To calculate the friction sensitivity, the threshold was measured by scraping the powder (10 mm^3) between two ceramic pieces. The force of the ceramic stick (piece located on top of the powder) was determined by the position of weights suspended from the lever bearing the stick. The selected sensitivity threshold values for the investigated material and for all tests corresponded to the value of six consecutive “no-reactions”, i.e., no color change, clapping sound, burning reaction etc. The probability of obtaining a total absence of combustion was 98.4% at these thresholds.

The ignition capability was tested by burning 10 mg of powder with an optical flash igniter. A detailed protocol is given in [31]. Video data of combustion events were collected using a Photron FASTCAM high-speed camera (104 frames per second).

Flame propagation experiments were performed using the apparatus described in [13,19]. Typically, the powdered sample was poured into a polymethylmetacrylate tube (PMMA, outer diameter = 25 mm, inner diameter = 3 mm, length = 150 mm) and, with 50 mg additions, was closed at one end by an adhesive. Then, the progressive filling height was measured. An approximate mass of 689 ± 5 mg of energetic mixture was poured in a PMMA tube. The tube was horizontally placed in a detonation tank and a laboratory-made electric igniter (a bi-layer energetic composition made of an Al/WO₃ ($\Phi = 1.4$) mixture followed by a B/Bi₂O₃ (10 wt. % of boron) composition) was placed at the other end. The Photron FASTCAM high-speed camera was set to 5×10^4 frames per second for video recording. The high-speed images allow for the observation of the progression of the reaction front during the combustion process. The combustion velocity of the Al/ITO nanothermite, averaged on four tests, was determined by tracking the front position as a function of time.

A C2000 IKA calorimeter equipped with a C62 calorimetry bomb was used to determine the heat of reaction of the Al/ITO energetic nanocomposite. For that, approximately 1 g of the sample was tested and the experiment was triplicated.

3. Results and Discussion

3.1. Individual Ingredients and Energetic Mixture Characteristics

Scanning and transmission electron microscope analyses were used to describe the morphologies and sizes of individual indium tin oxide (ITO) and aluminum (Al) particles, as well as the homogeneity/intimacy of the derived Al/ITO energetic composite materials. Representative images are shown in Figure 1. The Al nanoparticles were spherical in shape, with a core-shell microstructure and an average size ranging from 50 to 300 nm, as shown in Figure 1a,b. The 2–3 nm-thick shell corresponded to a layer of native amorphous alumina (Al₂O₃) [32]. The specific surface area was determined to be 24 m²/g. Figure 1c,d show ITO powders which differ in particle size. The micron-sized ITO powder (ITO_μm, Figure 1c) consisted of particles of undefined morphology with a size of approximately 0.1–0.5 μm, whereas the nano-sized ITO material (ITO_nm, Figure 1d) had quasi-spherical spheres of < 50 nm. Their specific surface areas were determined to be equal to 2 and 35 m²/g, respectively. Figure 1e,f show the Al/ITO_μm and Al/ITO_nm energetic composites, respectively. Clearly, both showed excellent surface contact between indium tin oxide and aluminum particles. This fact, with intimacy of components, is a key point for the kinetic combustion reactions [3,4,13,14].

