One-step solvent-free mechanochemical synthesis of metal iodate fine powders

Haiyang Wang, Jeffery B. DeLisio, Tao Wu, Xizheng Wang, Michael R. Zachariah *

Department of Chemical and Biomolecular Engineering and Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, United States

A R T I C L E   I N F O
Article history:
Received 23 June 2017
Received in revised form 2 October 2017
Accepted 8 October 2017
Available online 14 October 2017

Keywords:
Mechanochemical synthesis
Metal iodate
Solid-state
Superfine powders
Solvent-free

A B S T R A C T
Metal iodates are strong iodine rich oxidizers which can be used in the formulation of biocidal energetic materials. Generally, metal iodates particles were synthesized by chemical precipitation methods with a large size distribution. In this work, we developed a one-step and solvent-free, high yield method to synthesize metal iodate fine powders by mechanochemistry. Compared to the conventional chemical precipitation method, the size of final products can be reduced by 20–500 times. The method generates particles with a narrower size distribution and high yield, and is sufficiently generic as to enable creation of a variety of metal iodates including AgIO₃, Ca(IO₃)₂, Mn(IO₃)₂ and Cu(IO₃)₂. Moreover, the synthesis is conducted in the solid states with little to no solvent. The role of process conditions (temperature, hydration state, and milling time) on reaction products was investigated by TG/DSC and XRD. We believe that crystalline water bound to the metal nitrates precursor lowers the Tammann’s temperature sufficient to unbind water so as to promote ion diffusion and thus facilitate reaction in the absence of a solvent. The reaction is promoted by the milling process which attrits the particles to expose fresh unreacted surfaces and reduces particle size.

© 2017 Published by Elsevier B.V.

1. Introduction

“Mechanochemistry” refers to a technique that uses mechanical energy to induce physicochemical transformations and chemical reactions between solids [1–4]. So called “Green Manufacturing” approaches hope to minimize the use of solvents, particularly those that are petroleum based [2].Mechanochemistry, particularly if conducted in a dry state offers the potential to significantly decrease the environmental footprint, from both an energy and chemical usage and disposal [1,2]. In recent years, mechanochemical techniques have evolved into a mainstream synthesis technique to produce various materials including inorganic solids [5,6], cocrysalts [7], organic [8], and metal-organic frameworks (MOFs) [9]. In a mechanochemical process, chemical reactions occur at the interfaces of nanoscale layers that are continuously re-generated owing to repeated welding, deformation and fracture of the reactants mixture [10]. As a result, the temperature for inducing a chemical reaction in a mechanochemical process is lowered [10–15].

In this study, we focus on energetic material components that can be used in the neutralization of bacterial spores. Among different energetic systems, one of the most interesting are nanothermites, also known as metastable interstitial composites (MICs), consisting of nanosized fuel (normally aluminum nanoparticles, Al NPs) and nanosized metal oxides (such as CuO, Bi₂O₃, and Fe₂O₃), and shown to have >1000× higher reactivity when compared to conventional thermites [16–20]. Many techniques such as electrospray/electrospinning [21] and ball milling [22–24] (top-down), magnetron sputtering [25] and electrodeposition [26] (down-top), spray pyrolysis [27–29], precipitation [30,31] and combustion synthesis [32], etc. have been employed to generate the nanosized oxidizers in nanothermite systems. Using these methods, nanoparticles of various sizes and morphologies can be created. However, none of these methods simultaneously possess the three important characteristics for green manufacturing: solvent-free; low thermal budget, economical large-scale production.

Compared to metal oxides, metal iodates are much stronger oxidizers in thermitic applications because upon decomposition, not only is corresponding metal oxides formed, by oxygen and iodine gas are released at relatively low temperatures [30,31,33]. One very important aspect of this is that one of the by-products of reaction elemental iodine, is a very effective biocide [23,27,29,31,33]. The large exothermicity from reactions with metals such as aluminum and the large iodine content make metal iodates viable candidates for neutralization of biological warfare agents such as Bacillus anthracis (anthrax) spores [30,31,33]. Table 1 shows data of iodine content, energy density and adiabatic flame temperatures for different metal iodates based thermites (determined by NASA CEA and Cheetah codes). As shown in Table 1, metal iodate based thermites [with aluminum] have relatively high iodine content (~40 wt%), high energy densities (~5 kJ/g) and high adiabatic flame temperatures (~4000 K). Commonly, metal iodates particles such as AgIO₃, Ca(IO₃)₂, Mn(IO₃)₂ and Cu(IO₃)₂ are synthesized by

---

Footnotes:

* Corresponding author.
E-mail address: mrz@umd.edu (M.R. Zachariah).

