Core–Shell Al–Polytetrafluoroethylene (PTFE) Configurations to Enhance Reaction Kinetics and Energy Performance for Nanoenergetic Materials

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Energetic Materials

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Abstract: The energy performance of solid energetic materials (Al, Mg, etc.) is typically restricted by a natural passivation layer and the diffusion-limited kinetics between the oxidizer and the metal. In this work, we use polytetrafluoroethylene (PTFE) as the fluorine carrier and the shielding layer to construct a new type of nano-Al based fuels. The PTFE shell not only prevents nano-Al layers from oxidation, but also assists in enhancing the reaction kinetics, greatly improving the stability and reactivity of fuels. An in situ chemical vapor deposition combined with the electrical explosion of wires (EEW) method is used to fabricate core–shell nanostructures. Studies show that by controlling the stoichiometric ratio of the precursors, the morphology of the PTFE shell and the energy performance can be easily tuned. The resultant composites exhibit superior energy output characters than that of their physically mixed Al/PTFE counterparts. This synthetic strategy might provide a general approach to prepare other high-energy fuels (Mg, Si).

Introduction

Solid fuels with high energy density and superior extraction efficiency are strongly desired in the application fields of energy storage and transfer,[1] fuel cells,[2] aerospace propulsion systems,[3] super-thermites,[4] and micro-electromechanical systems (MEMS) etc.[5,6] For Al-based solid fuels,[7,8] nano-Al has higher specific surface areas than that of its micrometer-sized powder, and thus has improved combustion efficiency and reaction rate. However, nano-Al is easily oxidized and the produced passivation Al2O3 layer (usually 4–6 nm) on the nano-Al surfaces has a high melting point (2072 °C),[9,10] leading to higher ignition temperature and longer ignition time. In addition, this Al2O3 layer can cause some dead weight and then inhibit the diffusion of reactants, significantly reducing the energy density and extraction efficiency of the fuels.[11–13]

Polytetrafluoroethylene (PTFE) is usually used as the fluorine carrier and typical oxidizer for aluminum, with a high content of fluorine (76%) and an ultrahigh energy density (21 kJ cm−3).[14,15] The reaction product AlF3 has a relatively low melting point (1272 °C) compared with Al2O3, and the released gas in the reaction potentially facilitates the mass transfer process.[16,17] Generally, it is believed that the distance of mass transport, homogeneity of components, as well as the interfaces between fuel and oxidizer are important factors in determining the energy release rate for the nano-Al solid-state reactions.[18–20] R. R. Naik et al. used proteins to adjust the oxidizer and Al, and the mass transport distance was shortened and the energy release rate was improved.[21] C. Rossi et al. employed DNA to assemble CuO-Al and they found the initial reaction temperature decreased while the contact area and the energy release rate are strongly improved in comparison with the physically mixed CuO-Al configurations.[22] Tse et al. used WO3/Al nanoarrays to eliminate the Al2O3 interfaces and improve the performance.[11] In our recent work, we used the energetic superlattice PTFE-Al to realize an enhanced energy output.[22] These efforts greatly improved the performance of Al-based fuels, but there still remain large margins to be exploited, for example, the energy release rate.

Core–shell nanostructures containing different components with increased interfacial areas and intimacy of reactive components are considered as good options to enhance the energetic performance.[23–26] We envisioned that if the PTFE serves as the passivation layer of nano-Al, the oxidation of Al can be suppressed and then the sensitivity to any unintended initia-
tions can be reduced, due to the high hydrophobicity and soft mechanical properties of PTFE. Furthermore, the energy performance is expected to be tuned over a relatively large dynamic range by changing the thickness of the PTFE shell.

Herein, we design and prepare a nano-Al/PTFE core–shell structure by an in situ and continuous synthesis process. This route ensures the active nano-Al particles immediately being coated with PTFE and then being protected as long as the nanosized Al powder is synthesized. Our investigations show that the reactivity and stability are dramatically enhanced with this configuration. The mass transport limitations are relieved and the reactions become kinetically controlled. Thermal analysis and combustion tests indicate that our new structures are with significantly enhanced energy output.

Results and Discussion

Characterization of core–shell Al-PTFE

A typical core–shell nanostructure is confirmed by the TEM observations (Figure 1a and 1b). The average size of the aluminum nanoparticles is about 100 nm (note that by controlling the fabrication process in EEW (i.e., pressure), nano-Al with different sizes can be obtained). The PTFE is uniformly coated on the nano-Al surface, with a shell thickness of about 10 nm (Figure 1c). The lattice fringe image shows the crystalline nature and the interplanar spacing of 0.232 nm, corresponding to the (1 1 1) plane of aluminum (Figure S1 in the Supporting Information).

