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A combination strategy targeting combustion enhancement for electrically controlled rocket fuel exerts synergistic divestiture against zirconium’s electrostatic hazards

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Reliable strategies to enhance the energy density of electrically controlled solid propellant (ECSP), a promising intelligent propulsion fuel, is a challenge due to potential hazards for typical high-reactivity micro-nano metal fuels induced by manufacturing procedure involving water. Herein, we reversed the detrimental effect of water to a safety protection characteristic by doping micron-sized Zr@PVP fuel into ECSP. Zr@PVP composite particles with low electrostatic discharge (ESD) sensitivity were fabricated by coating Zr with PVP containing hydrophilic groups, which were suitable for one-pot fabrication of fully electrostatically isolated ECSP owing to the contribution of water to electrostatic shielding. Pyrolysis characteristics revealed that Zr could promote concentrated-rapid exothermic decomposition of the propellant due to possible compositional catalytic effects. Electrically controlled combustion diagnosis demonstrated that Zr significantly enhanced propellant combustion. Accordingly, we proposed the potential mechanism of excited-Zr to form fireballs as a “hot spot” that continuously triggers the diffusion combustion of highly reactive intermediates. Our efforts provide a prospect-fate for the zirconium powder with high ESD sensitivity and water-containing electrically controlled propellants possessing poor compatibility with typical high-activity metal powders.

Introduction

Electrically controlled solid propellant (ECSP), as a novel intelligent fuel, possesses admirable safety and controllable combustion characteristics. Despite tons of enthusiasm being invested in this propellant, the lack of high heat-value metal powder in the material system results in low energy density and slow regression rate of the burning surface,1,2 which limits its practical thrust output in solid rocket motor (SRM). Meanwhile, the metal powder can generate inert and high-density gas oxides during the combustion process, reducing gas vibration, thereby enhancing the stability and controllability of the propulsion system.3,4

Reactive micro-nano sized metal powders (such as Al, Mg, Li) are commonly used in composite propellants.5-10 Nevertheless, these metal fuels may potentially undergo water reduction reactions,11-15 which could hinder their application in water-containing electrically controlled solid propellant systems. High hazards and compatibility issues have long impeded research on the introduction of highly active metal fuels into ECSP. Researchers have adopted strategies involving the introduction of inert metal powders such as tungsten and copper to circumvent the interference of water with the metal powders.16-18 These methods can reduce the internal impedance of the propellant, but not conducive to increasing the energy density of the propellant, due to the low combustion heat value of these metal powders.19,20 Recently, zirconium (Zr) powder and its hydride have been exploited as a promising fuel for composite propellants, due to its outstanding volumetric energy density and easy ignitability characteristics.21-24 This is a very good train of thought. Unfortunately, the extremely high electrostatic discharge (ESD) sensitivity of Zr makes it more likely to induce accidental initiation of composite energetic materials.25-27 Nevertheless, it is noted that Zr powder exhibits excellent compatibility with water,28 and the presence of water can also reduce the ESD sensitivity of Zr.29,30 Therefore, Zr powder may be highly suitable for ECSP, combining safety and high energy output characteristics.

Herein, PVP-coated Zr powder (Zr@PVP) was used to reduce the electrostatic hazards in the raw material handling procedure, while also improving the powder’s dispersibility in water to form a homogeneous energetic hydrogel-electrolyte. A one-pot method was employed to prepare ECSP with a three-dimensional network structure. Morphology, functional group distribution, ESD sensitivity, and pyrolysis characteristics of the raw Zr, Zr@PVP and propellant were investigated. Importantly, comprehensive combustion characteristics of the propellant were extensively studied to fully evaluate this novel composite material, utilizing electrically controlled combustion diagnostic systems. Our efforts simultaneously provide a fate for the Zr powder with high ESD.
sensitivity and the water-containing ECSP possessing poor compatibility with typical high activity metal powders.