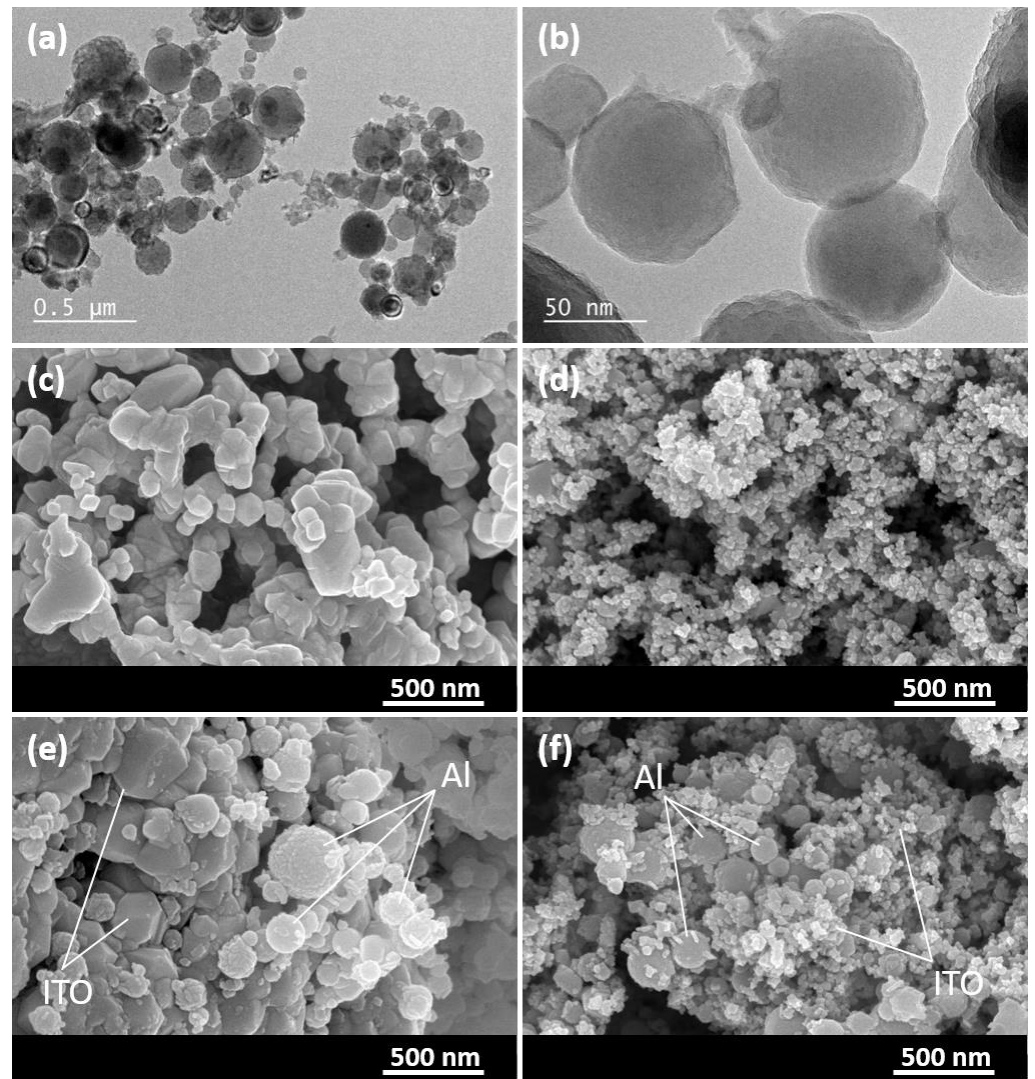


Figure 1. TEM pictures (a,b) of Al nanopowder and SEM images (c–f) of ITO_μm, ITO_nm, Al/ITO_μm, and Al/ITO_nm materials, respectively.

However, the spatial distribution of the fuel and oxidizer particles was more homogeneous in the case of the Al/ITO_nm energetic composite material than in its micron-sized counterpart, because at a low scale, both ingredients were easily observable, which was not as obvious in the second composite. In the latter case, the aluminum did not completely cover the micrometric oxidizer particles. This fact could be detrimental for combustion experiments where homogeneity between the fuel and oxidizer particles is critical to ensure an extremely fast self-propagating front flame [3].

Further characterizations were performed on both energetic composite materials, including the determination of the textural and electrical properties. Regarding the textural properties, the SSA of the two energetic composite materials was determined by nitrogen physisorption measurements at 77 K. Values of 5 m²/g and 22 m²/g were obtained for the thermites Al/ITO_μm and Al/ITO_nm, respectively—a trend expected for fuel–oxidizer systems with nm/μm and nm/nm particle sizes. This may result in a higher reactivity for the Al/ITO_nm system than for the Al/ITO_μm composite material, since a_{BET} reflects the surface where combustion reactions can occur [31].

For the electrical conductivity properties, a two-probe method was used, as described earlier in the experimental section. The electrical conductivity of the pelletized Al/ITO_μm energetic composite was an order of magnitude higher than that of the Al/ITO_nm system, with data of 8.91×10^{-1} S/cm (2.37 g/cm³, 47% TMD) versus 3.79×10^{-2} S/cm (2.11

g/cm³, 42% TMD), respectively. These data follow the trend described for conductivity measurements performed on ITO powders taken alone, where values of 4.74 S/cm (37.5% TMD) and 2.27×10^{-2} S/cm (34.1% TMD) were obtained for ITO_μm and ITO_nm, respectively. Note that the volume percent of ITO within Al/ITO energetic mixtures ($\Phi = 1.2$) was close to 52%. The conductivity of aluminum was found to be that of an insulating material with a value of 10^{-8} S/cm, which is explained by the insulating alumina layer covering the aluminum metal core [32].