Abbreviations: XRD, X-ray diffractometer; SEM, scanning electron microscope; EDS, Energy-dispersive X-ray spectroscopy; DI water, deionized water; Tm, melting point.

© 2017 Published by Elsevier B.V.
high reactivity when formulated with nano aluminum. Previously, our superballs, 7/32″ diameter, were used in ambient conditions using plastic centrifuge tubes purchased from Omega, after stirring for 24 h. The frequency of milling varied from 3.0 to 0.4 g, each respectively. All the experiments were conducted at room temperature (~25 °C). The average size of the produced Ca(IO₃)₂, Mn(IO₃)₂ and Cu(IO₃)₂ crystals are ~1.7 mm, ~0.1 mm and ~0.4 mm (Fig. S2). To obtain smaller particles, the concentration of the three metal nitrates and potassium iodates used was increased to 1 mol/L and 0.3 mol/L, respectively. The precipitation reaction temperature and time were also elevated to 70 °C and 50 min in a water bath. The average size of the produced Ca(IO₃)₂, Mn(IO₃)₂ and Cu(IO₃)₂ crystals are ~100 μm, ~5 μm and ~2 μm (Fig. S3). The Mn(IO₃)₂ needles and Cu(IO₃)₂ plates also agglomerate into large spheres with a diameter of >20 μm and >10 μm, respectively. These needles and plates are not easy dispersed using ultra-sonication.

2.4. Washing/drying process

The product made by the above methods need to be processed by a simple washing and drying process. The samples were loaded into a large centrifuge tube (15 mL, FisherBrand) with 15 mL deionized water (DI water) and sonicated for 5 min, and centrifuged for 10 min at 7000 rpm (Labnet, Model: Hermle Z300) to obtain the final product. The whole process was repeated 3 times to enable full removal of any impurities. The sample was then dried overnight in a vacuum oven to remove free water. The final products were gently broken apart into powders with a spatula.

2.5. XRD, SEM/EDS, and TG/DSC

A Bruker X-ray diffractometer (XRD, D8 with Cu-kα radiation) was used to determine the crystallinity state of each metal iodate. A Hitachi S-4700 scanning electron microscope (SEM) attached with Energy-dispersive X-ray spectroscopy (EDS) was employed to analyze the particle size/morphology and elemental composition, respectively. The size of particles was directly measured from the SEM images by Nano Measurer 1.2. At least 200 particles for each sample were measured and the average reported. The metal iodate powders were attached to the SEM stage using carbon tape. A thin layer of Au (~3–5 nm) was deposited on the surface to increase the samples’ conductivity before testing. Thermogravimetric/differential scanning calorimetry (TG/DSC) results were obtained with a TA Instruments Q600 at a rate of 10 ºC/min up to 1000 ºC in an argon atmosphere (100 mL/min).

3. Results and discussion

Generally, metal iodates precipitation can be obtained by mixing metal nitrate and potassium iodate solution as Eq. (1) shows. Table S1 shows the heat of formation of all the reactants and products and the Gibbs free energy change of each reaction. The latter is estimated as the change of reaction enthalpies (entropy change was assumed ~0). All the values of Gibbs free energy changes are negative, which means that based on Eq. (1), metal iodates form spontaneously.

$$M(NO_3)_x + xKIO_3 \rightarrow M(IO_3)_x + xKNO_3$$  \hspace{1cm} (1)

Six different metal iodates with cations spanning the periodic table from alkaline earth metals (such as Calcium) to transition metals (such as Iron) to post-transition metals (such as Bismuth) were synthesized by dry mechanochemistry and the corresponding SEM images in Fig. 1 shows a relatively narrow size distribution. For comparison, these metal iodates were also synthesized using a chemical precipitation method as shown in Fig. S1–S3. The details can be found in the
Experimental section. Using chemical precipitation $\text{AgIO}_3$ can be prepared at room temperature. However, $\text{Cu(IO}_3\text{)}_2$, $\text{Mn(IO}_3\text{)}_2$, and $\text{Ca(IO}_3\text{)}_2$ typically required heating to 70 °C, for ~1 h. The resulting particles are quite large, with significant agglomeration (Fig S3).