**Experiment**

**Materials**

Sodium perchlorate (SP, >99%, used as oxidant I) was purchased from Sinopharm Chemical Reagent Co., Ltd. Lithium perchlorate (LP, 98%, used as oxidant II) was commercially available from Aladdin (Shanghai, China). PVA-124 (used as binder, with a number-average molecular weight of 195,000) was acquired from Meryer Chemical Technology Co., Ltd (Shanghai, China). Zirconium micropowders (Zr MPs, ~1 μm) was produced by Naiou Nano Technology Co., Ltd (Shanghai, China). Polyvinylpyrrolidone (PVP, used as coating agent, with a number-average molecular weight of 850,000) was purchased from Yuanye Bio-Technology Co., Ltd (Shanghai, China). Glycerol (C\textsubscript{3}H\textsubscript{8}O\textsubscript{3}, analytically reagent, used as plasticizer) was supplied by Nanjing Chemical Reagent Co., Ltd (Nanjing, China). Boric acid (H\textsubscript{3}BO\textsubscript{3}, >99.5%, used as cross-linker) was produced by Shanghai Macklin Biochemistry Co., Ltd (Shanghai, China). Deionized water was prepared by ultra-pure water system.

**Preparation of Zr@PVP and ECSP**

The safety and dispersibility issues of Zirconium in the manufacturing process of propellants need to be considered, as it is highly prone to spontaneous combustion or explosion in air. The manufacturing process involves the intense collision between the stirring blade and solid particles, and the tendency of micro-nano powders to agglomerate. Polyvinylpyrrolidone (PVP) with hydrophilic groups (-CONH-) on the surface is used to coat Zr, forming a dense coating layer and obtaining micron-sized Zr@PVP composite particles (Zr@PVP MPs). This approach can simultaneously isolate Zr particles from high-frequency interface collisions the with the surroundings and allow the composite particles to be more uniformly distributed in the aqueous manufacturing system, thus preventing aggregation caused by water resistance and high surface energy. The schematic diagram of the Zr@PVP MPs manufacturing process is exhibited in Fig. 2A. The preparation process of Zr@PVP MPs involved sophisticated chemical operations and precise material ratios, aiming to achieve uniform coating on the surface of raw Zr particles. The Zr@PVP MPs were manufactured using a mechanical mixing method. Firstly, according to the target liquid volume ratio (ethanol:DMF=3:1), the required amounts of ethanol and DMF were accurately measured into a stirring beaker and stirred for 5 min, ensuring no obvious stratification of the solution based on its color and transparency, to obtain the ethanol/DMF reconstituted solution.

<table>
<thead>
<tr>
<th>Samples</th>
<th>SP</th>
<th>LP</th>
<th>Zr@PVP</th>
<th>Zr MPs</th>
<th>PVA-124/H\textsubscript{2}O/Glycerol/H\textsubscript{3}BO\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>28.8</td>
<td>19.2</td>
<td>-</td>
<td>-</td>
<td>52</td>
</tr>
<tr>
<td>1%Zr@PVP</td>
<td>28.8</td>
<td>19.2</td>
<td>1</td>
<td>-</td>
<td>51</td>
</tr>
<tr>
<td>2%Zr@PVP</td>
<td>28.8</td>
<td>19.2</td>
<td>2</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>3%Zr@PVP</td>
<td>28.8</td>
<td>19.2</td>
<td>3</td>
<td>-</td>
<td>49</td>
</tr>
<tr>
<td>5%Zr@PVP</td>
<td>28.8</td>
<td>19.2</td>
<td>5</td>
<td>-</td>
<td>47</td>
</tr>
<tr>
<td>5%Zr</td>
<td>28.8</td>
<td>19.2</td>
<td>-</td>
<td>5</td>
<td>47</td>
</tr>
<tr>
<td>7%Zr@PVP</td>
<td>28.8</td>
<td>19.2</td>
<td>7</td>
<td>-</td>
<td>45</td>
</tr>
</tbody>
</table>