3.2. Sensitivity Properties of the Al/ITO Energetic Composites

One major safety concern in the application of energetic composite materials is their high sensitivity to spark or electrostatic discharge (ESD). Therefore, the sensitivity levels of both Al/ITO energetic mixtures were determined from the protocol defined in the experimental part. The mechanical sensitivities (impact and friction), although less problematic for nanothermites, were also evaluated and attached to the ESD data in Table 1.

Table 1. Sensitivity thresholds of the Al/ITO thermites (at an equivalence ratio ϕ of 1.2) with respect to the oxidizer granulometry.

Sensitivity Test	ESD (mJ)	Impact (J)	Friction (N)
Al/ITO_μm	13.70	>100	>360
Al/ITO_nm	<0.21	>100	324

For impact and friction sensitivity tests, the values were noticeably high, i.e., > 100 J, and at least equal to 324 N, respectively, making Al/ITO energetic mixtures insensitive to impact, and insensitive/moderately sensitive to friction, as defined by NATO standards [6,7]. In contrast, the ESD threshold value of the Al/ITO_nm thermite was extremely low, with a value well below the energy that can be generated by a human body (<0.21 mJ compared to 8–20 mJ) [9–11]. This result is consistent with the results obtained for an energetic formulation based on fuel and oxidizer nanoparticles since the sensitivity thresholds are generally low, as noted for many reactive pairs mentioned in the introduction. However, when the ITO_μm oxidizer was involved in nanothermite, this value considerably increased (at least two orders of magnitude), since the ESD threshold value was 13.70 mJ for the Al/ITO_μm energy composite. It should be noted that despite this trend, the latter mixture should also be considered dangerous to handle with an ESD value not exceeding the upper discharge limit of the human body. Usually, in order to observe a similar trend, the addition of a ternary conductive component (carbon structures, conductive polymers) is necessary [15,16,19,20,22]. As the fuel ingredient and the experimental procedure were the same for both energetic composite materials, this result may be attributed to the oxidizer material. In this case, two hypotheses can be suggested: the size effect (μm vs. nm) and the electrical properties of the oxidizer component (conductive, semi-conductive, or insulating). Regarding the former, previous works have shown that the use of micrometer-sized oxidizer particles does not have a significant impact on the ESD threshold value compared to oxidizer nanoparticles [33,34]. For example, when Cr₂O₃ (Sigma-Aldrich, PS > μm, SSA = 3 m²/g) and WO₃ (Sigma Aldrich, PS = 20 μm, SSA = 1 m²/g) microparticles were used in Al nm-based thermites (Al, Nanotechnologies Inc., PS = 50 nm, SSA = 40 m²/g), instead of nanoparticles, the ESD threshold was determined to be 0.14 mJ, i.e., widely lower than the ESD value determined in the present case for the Al-nm/ITO μm energetic system (13.70 mJ). In addition, Cr₂O₃ and WO₃ materials exhibited low electrical conductivities, as experimentally determined (according to the procedure described in this work), equal to 6.5×10^{-7} S/cm (54.1% TMD) and 3.6×10^{-6} S/cm (55.2% TMD), respectively. Consequently, given this result, it seems reasonable to attribute the mitigation of the spark sensitivity of the Al/ITO energetic system to the intrinsic electrical conductivity of the ITO material, which was higher at the micro than at nanometer scale (~4.74 S/cm versus 2.27×10^{-2} S/cm).

Another aspect that can be considered is the possible simplicity of building a continuous conductive network with ITO micro-sized particles rather than nano-sized particles (in agreement with previous SEM analyses), allowing for an easy and quick dissipation of electrical charges. However, it is accepted that the accumulation of electrostatic charges at the fuel–oxidizer interface may be responsible for the ignition of energetic compositions following thermal heating created by the Joule effect. Therefore, if the charges are rapidly removed from the energy mixture, thanks to the presence of a continuous conductive network, it becomes more difficult to ignite the compositions by an electrostatic stimulus. The compositions thus require more energy to combust.