Table 2 tabulates results for both ball milled and precipitation synthesis. Mechanochemistry produces much smaller sizes with narrower size distribution than precipitation growth. The average size of $\text{AgIO}_3$, $\text{Cu(IO}_3\text{)}_2$, $\text{Mn(IO}_3\text{)}_2$, and $\text{Ca(IO}_3\text{)}_2$ particles was reduced by a factor 20, 40, 100 and 500, respectively, when using mechanochemistry as compared to chemical precipitation. However, $\text{Bi(IO}_3\text{)}_3$ and $\text{Fe(IO}_3\text{)}_3$ mechanochemically generated particles were 6 and 3 times larger than those made from chemical precipitation, respectively. The latter result is presumably because the low solubility of $\text{Bi(IO}_3\text{)}_3$ and $\text{Fe(IO}_3\text{)}_3$ in water leads to a higher nucleation rate. Both $\text{Bi(IO}_3\text{)}_3$ and $\text{Fe(IO}_3\text{)}_3$ particles obtained by the chemical precipitation method are amorphous supporting this claim [31].

The XRD results of all the products after only 10 min's milling (25 Hz: milling frequency) are shown in Fig. 2 (except $\text{Bi(IO}_3\text{)}_3$ and $\text{Fe(IO}_3\text{)}_3$ cases) and clearly confirm that all the products are a mixture of metal iodates and the other by-product $\text{KNO}_3$, with no evidence of unreacted precursor. Washing (with water) is shown to leave only the desired metal iodate. (Fig. S4 and S5). The $\text{Bi(IO}_3\text{)}_3$ and $\text{Fe(IO}_3\text{)}_3$ cases are more complex which will be discussed later in this paper. The yields of metal iodates made by the two methods are also listed in Table 2. In general, the yields from the mechanochemical approach are >75%, and higher than chemical precipitation and in some cases, such as $\text{Ca(IO}_3\text{)}_2$ and $\text{Cu(IO}_3\text{)}_2$, the yield was almost doubled.

3.1. The role of thermal properties on the reaction

Generally, solid-solid reaction chemistry needs high pressure and/or high temperature for a sustained period to overcome the diffusion bottleneck for reaction. However, in this work, we achieve efficient reactions between solids at near ambient pressure and temperature. It is well accepted that the Tammann temperature ($T_s$) is a good metric to determine when atoms or molecules in a solid acquired sufficient energy for their bulk mobility and reactivity to become appreciable (such as to sinter) [39]. Therefore, the Tammann temperature is related to the melting point ($T_m$) of the solid. For example, the Tammann temperature for salts is usually evaluated as $\sim 0.57 T_m$ (Kelvin scale) [39]. Table 3 shows the melting temperature, the calculated Tammann temperature and decomposition temperature ($T_d$) of various metal nitrates.

From Table 3, we see that all the hydrated metal salt except $\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O}$ have a low melting point ($<323 \text{ K (50 °C)}$). This makes the corresponding Tammann temperature below 223 K (−50 °C). Direct measurement of temperature after 5 min of milling showed that the sample temperature was $>318 \text{ K (45 °C)}$ owing to the mechanical energy input, which is $>100 \text{ K}$ higher than the Tammann
temperature of the most metal nitrates. Therefore, according to the definition of Tammann temperature, the diffusion speed of mobile species into crystalline lattice should increase significantly when the temperature is higher than this critical point. Moreover, metal nitrates such as Cu(NO₃)₂·3H₂O are strongly hygroscopic which further promotes ion transport between the reactants. AgNO₃ and KIO₃ have a much higher melting point of 483 K and 833 K, raising their Tammann’s temperatures as 275 K and 475 K, respectively.