4 mL of the reconstituted solution was taken into a magnetic stirring beaker containing 37 mg of PVP, accompanied by incubation of 30 °C. A continuous 30 min stirring is required to ensure all PVP particles are completely dissolved without any precipitation or suspension. Furthermore, add 563 mg of Zr, continue stirring for 12 h to evenly disperse the Zr particles in the solvent, forming a stable suspension. An open container lined with aluminum foil containing suspension was placed in a 60 °C oven for 4 hours of drying treatment, evaporating the solvent to obtain dry Zr@PVP composite MPs. Continuous manufacturing was conducted to obtain all the Zr@PVP MPs required for the production of all propellants. Particularly, a low PVP content may lead to the rupture of the coating layer, while a high PVP content can result in the formation of crosslinked films that prevent the obtainment of usable particles. The concentration of the PVP solution has been repeatedly adjusted to regulate the thickness of the coating layer. The above material ratio is ultimately considered to be the optimal choice.

To better investigate the influence of Zr on the combustion of ECSP, an additive gradient ranging from 1% to 7% was set, as detailed in Table 1. The propellant was manufactured using a one-pot method manufacturing device, as depicted in Fig. 2C. Firstly, all dry materials were dried, sieved, and pre-treated, and the pre-treatment of raw materials was conducted at the Energetic Materials Key Laboratory of Nanjing University of Science & Technology. Zr@PVP MPs and PVA-124 were dry-mixed according to the ratio. Subsequently, all dry materials (Zr@PVP MPs, PVA-124, SP, LP, boric acid) and reconstituted solution (glycerol and deionized water) were added to a vacuum stirring beaker (< 1 kPa) with an external water bath at a temperature of 0-5 °C. After being mixed and stirred for 15 min, the water bath temperature was gradually raised to 60 °C. Meanwhile, the stirring speed was reduced to 40 rpm, and stirred for 30 min to obtain a flowable slurry, which was then poured into a polytetrafluoroethylene mold with a size of 10×10×100 mm. All samples were manufactured in one batch, cured in a 60°C oven for 4 d to obtain formed propellants. The propellant strands were wire-cut to 10×10×10 mm for testing purposes.

**Characterization method**

The morphology of Zr@PVP and ECSP was examined by field emission scanning electron microscopy (FESEM, Quant 250F, FEI) at an acceleration voltage of 20 kV, and the elemental distribution was determined with energy dispersive spectroscopy (EDS, Quanta 200, Bruker). The crystalline-species of Zr@PVP and ECSP were inspected through powder X-ray diffraction (XRD, D8 Advance, Bruker), and the data were collected from 5°-80° 2θ with a step size of 0.05°. The compound-species of Zr@PVP and ECSP were investigated by X-ray
photoelectron spectroscopy (XPS, Scientific K-Alpha, Thermo) and microscopic infrared spectroscopy (μ-FTR, In 10, Thermo). The exothermic reaction of ECSP was measured by differential scanning calorimetry (DSC, STA 449C, NETZSCH) from 30°C to 750°C at the heating rate of 5, 10, 15 and 20°C·min⁻¹ under flowing argon (30 mL·min⁻¹). The kinetic parameters of ECSP with 5% Zr@PVP were calculated using Kissinger’s model and Flynn-wall-Ozawa’s model.

ESD sensitivity measurement

ESD sensitivity of Zr, Zr@PVP and ECSP with 5% Zr@PVP were measured by the ESD Sensitivity meter (self-design, NJUST-ESD-24) with a discharge-circuit inductance of 5 μH. A high-voltage polystyrene capacitor with a capacity of 500pF or 10000pF was charged by an adjustable electrostatic generator (0-30kV) to precisely-instantaneously release charging energy into the sample through logical control subsystem. Particularly, a H70 brass mold containing the sample was placed on a grounding base, and the distance between the electrode probe and the sample surface was fixed at 0.12mm. Neyer p-optimal method was adopted to evaluate the electrostatic energy for 50% excitation probability (Eₐ₀) accompanied by