The thickness of the shell is important to improve stability and enhance energy output efficiency of such core–shell nanostructures. From the stoichiometric reaction \((4\text{Al} + 3(-\text{C}_2\text{F}_4)n \rightarrow 4\text{AlF}_3 + 6\text{C})\), it is possible to estimate the theoretical thickness and the mass of the PTFE shell by the reaction time and the flow rate of HFPO (Figures S2 and S3 in the Supporting Information). For instance, when the average particle size of aluminum is 100 nm, the theoretical thickness of the PTFE shell is about 34 nm.

We then examined the formation mechanism of the PTFE shell, as schematically shown in Figure 1g. Firstly, CF\(_2\) radicals generated from HFPO polymerize on the surface of aluminum will form initial nucleation sites, followed by further growth to give PTFE nanoparticles.\(^{[28, 29]}\) Then, more PTFE nanoparticles are accumulated and gradually connected to construct a PTFE nanofilm. Finally, integral core–shell Al-PTFE is formed with the continuous deposition and diffusion of CF\(_2\) radicals on aluminum surface. TEM (Figure 1f) confirms the growth of PTFE nanoparticles on the surface of aluminum. In the experiments, we found that a certain minimum amount of CF\(_2\) radicals is necessary and the shell thickness could be controlled by the reaction time and the flow of HFPO (see Figures S3 and S5 in the Supporting Information).

Figure 2a shows the Fourier transform infrared absorption spectra of the PTFE shell (red line) and the core–shell Al-PTFE (green line). Clear characteristic absorption signals for PTFE are
observed as CF₂ bonds, such as CF₂ wagging mode (634.2 cm⁻¹), CF₂ symmetric stretching mode (1153.6 cm⁻¹), and CF₂ asymmetric stretching mode (1206.9 cm⁻¹). The signal at 2337.5 cm⁻¹ may be attributed to the absence of the carbonyl (C=O) stretching mode of CF₂COF from the pyrolysis of hexafluoropropylene oxide. The XPS spectrum for the core–shell Al-PTFE sample (Figure 2b) consists of fluorine and carbon signals (689.6 and 295.9 eV), whereas the PTFE deposited on aluminum can cause a weak signal, which was attributed to oxygen (531.6 eV) with atomic percentage around 0.3%. Aluminum signals (77.45 eV) are extremely weak and this reveals that the aluminum particles are completely coated by PTFE films. The F/C ratio stoichiometry (1.97:1) of shell material is close to the value of theoretical PTFE (F/C ratio 2:1; see Figure S4 in the Supporting Information).

An XRD spectrum for the core–shell Al-PTFE is shown in Figure 2c. The spectrum matches well with that of crystalline aluminum; only few aluminum oxide signals are observed. A typical energy-dispersive spectrum (Figure 2d) of the as-prepared Al-PTFE composites indicates the presence of aluminum, carbon, and fluorine. Elemental oxygen is not detected in the sample, revealing that the PTFE shell provides good protection for aluminum. To further investigate the uniformity of the PTFE nanofilm on aluminum spheres, STEM mapping analysis is conducted. Figure 2e shows the STEM elemental map of Al and F, in which the distribution of F is consistent with that of Al, proving that the PTFE on the aluminum is uniformly distributed. Based on the above characterizations, we can safely conclude that nano-Al particles are completely coated with a PTFE shell, and the aluminum is effectively protected.

Stability of core–shell Al-PTFE

When deionized water (25°C) drops directly onto the aluminum surface, it gradually spreads due to the reaction between the water drop and the highly reactive nano-aluminum (Figure 3a left). Remarkably, the contact angle of the core–shell Al-PTFE (30 nm thickness shell) is over 118° (Figure 3a right). Typically, the contact angle increases with the shell thickness and will not change too much once the PTFE is over 30 nm. This indicates that, with the aid of hydrophobic PTFE, the core–shell structures would provide good resistance against moisture.

To further illustrate the stability of our core–shell PTFE-Al structures, the dissolution in sodium hydroxide (NaOH) is examined (2Al + 2NaOH + 2H₂O = 2NaAlO₂+3H₂). The dissolution reaction is monitored via the mass change of the powder samples. The reduction of the dissolution “rate constant” of aluminum in stoichiometric quantities of 0.01 M NaOH solutions upon the PTFE shell is used as a quantitative evaluation of the protective property. The effect of the PTFE shell on the dissolution rate of aluminum in NaOH solution is illustrated in Figure 3b. Compared with pure aluminum nanoparticles, the dissolution rate of core–shell Al-PTFE is 8.6 times lower than that of pure Al particles (typically, for the core–shell structure with 30 nm PTFE, the dissolution rate is 2.81 x 10⁻³ g·min⁻¹; for pure Al nanoparticles, the dissolution rate is 24.37 x 10⁻³ g·min⁻¹). From the above tests, it is observed that the PTFE shell can provide good protection to nano-Al, and further enhance the resistance against complex and variable environmental conditions.