3.3. Ignition Ability of the Al/ITO Energetic Composites

The ignition ability of the two Al/ITO formulations was tested in an open configuration using a portable optical flash igniter. The combustion movies are shown in Supporting Information—Videos S1 a, b for the Al/ITO_μm and Al/ITO_nm energetic systems, respectively. Combustion reactions were complete, but the energetic formulations behaved differently. The energetic composite made of indium tin oxide at the micron scale (ITO_μm) was more difficult to ignite after the thermal pulse. The combustion reaction was characterized by cracklings, characterizing multiple and successive combustion starts. Each crackling was represented by the generation of a small fireball that grows with time before leading to the formation of a large and single incandescent particle cloud. In contrast, for the Al/ITO_nm composite, the ignition occurred more quickly and the combustion reaction was faster and more violent. The combustion phenomenon was represented by the formation of an extremely bright yellow–white and dense spray of incandescent particles. This result is supported by a reduction in the particle size implemented in energetic composite nanomaterials (nm vs. μm). This then enhanced the reactive properties due to an increase in the contact surface between the fuel and oxidizer particles and reduced the diffusion path of the oxygen moving from the oxidizer to the fuel during the redox reaction. As a result, the ignition capacity and propagation of the front flame considerably improved. Combustion images, illustrating the most intense moments, were extracted from the respective video recordings and shown in Figure 2. They clearly illustrate the different reactive behaviors of the two energetic Al/ITO composites.

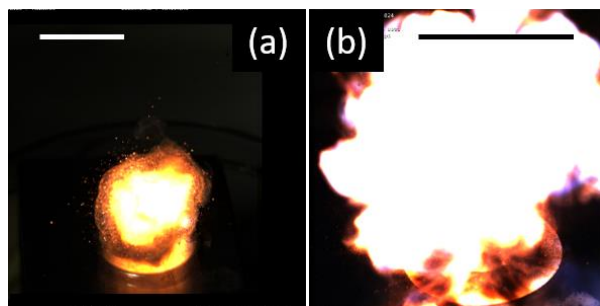


Figure 2. Combustion images of the (a) Al/ITO_μm and (b) Al/ITO_nm energetic composite materials ($\phi = 1.2$) recorded at 20 ms and 1 ms after the thermal impulse provided by the optical igniter. The white or black scale bar (on top on images) represents 20 mm.

The experimental heat of reaction of the energetic Al/ITO nanocomposite, by means of calorimetry bomb, was determined to be equal to $11.5 \pm 0.6 \text{ kJ/cm}^3$ ($2275 \pm 133 \text{ J/g}$). According to the work of Fisher et al. [2], the studied formulation presents an intermediate heat reaction among aluminum-based thermites if the equivalence ratio was not considered, i.e., between the two extremes (stoichiometric aluminum–titanium oxide (Al/TiO₂) and aluminum–iodine pentoxide (Al/I₂O₅) energetic mixtures, for which theoretical heat reactions of 5.5 kJ/cm^3 and 25.6 kJ/cm^3 were calculated, respectively).

3.4. Combustion Speed of the Al/ITO Energetic Composites

Combustion experiments in polymethylmetacrylate tubes were performed at 12.9% of the theoretical maximum density (TMD) for the Al/ITO_{nm} system. The TMD for Al/ITO_{nm} was 5.08 g/cm³. The Al/ITO_{μm} system could not be studied because no self-propagating combustion reaction was available for these experimental conditions. Since nano-aluminum (fuel) was present in the energetic composite, low-density loadings (<20%) could favor the highest reactive performance (for the equivalence ratio considered), since a fuel melt dispersion mechanism (MDM) could be expected [4]. Video recordings of the Al/ITO composite are presented in Supporting Information (Video S2). The ignition front appeared at the section of the tube exposed to the igniter and rapidly moves to the end of the PMMA tube. No extinction of the reaction or decelerating of the combustion front propagation was observed for the studied system. Figure 3 shows images extracted from the combustion video in confined medium of the Al/ITO_{nm} nanothermite. From a series of four tube experiments, an average combustion velocity of 657 ± 31 m/s was determined for the prepared Al/ITO_{nm} energetic material, with an equivalence ratio of 1.2. This was achieved by excluding the acceleration zone (the first 30 mm) and the end of the tube (the last 10 mm).