Combustion diagnosis

Institute of Space Propulsion (ISP), Nanjing University of Science & Technology established an electrically controlled combustion system to investigate the combustion characteristics of ECSP with electricity. The schematic diagram of the electrically controlled combustion system is illustrated in Fig. 1. The system mainly included optical platform, high-pressure combustion chamber (HPCC, self-designed, CNC machining) with four sapphire glass observation windows (two rectangles/two circles), PLC-pressure control system (customer-made/programmed, included PLC control processor, pressure sensor, solenoid valve), programmable DC voltage source (Itech IT6726G, 600 V, 10 A), PCO high-speed camera, photoelectric sensor (LeCroy 104Xi-A, 1 GHz bandwidth, sampling rate of 10 GS/s) and customer-made relay circuit control system. All the above devices/subsystems completed communication-recognition commands through the TTL level to form an intelligent synchronous electrically combustion diagnosis system. The sandwich configuration ignition device was fixed on the quick loading-unloading bottom plug of HPCC, achieving the ignition of the propellant with the action of programmable DC voltage (100V~200V) under a high-pressure atmosphere created by nitrogen. The more detailed description of the sandwich ignition device (electrode layout, electrode configuration, dynamic-push mode, flame/gas release method, etc.) can refer to our previous introduction related to the electrically combustion system. The voltage probe was used to record the voltage applied at both ends of the positive and negative electrodes. Simultaneously, the current probe was used to monitor the current variation in the circuit. The flame intensity was measured using a photoelectric sensor. The above voltage, current and flame intensity signals were recorded on the oscilloscope (set the acquisition frequency to 10 kHz). The combustion process was recorded by a high-speed camera (PCO. dimax HS) capturing 1000 frames per second, uploading the image to the PC. High precision balance was used to record the mass of propellant before and after combustion.

Results and discussion

Morphology and chemical composition of Zr@PVP and ECSP

A systematic characterization of the morphology, coating layer, and surface functional group distribution of Zr@PVP MPs was conducted to evaluate the quality of the coating. The microstructure of Zr@PVP MPs is shown in Fig. 2B. The TEM images indicated that the Zr particles were encapsulated within PVP microspheres, achieving complete encapsulation. Furthermore, EDS images and the XPS spectrum peak intensity of O1s (as shown in Fig. 3C, with strong peaks for ZrO₂ (529.8eV) and -OH (531.2eV) in surface zirconium, along with a weak peak for CeO (533.7eV)) collectively indicated that PVP (element N) tightly encapsulated Zr, resulting in a thin coating layer, which was instrumental in enhancing the mass fraction of Zr in Zr@PVP MPs. XPS spectrum of N1s (as shown in Fig. 3A) demonstrated the presence of hydrophilic functional groups (-CONH(C), 399.7eV, as shown in Fig. 3D) on the surface of Zr@PVP MPs. Additionally, as depicted in Fig. 3B, the peak intensity (Zr3d) of ZrO₂ (184.4eV, 182eV) was significantly higher than that of Zr (178.7eV), indicating the oxidation of the Zr surface at a certain depth due to the high activity of micron-scale raw materials. The oxide layer can assist in reducing the ESD sensitivity characteristics, but simultaneously prolong the ignition delay.
Fig. 2. The manufacturing process and morphology characterization. (A) The schematic diagram of the preparation process for Zr@PVP MPs. (B) Morphology and elemental distribution characterized by TEM, SEM, and EDS for Zr@PVP MPs. (C) The schematic diagram of the preparation process for Zr@PVP-based ECSP. (D) Morphology and elemental distribution characterized by SEM and EDS for Zr@PVP-based ECSP.

Morphology and element distribution of the ECSP manufactured by the one-pot method are shown in Fig. 2D. Matrix morphology suggested abundant 3D cross-linked meshwork were formed, contributing to simultaneously enhance the mechanical properties and conductivity of propellant. EDS spectra indicated propellant fulfilled excellent uniformity of mixing with components, which was conducive to stable combustion. Furthermore, X-ray diffraction (XRD) was employed to analyze the binding form and bulk structure of Zr@PVP with varying contents, aiming to evaluate the existence of Zr@PVP in the propellant under the interference of other components (Fig. 3E). The gradual increase in the diffraction peak intensity of ZrH$_{1.66}$ (2θ = 32.40°) with the augmentation of its addition manifested that the surface of Zr particles (2θ = 36.31°) was adorned with copious hydrides originating from the hydroxyl-rich components (water, PVA, glycerin) present in the propellant, which facilitated the progress of the reaction. Microscopic infrared scanning (Fig. 3F) of the carbonyl groups in ECSP revealed that the main distribution of the carbonyl groups was in the folds and gullies (Fig. 3G), suggesting that the surface film-forming capability of PVA was weaker than PVA, which might be detrimental to the ignition during interfacial contact since Zr could only be exposed and react after the decomposition of the film-forming PVA.