Performance of core–shell Al-PTFE

To evaluate the reactivity and the energy output efficiency, the exothermic reactions of the Al-PTFE composites have been obtained using differential scanning calorimetry (DSC) analysis. The DSC profile of physically mixed Al-PTFE (showing a wide exothermic signal occurring between 450°C and 550°C and a sharp endothermic signal at 670°C as well as mild exothermic behavior (heat of reaction: 0.47 kJ·g⁻¹, resulting from the low mass transport rate and long diffusion distance and limitation of the reaction between fluorine and aluminum) is used as a baseline for comparison (Figure 4a). Surprisingly, for the core–shell nanostructure (PTFE ca. 10 nm), the exothermic signal appears at 410°C with a much larger heat output (1.81 kJ·g⁻¹). By changing the shell thickness, the heat of reaction, and the onset temperature, the core–shell Al-PTFE (2.43 kJ·g⁻¹, 386°C for a 30 nm shell) can be further tuned. We then get insights into this phenomena: 1) In the DSC analysis, we can see that PTFE is firstly decomposed to CF₂. Typically, the existence of CF₂ (or F) could assist in improving the reaction rate. 2) On the other hand, solid–solid diffusion-based exothermic reactions between the PTFE and aluminum could greatly reduce the onset temperature, which would lead
to the PTFE producing an oxide layer and increasing the expansion of the Al core. 3) As the core–shell can provide a particular thermal signature, we believe that the heterogeneous and well-defined interfaces between reactants also play important roles in the improved performance. In our experiments, the energy output increases almost linearly with the shell size when the thickness is less than 30 nm. This also indicates the limitations of the output performance in this configuration.

It is widely accepted that the interfacial contact between the fuel and the oxidizer plays an important role in the combustion behavior of nanomaterials. The reactivity of Al-PTFE was then evaluated by igniting a sample (2.0 g) in an combustion cell. Figure 4b shows the temporal pressure traces at selected time frames using high-speed camera: a) PTFE-Al mixtures, d) core–shell Al-PTFE (with 10 nm shell), e) core–shell Al-PTFE (with 30 nm shell). The heat of reaction (2.43 kJ g⁻¹) of the energetic core–shell nanomaterial (ca. 30 nm shell thickness) is much larger than that of the physically mixed Al-PTFE (0.47 kJ g⁻¹). Pressurization and combustion rate are significantly increased because of improved reaction kinetics resulting from increasing the interfacial contact area and the reduction of the diffusion distance between the reactants in the core–shell nanostructure. The results reveal the core–shell displays superior energetic properties, which can be tuned with the thickness of the PTFE shell.

Figure 4. a,b) Energetic properties of Al-PTFE composites. a) DSC profile, (black line: nano-Al coated by 30 nm PTFE, red line: nano-Al coated by 10 nm PTFE, blue line: physically mixed Al-PTFE). b) Simultaneous pressure as measured during combustion in a constant-volume pressure cell (black line: physically mixed Al-PTFE, red line: nano-Al coated by 30 nm PTFE, blue line: nano-Al coated by 10 nm PTFE). c–e) Visualization of combustion at selected time frames using high-speed camera: a) PTFE-Al mixtures, d) core–shell Al-PTFE (with 10 nm shell), e) core–shell Al-PTFE (with 30 nm shell). The heat of reaction (2.43 kJ g⁻¹) of the energetic core–shell nanomaterial (ca. 30 nm shell thickness) is much larger than that of the physically mixed Al-PTFE (0.47 kJ g⁻¹). Pressurization and combustion rate are significantly increased because of improved reaction kinetics resulting from increasing the interfacial contact area and the reduction of the diffusion distance between the reactants in the core–shell nanostructure. The results reveal the core–shell displays superior energetic properties, which can be tuned with the thickness of the PTFE shell.