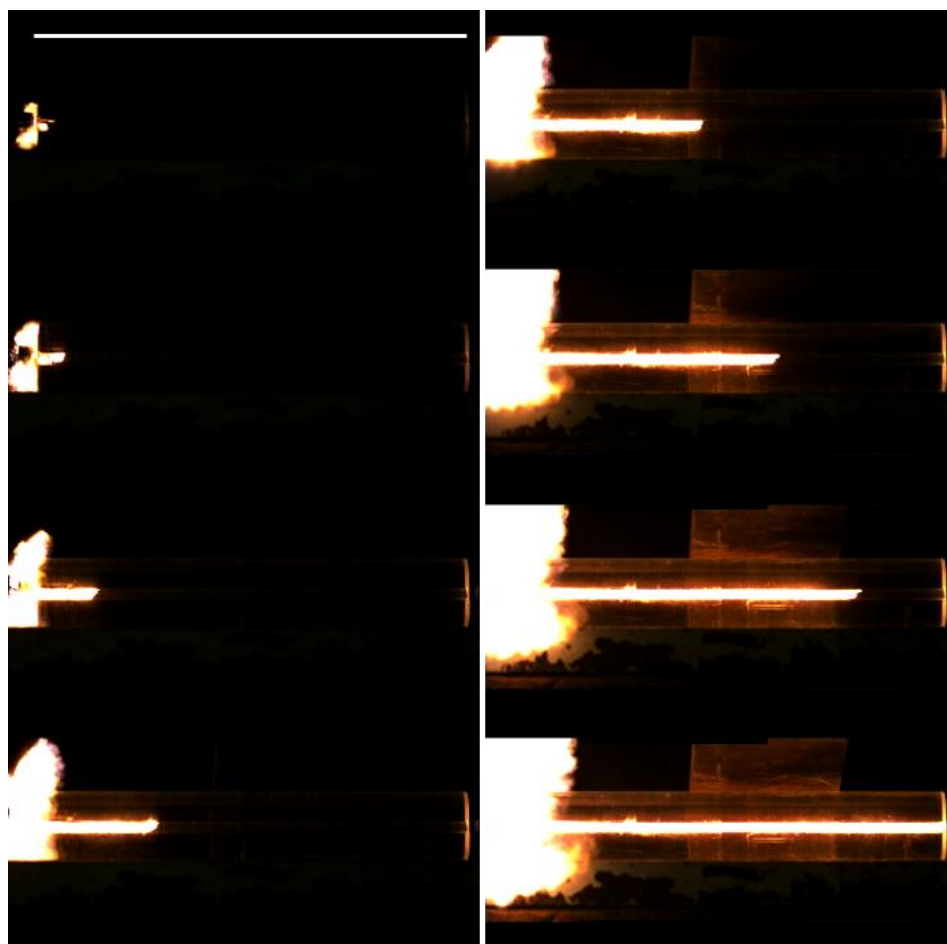


Figure 3. Photographs extracted from the combustion video of the Al/ITO_{nm} energetic composite material. The equivalence ratio (ϕ) was fixed at 1.2. The elapsed time between images was 40 μ sec. The white scale bar (on top on first) represents the tube length (150 mm).

In summary, ITO-based energetic aluminum thermites were insensitive to the impact test (>100 J), like many energetic composites. With regard to the friction sensitivity, the Al/ITO formulations were moderately sensitive to insensitive (≥ 324 N). This is common for energetic formulations, such as Al/In₂O₃, Al/SnO₂, and Al/Nb₂O₅, but better than