Fig. 3. The systematic characterization. (A) XPS full-spectrum of raw Zr and Zr@PVP. XPS peaking-spectrum (Zr@PVP) of (B) Zr 3d, (C) O1s, and (D) N1s. (E) XRD spectra of ECSP with different Zr@PVP content. (F) Microscopic infrared mapping of ECSP. (G) Morphology of infrared scanning area.

Thermal analyses

ECSPs with different Zr@PVP content underwent thermal analysis, as shown in Fig. 4E. With the addition of Zr@PVP (relative to the baseline), the most direct-significant conclusion was that the exothermic peaks of the propellant were highly concentrated in a very small exothermic range. The low temperature decomposition peak (T$_{LTD}$) and high temperature decomposition peak (T$_{HTD}$) of Baseline were both lower than T$_{HTD}$ of Zr-based ECSP (Table 3), with the low-temperature decomposition peak being closer to the ECSP.
decomposition peak in terms of temperature, indicating that Zr might have a strong catalytic effect on the rapid reaction and heat release of the other components in the ECSP. The two exothermic peaks in the baseline were mainly due to the time difference in the decomposition of SP and LP, while the thermal decomposition of PVA producing acetic acid/acetaldehyde and other highly reducing carbon compounds was a multi-step process. Of particular note was that within the temperature range of 75-150°C, a heat absorption was occurred as moisture in the propellant was thermally evaporated. Thus, moisture was not absent in ECSP during the main reaction phase, which also contributed to the release of high reactivity Zr, triggering rapid chemical reactions among the components of the propellant. With an increase in the addition of Zr@PVP, the main exothermic peak of ECSP slightly shifted to the right, possibly due to Zr enhancing the thermal conductivity efficiency from the surface to the interior of the propellant. Furthermore, the kinetic parameters of 5%Zr@PVP ECSP were investigated based on DSC curves with different heating rates, as shown in Fig. 4F. Increasing the heating rate can gradually shift the main exothermic peak to the right owing to the effects of heating relaxation.

Fig. 4. The thermal decomposition characteristics and ESD sensitivity of Zr, Zr@PVP MPs and 5%Zr@PVP ECSP. (A) The ESD meter (NJUSTR-ESD-24) with logical control subsystem. (B) The electrode needles and molds with Zr/Zr@PVP before and after discharge. (C) Typical discharge-excited ignition sequence. (D) ESD sensitivity (H50) for Zr, Zr@PVP, and 5%Zr@PVP ECSP. (E) DSC curve with different doping amount of Zr@PVP. (F) Non-isothermal DSC curve of 5%Zr@PVP ECSP.
Aizing small molecules ease in the energy barrier when the dual
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of ESD sensitivity within the ECSP system, attributed to the inhibition
of ECSP indicated the remarkable performance of Zr@PVP in terms
sensitivity of the composite material by isolating static electricity or
applications are extremely high. PVP c
results demonstrated that the ESD sensitivity threshold of Zr was
required to ignite the sample, resulting in lower ESD sensitivity and
is illustrated in
4B
of the samples was carried out using the discharge tip depicted in
manufacturing and usage processes of propellants. Discharge te
safety enhancement capability of the composite particles during the
pyrolysis reactions.
Furthermore, the self
ESD sensitivity
pyrolysis reactions.