The rapid reaction between metal nitrate and potassium iodate can be achieved mechanochemically, in part because the mechanical energy input will exothermically accelerate the ion diffusion after the temperature is raised above the Tammann temperature. To further confirm this, a simply mixed Ca(NO₃)₂·4H₂O/KIO₃ and a ball milled product (25 Hz, 10 min) of Ca(NO₃)₂·4H₂O/KIO₃ (both in stoichiometric ratio) were heated in a TG/DSC at 10 °C/min till to 1000 °C in argon. The simply mixed case was kept at ~50 °C for 30 min to complete the reaction. For a better comparison, all the reactants and products (Ca(NO₃)₂·4H₂O, KIO₃, KNO₃ and Ca(IO₃)₂·H₂O) and a simply mixed KNO₃/Ca(IO₃)₂·H₂O (same amount produced according to Eq.(1)) were also heated in the TG/DSC in the same procedure. As Fig. 3 shows, for the ball milled case, the TG/DSC curves are almost the same as that of KNO₃/Ca(IO₃)₂·H₂O, which indicates that the mechanochemical reaction is complete. For the simply mixed case, the TG/DSC curves are similar to that of the mixture of KNO₃/Ca(IO₃)₂·H₂O. That is, after being heated at 50 °C for 30 min, the simply mixed Ca(NO₃)₂·4H₂O/KIO₃ has partially transformed to KNO₃/Ca(IO₃)₂·H₂O. One direct evidence is that the dehydration endothermic peak of Ca(IO₃)₂·H₂O (~200 °C) and melting endothermic peak of KNO₃ (~330 °C) were all detected in the three curves. One interesting point is that there is a wide and deep endothermic peak around 50 °C for simply mixed Ca(NO₃)₂·4H₂O/KIO₃ case while that peak for just Ca(NO₃)₂·4H₂O case is sharper. The shape change of this peak might be attributed to the reaction between Ca(NO₃)₂·4H₂O and KIO₃.

As we saw in Table 3, precursors at room temperature are already above the Tammann temperature in most cases. Simple mixing the two reactants of metal nitrates (except AgNO₃) with KIO₃ at room temperature will lead to interfacial reaction, however the reaction is limited by diffusion and thus milling is necessary to remove the reacted (product) interfacial layers to expose fresh material for continued reaction.

### Table 3

<table>
<thead>
<tr>
<th>Reactant 1</th>
<th>Tₘ, K</th>
<th>Tₛ, K</th>
<th>Tₐ, K</th>
<th>Obtained iodate by mechanochemistry?</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNO₃</td>
<td>483</td>
<td>275</td>
<td>523–713</td>
<td>Yes with 0.1 mL DI water</td>
</tr>
<tr>
<td>Bi(NO₃)₃·5H₂O</td>
<td>303</td>
<td>173</td>
<td>323–333</td>
<td>Yes with Al₂O₃ balls</td>
</tr>
<tr>
<td>Cu(NO₃)₂·3H₂O</td>
<td>388</td>
<td>221</td>
<td>443</td>
<td>Yes</td>
</tr>
<tr>
<td>Fe(NO₃)₃·9H₂O</td>
<td>320</td>
<td>182</td>
<td>398</td>
<td>Yes</td>
</tr>
<tr>
<td>Mn(NO₃)₂·4H₂O</td>
<td>310</td>
<td>177</td>
<td>433–473</td>
<td>Yes</td>
</tr>
<tr>
<td>Ca(NO₃)₂·4H₂O</td>
<td>316</td>
<td>180</td>
<td>475</td>
<td>–</td>
</tr>
<tr>
<td>KIO₃</td>
<td>833</td>
<td>475</td>
<td>833</td>
<td>—</td>
</tr>
</tbody>
</table>

### 3.2. The role of hydration in the reaction

Fig. 4 shows, that the Tammann’s temperature of AgNO₃ is as low as 275 K, however milling AgNO₃ and KIO₃ does not produce AgIO₃, which suggests the importance of crystal water. As shown in Table 3 and described above, AgIO₃ can be synthesized by milling with 0.1 mL DI water (Fig. 4). We note at this point that addition of 0.1 mL of water only dissolves a negligible amount of the two reactants, but should provide a pathway for ion transport.