Al/WO₃, Al/MnO₂, Al/Bi₂O₃, and Al/CuO composites whose thresholds are <5 N (for the first three listed) and 9 N, respectively [13,16,34–37]. With respect to the spark sensitivity, Al/ITO materials showed a similar trend compared to the Al/In₂O₃ system, with a high sensitivity at the nanoscale (like many binary energetic compositions reported in the literature) and a mitigation of the ESD sensitivity when oxidizing microparticles are involved. This result may be due to the fact that a continuous conductive network is easier to design with micro-sized ITO particles than with nano-sized ITO particles, mixed with (non-conductive) fuel particles. The existence of this conductive pathway makes it easier to conduct electrical discharges through the volume of the composite. Finally, regarding the burning speed in the confined test, the fastest phenomenon was recorded for the Al/ITO_nm energetic system with a burning speed close to 650 m/s. In order of magnitude, the measured velocity was similar to that given in the literature for other nanothermite compositions, such as Al/Fe₂O₃ (550 m/s) and Al/MoO₃ (950 m/s) composite materials [38,39]. Note that this comparison is made for indicative purposes only, as the fuel and oxidizer particle sizes, equivalence ratios, loading densities, and mixture preparation methods are not entirely similar in the various works.

4. Conclusions

In this study, indium tin oxide (ITO), an n-type semiconductor material, was chosen as an oxidizer and mixed with aluminum to formulate thermite. It showed attractive electrical conductivity, making it ideal for antistatic applications. ITO nanoparticles and microparticles were used to evaluate the size effect on the sensitivities and reactive properties of as-prepared Al/ITO energetic composite materials. Two major differences can be noted in terms of energetic behavior.

First, in terms of sensitivity properties, while the energetic Al/ITO_μm and Al/ITO_nm formulations showed insensitivities to impact and friction tests and can be classified as safe, the ITO_μm particle-based formulation was strongly desensitized to electrostatic discharges compared to its nano-sized counterpart (13.70 vs. <0.21 mJ). This result can be interpreted by taking into account the higher electrical conductivity of ITO_μm compared to ITO_nm. Furthermore, it represents an easier formation of an electrical conductive pathway with large ITO particles. Second, as the ITO particle size decreased, the reactivity behavior improved with a shorter ignition delay and an improved combustion event. In a confined environment, the burning rate of the Al/ITO_nm energetic thermite was determined to be close to 650 m/s.

Reactive and spark-desensitized nanothermites can be formulated using an oxidizer in micrometric dimensions form but structured at the nanoscale. The controlled sintering (porosity preservation) of oxidizer nanoparticles may represent a solution. Mixed with an aluminum fuel, this type of architecture can combine the reactivity and insensitivity from the nanoscale and the micro-scale, respectively.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1. Video S1: Combustion videos in unconfined configuration of the (a) Al/ITO_μm and (b) Al/ITO_nm energetic systems, respectively. Equivalence ratio of 1.2. Video S2: Combustion videos in unconfined configuration of the (a) Al/ITO_μm and (b) Al/ITO_nm energetic systems, respectively. Equivalence ratio of 1.2.

Author Contributions: E.P. and P.G. carried out the experimental work. B.L. and F.O. performed scanning electron microscopy analysis and sensitivity tests, respectively. P.G. interpreted corresponding data, suggested and guided this research, and wrote the paper. All authors read and agreed to the published version of the manuscript.

Funding: The authors wish to thank the French National Centre for Scientific Research (CNRS), the French German Research Institute of Saint-Louis (ISL, Saint-Louis, France), and the University of Strasbourg (UNISTRA, Strasbourg, France) for funding.

Institutional Review Board Statement:

Data Availability Statement: Not applicable.