Conclusion

In summary, a nano-Al based core–shell structure has been designed and successfully prepared by an in situ and continuous synthetic method. Introducing PTFE as oxidizer and shielding layer on nano-Al overcomes challenges of oxidation, and eventually improves energy release efficiency. By changing the thickness of the shell and the reaction stoichiometry, the reactivity of the core–shell Al-PTFE configuration can be further tuned. Our strategy could provide a general route to the synthesis of other energetic materials (Mg, Si), and have great potential in the design of energy devices, MEMS, underwater propulsion systems, as well as composite fuels (AP or HTPB binder system) etc.

Experimental Section

Preparation of core–shell Al-PTFE

The synthesis procedure is schematically shown in Scheme 1. Nano-Al particles were prepared by the EEW method with high purity aluminum wire (99.9999 %) under an Ar atmosphere in an explosion chamber. Then, the produced nano-Al particles were transferred to a powder filter to obtain the desired sizes, followed by coating with PTFE in the reactor chamber. Note that the coating process is line-of-sight and directional.

First, the undiluted hexafluoropropylene oxide (HFPO; CF₂CF(O)CF₂) was decomposed in a pyrolysis reactor at 200 °C to produce CF₂ radicals. Then, the radicals were polymerized onto the surfaces of nano-Al particles. To prevent aluminum reacting with the CF₂ radicals, the temperature in the reactor chamber was controlled at 25–30 °C by the circulating cooling water. The flow and reaction time were adjusted based on the required thickness of the PTFE film. The PTFE nanofilm was synthesized as follows.

$$\text{CF}_2 + \text{CF}_2 \rightarrow \text{CF}_2 + \text{CF}_2 \text{CF}_2$$

$$\text{CF}_2 + \text{CF}_2 \text{CF}_2 \rightarrow \text{CF}_2 + \text{CF}_2 \text{CF}_2 \text{CF}_2$$

show that the core–shell nanostructure is capable of modulating the reactivity by varying the shell thickness. Compared to the physically mixed counterparts, we believe that the enhanced combustion performance of core–shell structures is attributed to the superior interfacial contact and mass transport in such core–shell configurations.¹,¹²

A combustion test was carried out to qualitatively determine the energetic behavior and reaction kinetics of the materials under normal combustion conditions (Figure 4c–e). The average combustion speed for the physically mixed Al-PTFE is as low as 0.98 m s⁻¹. By contrast, a much faster combustion speed (3.85 m s⁻¹) is observed for core–shell Al-PTFE, indicating that the core–shell nanostructure can lead to faster combustion and then higher energy release rate. The result supports the enhanced role of the core–shell structure on the reaction kinetics. Therefore, our configurations provide superior performance in storing and releasing energy. Note that in this work, the combustion wave speeds of PTFE-Al nanoenergetic materials were tested at the micro-channels and thus the values are lower than that observed for general nanothermites.
Characterization of structure and chemical composition

The structures of the products were analyzed by using a FE-SEM (Ultra 55) coupled with an EDX-spectroscopy system and a TEM (transmission electron microscope, Tecnai F20). An X’Pert PRO X-ray diffractometer with monochromatized Cu Kα (λ = 1.54059 Å) radiation was used to obtain the XRD data. The chemical compositions were studied by using a PHI ESCA7000 X-ray photoelectron spectrometer (XPS) with a take-off angle of 75° and a Fourier transform infrared spectrometer (FTIR, Spectrum One (Version BM)) equipped with an attenuated total reflectance (ATR) attachment.

Contact angle tests and dissolution in NaOH

Core–shell Al-PTFE was directly pressed to slice for static contact angle tests. The contact angle was measured by a ramé-hart Model 500 Advanced Goniometer attached to a CCD camera (30 fps), and the deionized water droplet with a volume of 5 μL was used. A 10.0 g sample was added into a 1000 mL NaOH solution (concentration 0.01 M). To achieve a suitable reaction rate, the temperature was adjusted to 50 °C. After reacting for 40 min, the insoluble solid was weighed. This was repeated several times to obtain the dissolution “rate constant” of aluminum in 0.01 M NaOH solutions.

DSC test

DSC measurements were performed on a Mettler Toledo system under an Ar flow (70–75 mL min⁻¹) over the temperature range from 200 °C to 700 °C and at a heating rate of 5 °C min⁻¹. The sample masses were about 2.0–3.0 mg.

Combustion-cell characterization

A constant-volume combustion cell (78 mL) was used to measure the pressure. A 2.0 g sample was placed inside the cell and ignited by an electric initiator.

High-speed imaging

A high-speed camera was used to capture the visible emission light and record the ignition and flame propagation at a speed of 100,000 frames per second. The sample (~0.60 g) was confined in a open steel tube to allow the visual inspection of the combustion. (The tube length was 20 cm, with the inner and outer diameter of 3.3 and 5.5 mm, respectively).

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