To further explore the role of hydration in the diffusion and reaction, Cu(NO₃)₂·3H₂O and Ca(NO₃)₂·4H₂O were mixed with KIO₃ separately and characterized by SEM. In this experiment, the metal nitrate salts and KIO₃ crystals were freshly mixed before loading into the SEM without any other treatment. Fig. 5 shows that upon beam heating in the
Fig. 5. SEM showing fast diffusion of KIO₃ into Cu(NO₃)₂·3H₂O (a and b) and Ca(NO₃)₂·4H₂O (d and e). The products after 10 min's milling of Cu(NO₃)₂·3H₂O/KIO₃ mixture (c) and Ca(NO₃)₂·4H₂O/KIO₃ mixture (f).

Fig. 6. Temporal XRD of milling Bi(NO₃)₃·5H₂O/KIO₃ after 3 washings with DI water. Note: 25/s (25 Hz) is the frequency of shaking during ball milling.
The metal nitrates began to melt with bubbling, resulting from evaporation of water from nitrates. (confirmed by EDS) The spreading bubbles rapidly dissolved the exterior surface of KIO₃ crystals (Fig. 5a to Fig. 5b, Fig. 5d to e), which reacts to produce metal iodate NPs (confirmed by EDS) within a KNO₃ matrix. After washing away the KNO₃ (dark part in Fig. 5c and f), the monodisperse metal iodate NPs can be seen in Fig. 5f.

3.3. The role of milling time on the reaction

The milling products of Bi(NO₃)₃·5H₂O/KIO₃, Cu(NO₃)₂·3H₂O/KIO₃ and Fe(NO₃)₃·9H₂O/KIO₃ with different milling durations and frequencies are shown in Fig. 6 and S5, respectively. Fig. 6 shows temporal XRD patterns of the effect of milling on Bi(NO₃)₃·5H₂O/KIO₃. We note that Al₂O₃ balls were used instead of hardened steel balls (used for the others five metal iodates) in the synthesis of Bi(IO₃)₃. This is because the decomposition temperature of Bi(NO₃)₃·5H₂O is as low as 323–333 K. With hardened steel balls (~318 K), the temperature can temporarily reach the point of the decomposition of Bi(NO₃)₃·5H₂O. And in fact, with hardened steel balls, Bi₂O₃ was detected in the final products, which confirms the above assumption. With Al₂O₃ balls, the temperature reached is only ~308 K, which is lower than the decomposition temperature (323–333 K) of the nitrates, but still much higher than its Tammann temperature (173 K). There is a decrease in Bi(NO₃)₃·5H₂O and KIO₃ intensity, with increased milling duration from 10 s to 360 s (25/s), which is essentially completely gone by 450 s. This decrease implies reaction is occurring, but the lack of any product diffraction pattern indicates an amorphous product or intermediate. New product diffraction patterns appear around 600 s which indicate nucleation of the reactant temperature is measured to increase rapidly to 318 K, which is ~100 K higher than the Tammann temperature. This significantly enhances diffusion rates and reaction speed mediated by water as an ion conductor. The most interesting part of this work is that superfine metal iodates can be produced with a totally dry mechanochemical process with high efficiency (~600 s for a production of ~2500 mg). One key factor for the fast reaction is water (crystal water and free water) inside the metal nitrate salts. Metal nitrate salts with crystal water have a much lower Tammann temperature than those without crystal water. Most metal nitrate hydrates might contain some free water owing to their strong hygroscopic property, which further promotes the ion diffusion between the reactants. Milling attains the particles to expose fresh unreacted surfaces and reduces particle size. Milling may also introduce defects [2] that contribute to the nucleation of the final products, in turn creating smaller particles. The continually formed KNO₃ may also act as a buffering material to protect metal iodate particles from decomposition and agglomeration.

5. Conclusions

In this work, we use a solid-solid mechanochemical method to produce various metal iodate superfine powders. The formed particles have a much smaller and narrower size distribution compared to those made by the chemical precipitation method (except for Fe(IO₃)₃ and Bi(IO₃)₃). This method also has a high yield of ~75% and a high production rate (2.5 g in 600 s), which is easily scalable. This method provides an economical and green approach for superfine powders synthesis.

Acknowledgment

This work was supported by Defense Threat Reduction Agency (DTRA). We acknowledge the support of the Maryland Nanocenter and its NispLab. The NispLab is supported in part by the NSF as a MRSEC Shared Experimental Facility.

Appendix A. Supplementary data

Supplementary data to this article can be found at https://doi.org/10.1016/j.powtec.2017.10.024.

References