Acknowledgments: The authors express their acknowledgements to Y. Boehrer (ISL, Saint-Louis, France) for video recordings and to L. Vidal (IS2M, Mulhouse, France) for the transmission electron microscopy analysis.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Akhavan, J. *The Chemistry of Explosives*, 2nd ed.; Royal Society of Chemistry: London, UK, 2004.
2. Fischer, S.H.; Grubelich, M.C. Theoretical energy release of thermites, intermetallics, and combustible metals. In Proceedings of the 24th International Pyrotechnics Seminar, Monterey, CA, USA, 27–31 July 1998; pp. 231–286.
3. Pantoya, M.L.; Granier, J.J. Combustion Behaviour of Highly Energetic Thermites: Nano versus Micron Composites. *Propellants Explos. Pyrotech.* **2005**, *30*, 53–62.
4. Pantoya, M.L.; Levitas, V.I.; Granier, J.J.; Henderson, J.B. Effect of bulk density on reaction propagation in nanothermites and micronthermites. *J. Propuls. Power* **2009**, *25*, 65–470.
5. Agrawal, J.P. *High Energy Materials*, 1st ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2010.
6. No. 4489; NATO Standardization Agreement (STANAG) on Explosives, Impact Sensitivity Tests, 1st ed. NATO Standardization Agency: Brussels, Belgium, 1999.
7. No. 4487; NATO Standardization Agreement (STANAG) on Explosive, Friction Sensitivity Tests, 1st ed. NATO Standardization Agency: Brussels, Belgium, 2002.
8. United Nations. *Recommendations on the Transport of Dangerous Goods: Manual of Tests and Criteria*, 4th revised ed.; United Nations, New York, NY, USA; Geneva, Switzerland, 2007.
9. Talawar, M.B.; Agrawal, A.P.; Anniyappan, M.; Wani, D.S.; Bansode, M.K.; Gore, G.M. Primary explosives: Electrostatic discharge initiation, additive effect and its relation to thermal and explosive characteristics. *J. Hazard. Mater.* **2006**, *137*, 1074–1078.
10. Greason, W.D. Electrostatic discharge characteristics for the human body and circuit packs. *J. Electrostat.* **2003**, *59*, 285–300.
11. Moureaux, P.; Poyard, J.L. *Phénomènes Electrostatiques — Risques Associés Et Prévention*; INRS: Quebec City, QC, Canada, 2019; ED 6354.
12. Gibot, P.; Miesch, Q.; Bach, A.; Schnell, F.; Gadiou, R.; Spitzer, D. Mechanical desensitization of an Al/WO₃ nanothermite by means of carbonaceous coatings derived from carbohydrates. *C J. Carbon Res.* **2019**, *5*, 37.
13. Gibot, P.; Goetz, V. Aluminium/Tin (IV) oxide thermite composite: Sensitivities and reaction propagation. *J. Energ. Mater.* **2020**, *38*, 295–308.
14. Puszynski, J.A.; Bulian, C.J.; Swiatkiewicz, J.J. Processing and ignition characteristics of aluminum-bismuth trioxide nanothermite system. *J. Propuls. Power* **2007**, *23*, 698.
15. Poper, K.H.; Collins, E.S.; Pantoya, M.L.; Daniels, M.A. Controlling the electrostatic discharge ignition sensitivity of composite energetic materials using carbon nanotube additives. *J. Electrostat.* **2014**, *72*, 428–432.
16. Siegert, B.; Comet, M.; Muller, O.; Pourroy, G.; Spitzer, D. Reduced-sensitivity nanothermites containing manganese oxide filled carbon nanofibers. *J. Phys. Chem. C* **2010**, *114*, 19562–19568.
17. Thiruvengadathan, R.; Chung, S.W.; Basuray, S.; Balasubramaniam, B.; Staley, C.S.; Gangopahyay, K.; Gangopadhyay, S. A versatile self-assembly approach toward high performance nanoenergetic composite using functionalized graphene. *Langmuir* **2014**, *30*, 6556–6564.
18. Bach, A.; Gibot, P.; Vidal, L.; Gadiou, R.; Spitzer, D. Modulation of the Reactivity of a WO₃/Al Energetic Material with Graphitized Carbon Black as Additive. *J. Energetic Mater.* **2015**, *33*, 260–276.
19. Gibot, P.; Bach, A.; Vidal, L.; Schnell, F.; Gadiou, R.; Spitzer, D. Safer and performing energetic materials based on polyaniline-doped nanocomposites. *J. Energetic Mater.* **2017**, *35*, 136–147.
20. Gibot, P.; Goetz, V. SnO₂-polyaniline composites for the desensitization of Al/SnO₂ thermite composites. *J. Appl. Polym. Sci.* **2020**, *137*, 48947.
21. Foley, T.; Pacheco, A. Development of nanothermite composites with variable electrostatic discharge ignition thresholds. *Propellants Explos. Pyrotech.* **2007**, *32*, 431–434.
22. Yana, N.; Qin, L.; Hao, H.; Hui, L.; Zhao, F.; Feng, H. Iron oxide/aluminum/graphene energetic nanocomposites synthesized by atomic layer deposition: Enhanced energy release and reduced electrostatic ignition hazard. *Appl. Surf. Sci.* **2017**, *408*, 51–59.
23. Li, S.; Tian, M.; Gao, Q. Nanometre-thin indium tin oxide for advanced high-performance electronics. *Nat. Mater.* **2019**, *18*, 1091–1097.
24. Du, J.; Chen, X.; Liu, C.; Ni, J.; Hou, G.; Zhao, Y.; Zhang, X. Highly transparent and conductive indium tin oxide thin films for solar cells grown by reactive thermal evaporation at low temperature. *Appl. Phys. A Mater. Sci. Process.* **2014**, *117*, 815–822.
25. Luis, A.; Nunes de Carvalho, C.; Lavareda, G.; Amaral, A.; Brogueira, P.; Godinho, M.H. ITO coated flexible transparent substrates for liquid crystal-based devices. *Vacuum* **2002**, *64*, 475–479.
26. Betz, U.; Olsson, M.K.; Marthy, J.; Escola, M.F.; Atamny, F. Thin films engineering of indium tin oxide: Large area at panel displays application. *Surf. Coat.* **2006**, *200*, 5751–5759.