Table 2 Kinetic parameters of baseline, ECSP with 5%Zr@PVP and composite propellant calculated using nonlinear Kissinger and Flynn-Wall-Ozawa models.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( T_p ) (°C)</th>
<th>( E_k ) (kJ·mol(^{-1}))</th>
<th>( ln A ) (S(^{-1}))</th>
<th>( R^2 )</th>
<th>( E_w ) (kJ·mol(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%Zr@PVP</td>
<td>THTD</td>
<td>64.8±7.4</td>
<td>2.7</td>
<td>0.9747</td>
<td>69.6±4.0</td>
<td>0.9674</td>
</tr>
<tr>
<td>Baseline</td>
<td>THTD</td>
<td>12.8±2.3</td>
<td>3.3</td>
<td>0.9524</td>
<td>12.2±2.1</td>
<td>0.9418</td>
</tr>
<tr>
<td>Baseline</td>
<td>TLTD</td>
<td>20.3±2.8</td>
<td>8.2</td>
<td>0.9815</td>
<td>23.6±2.6</td>
<td>0.9881</td>
</tr>
<tr>
<td>Composite propellant [45]</td>
<td>THTD</td>
<td>182.8±26.0</td>
<td>34.3</td>
<td>0.9610</td>
<td>183.8±24.9</td>
<td>0.9647</td>
</tr>
</tbody>
</table>

Table 3 Detailed temperature parameters of exothermic decomposition peak for baseline and ECSP with 5%Zr@PVP.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( T_p ) (°C)</th>
<th>5 (K·min(^{-1}))</th>
<th>10 (K·min(^{-1}))</th>
<th>15 (K·min(^{-1}))</th>
<th>20 (K·min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%Zr@PVP</td>
<td>THTD</td>
<td>256.2</td>
<td>264.6</td>
<td>270.5</td>
<td>279.0</td>
</tr>
<tr>
<td>Baseline</td>
<td>THTD</td>
<td>276.5</td>
<td>298.6</td>
<td>326.7</td>
<td>330.2</td>
</tr>
<tr>
<td>Baseline</td>
<td>TLTD</td>
<td>250.2</td>
<td>263.2</td>
<td>-</td>
<td>284.1</td>
</tr>
</tbody>
</table>

Nevertheless, the propellant with a heating rate of 5K·min\(^{-1}\) exhibited a distinct exothermic curve similar to the baseline, indicating that the catalytic effect of Zr on the overall composition of the propellant was significantly reduced at slow heating rates. In addition, the reaction activation energy of the Zr-based ECSP was evaluated according to the Flynn-Wall-Ozawa\(^{62,63}\) and Kissinger models.\(^{44}\) Detailed reaction kinetic parameters are listed in Table 2. The activation energy of Zr-based ECSP was significantly higher than that of the Baseline, indicating an increase in the energy barrier when the dual-stage reaction of the propellant merges into a single-stage reaction. The catalytic contribution of Zr to ECSP was confined to facilitating the rapid progress of the propellant’s exothermic reaction, thereby reducing the duration of the segmented reaction phases. Furthermore, the activation energy of Zr-based ECSP was significantly lower than that of composite propellants,\(^{45}\) indicating that ECSP that had lost moisture could readily overcome the energy barrier to initiate reactions. Besides, to achieve complete combustion, Zr contributed to minimize the occurrence of slow pyrolysis reactions.

ESD sensitivity

The self-designed electrostatic sensitivity instrument, as shown in Fig. 4A, was employed to conduct ESD sensitivity tests on the raw Zr material, Zr@PVP composite MPs, and 5%Zr@PVP ECSP to assess the safety enhancement capability of the composite particles during the manufacturing and usage processes of propellants. Discharge testing of the samples was carried out using the discharge tip depicted in Fig. 4B. The typical excitation process of \( E_{50} \) energy discharge for Zr@PVP is illustrated in Fig. 4C. Higher \( E_{50} \) values indicate that more energy is required to ignite the sample, resulting in lower ESD sensitivity and higher safety. Detailed test results are presented in Fig. 4D. The results demonstrated that the ESD sensitivity threshold of Zr was significantly enhanced after being encapsulated by PVP. The static electricity generated by the human body is approximately 8 mJ.\(^{46}\) Thus, the hazards associated with raw Zr particles in practical applications are extremely high. PVP could effectively reduce the sensitivity of the composite material by isolating static electricity or suppressing hot-spot formation. Furthermore, the \( E_{50} \) ESD sensitivity of ECSP indicated the remarkable performance of Zr@PVP in terms of ESD sensitivity within the ECSP system, attributed to the inhibition of Zr’s electrostatic sensitivity in a moist environment. Notably, the voltage and capacitance capacity used for testing Zr here had already reached the maximum range of the instrument, indicating that the actual ESD sensitivity of ECSP might be even lower. From a safety perspective, Zr was an ideal additive with high reactivity for ECSP.