-
27. Wan, Q.; Dattoli, E.N.; Fung, W.Y.; Guo, W.; Chen, Y.; Pan, X.; Lu, W. High-performance transparent conducting oxide nanowires. *Nano Lett.* **2006**, *6*, 2909–2915.
 28. Sun, Y.; Chang, H.; Wu, S.; Leng, Y.; Wang, L. Study on electromagnetic shielding of infrared/visible optical window. *Mod. Appl. Sci.* **2015**, *9*, 231–236.
 29. Kerkache, L.; Layadia, A.; Mosser, A. Effect of oxygen partial pressure on the structural and optical properties of dc sputtered ITO thin films. *J. Alloys Compd.* **2009**, *485*, 46–50.
 30. Al-Dahoudi, N.; Bisht, H.; Gobbert, C.; Krajewski, T.; Aegerter, M. Transparent conducting, anti-static and antistatic—Antiglare coatings on plastic substrates. *Thin Solid Films* **2001**, *392*, 299–304.
 31. Gibot, P. Templated synthesis of Cr₂O₃ material for energetic composites with high performance. *Solid State Sci.* **2019**, *94*, 162–167.
 32. Martirosyan, K.S. Nanoenergetic gas-generator: Principles and applications, *J. Mater. Chem.* **2011**, *21*, 9400–9405.
 33. Gibot, P.; Comet, M.; Eichhorn, A.; Schnell, F.; Muller, O.; Cizek, F.; Boehrer, Y.; Spitzer, D. Highly insensitive/reactive thermite prepared from Cr₂O₃ nanoparticles. *Propellants Explos. Pyrotech.* **2011**, *36*, 80–87.
 34. Gibot, P.; Comet, M.; Vidal, L.; Moitrier, F.; Lacroix, F.; Suma, Y.; Schnell, F.; Spitzer, D. Synthesis of WO₃ nanoparticles for superthermites by the template method from silica spheres. *Solid State Sci.* **2011**, *13*, 908–914.
 35. Gibot, P.; Puel, E. Study on indium (III) oxide/aluminum thermite energetic composites. *J. Compos. Sci.* **2021**, *5*, 166.
 36. Gibot, P.; Oudot, F.; Lallemand, B.; Schnell, F.; Spitzer, D. Nanosized niobium (V) and tantalum (V) oxide ceramics as competitive oxidizers within aluminum-based nanothermites. *Energ. Mater. Front.* **2021**, *2*, 167–173.
 37. Pichot, V.; Comet, M.; Miesch, J.; Spitzer, D. Nanodiamond for tuning the properties of energetic composites. *J. Hazard. Mater.* **2015**, *300*, 194–201.
 38. Bezmelnitsyn, A.; Thiruvengadathan, R.; Barizuddin, S.; Tappmeyer, D.; Apperson, S.; Gangopadhyay, K.; Gangopadhyay, S. Modified nanoenergetic composites with tunable combustion characteristics for propellant applications. *Propellants Explos. Pyrotech.* **2010**, *35*, 384–394.
 39. Sanders, V.E.; Asay, B.W.; Foley, T.J.; Tappan, B.C.; Pacheco, A.N.; Son, S.F. Reaction propagation of four nanoscale energetic composites (Al/MoO₃, Al/WO₃, Al/CuO and Bi₂O₃). *J. Propuls. Power* **2007**, *23*, 707–714.