Flame morphology

The anode metal mesh side of the “sandwich structure” subjected to applied voltage ignited first after a period of ignition delay. The highly active Zr and the pyrolysis products of PVA/PVP/glycerol would be rapidly oxidized under the action of highly oxidizing small molecules generated by SP/LP electrolysis/pyrolysis, releasing massive heat and growing up to a strong combustion reaction. Increasing the voltage could enhance the combustion intensity of the propellant (as shown in Fig. 5A). Voltage enhancement could accelerate the transition of the propellant from condensed phase to gas phase through coupling raise of electrolysis/pyrolysis rate. Meanwhile, voltage could promote the ion generation/transmission speed and reactant concentration accumulation in the combustion reaction, improving the injection velocity of reactants to the gas-phase reaction zone, to form a larger flame area. As the amount of Zr@PVP increased, the most intuitive phenomenon was that the core brightness of the propellant flame significantly enhanced (as shown in Fig. 5B), which was related to more high-energy density substances participating in the combustion reaction within a unit time.\(^{47}\) The temperature and thermal radiation intensity of the flame also increased accordingly, leading to a significant enhancement in the brightness of the flame, which further affected the thermodynamic characteristics of combustion.

Additionally, ECSP leaned towards dynamic diffusion combustion, which was a hybrid of diffusion combustion and premixed combustion. The combustion participation of Zr powder might also alter the propellant combustion mode, triggering extensive thermal-core combustion (as shown in Fig. 5C). Localized fireballs centered on Zr powder particles might result in changes in flame morphology and propagation speed. We believe these fireballs were more analogous to “hot spots”, continuously initiating chain reactions of gaseous oxidizing/reducing substances invisible to the naked eye above the anode region, thereby forming localized flame diffusion. ZrO₂ can suppress deflagration.\(^{48}\) However, excessive Zr could induce detonation, interfering the combustion stability of the propellant.
ECSP with 7% Zr@PVP MPs had already formed multitudinous explosive combustion particles, accompanied by intense vibration noise. This instability was further amplified by increased voltage.

Comprehensive electrically controlled combustion characteristics

The combustion process of ECSP can be divided into: i) ignition, ii) combustion, and iii) extinguishment, constituting a cycle. Herein, an ignition-combustion-extinguishment cycle is referred to as a stage. The captured photoelectric time signal as shown in Fig. 6A can be utilized to determine the combustion parameters of the propellant, including ignition delay, extinguishment delay, and burning rate. Detailed calculation procedures are presented in the Supplementary Material.

As depicted in Fig. 6B, increasing the voltage applied to the dual-electrodes and the addition of Zr@PVP could simultaneously enhance the burning rate of propellant. The voltage rise facilitated the generation of electrolysis products per unit time. Meanwhile, the ohmic heating rate induced by the impedance at the propellant-electrode interface was positively correlated with the voltage. Increasing the voltage could be regarded as accelerating the transition of the condensed phase towards substances with a lower ignition point through these two pathways, which favored a rapid progression of the combustion reaction. Zr, with its rapid heat-release capability, could advance-concentrate the decomposition temperature of the condensed phase for propellant (as described in Section 3.2), thereby accelerating the regression of the burning surface. Among the tested formulations, excessively high doping levels did not compromise this burning rate enhancement characteristic.

Fig. 6. Comprehensive electrically controlled combustion characteristics. (A) Typical captured photoelectric signals during ECSP combustion process. (B) Burning rate. (C) Ignition delay time. (D) Extinguishment delay time.
Furthermore, the regulation capability of burning rate for electrically controlled solid propellant, which is of great significance, requires extra attention. The detailed regulation capability of burning rate for ECSPs with different Zr@PVP loadings is listed in Table 4. Overall, the regulation capability of the propellant’s burning rate with electricity decreased as the Zr@PVP loading increased. The greater enhancement in the burning rate of propellant during the low-voltage stage by Zr@PVP likely played a crucial role. The finding also implied that Zr can reduce the electrical energy requirements of ECSP, particularly during the low-voltage stage. This was highly conducive to practical applications, owing to the limited payload capacity of the power system imposed by the rocket as an isolated entity.

It was worth noting that the ignition delay time of Zr-based ECSP was much longer than that of the baseline, as shown in Fig. 6C. Despite the advantage of enhancing the burning rate, the addition of Zr@PVP composite MPs was not conducive to ignition delay. As voltage was applied to both sides of Zr@PVP-based ECSP, majority of electrical energy was transferred to the interior of the propellant with high conductivity, rather than the propellant-electrode interface. The slow accumulation of heat at the interface delayed the formation of strongly reducing pyrolysis species. Meanwhile, the heat caused by the interface impedance would rapidly diffuse due to the increased thermal conductivity of the propellant by metal particles. The ignition delay time exhibited an overall upward trend with the addition amount, but the increase was not obvious compared with the gap between the baseline and the ignition delay. The test results of burning rate and ignition delay both indicated that a lower content of Zr@PVP MPs was sufficient to have a prominent impact on the combustion characteristics of ECSP.

Moreover, the extinguishment delay, which determined the actuation accuracy, need to be evaluated. The detailed results are shown in Fig. 6D. Generally, the unhealthy heat accumulation of electrodes caused by excessive ignition delay were bad for the extinguishment of the propellant. However, it seemed that this was not the main factor affecting the difficulty of extinguishment for Zr@PVP-based ECSP. The extinguishment of 1%Zr@PVP propellant followed this rule, while the extinguishment delay of propellants with higher Zr@PVP loadings hardly changed significantly with the voltage and loading. Analysis suggested that the high heat transfer efficiency caused by the additive metal fuel further promoted the rapid diffusion of interfacial heat-deposition, reducing the burning surface temperature, thus facilitating the extinguishment.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Regulation capability of burning rate</th>
<th>Regulation ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( b_{\text{min}} ) (mm·s(^{-1}))</td>
<td>( b_{\text{max}} ) (mm·s(^{-1}))</td>
</tr>
<tr>
<td>Baseline</td>
<td>1.34</td>
<td>2.77</td>
</tr>
<tr>
<td>1%Zr@PVP</td>
<td>1.909</td>
<td>3.386</td>
</tr>
<tr>
<td>2%Zr@PVP</td>
<td>2.151</td>
<td>3.858</td>
</tr>
<tr>
<td>3%Zr@PVP</td>
<td>2.276</td>
<td>4.092</td>
</tr>
<tr>
<td>5%Zr@PVP</td>
<td>2.576</td>
<td>4.270</td>
</tr>
<tr>
<td>7%Zr@PVP</td>
<td>2.936</td>
<td>4.538</td>
</tr>
</tbody>
</table>

Mechanism for Zr-enhanced combustion

As a promising collaborative application in the future, elucidating the influence of Zr on the combustion mechanism of ECSP can facilitate the blossoming of optimized combustion strategies. Analysis considers that, from the point of electrical ignition to the cessation of combustion upon power-off, Zr-enhanced combustion for ECSP can be primarily divided into the following six stages (as illustrated in Fig. 7).

Once the propellant is subjected to voltage, oxidative/reductive intermediates are generated by electrolysis/pyrolysis, and these active species continuously accumulate in the anode-overhead region.

The interfacial impedance decreases due to the enhancement of ECSP’s electrical conductivity contributed by Zr, leading to a reduction in the rate of temperature rise at the propellant-anode interface, but favoring the progress of the oxygen evolution reaction (OER). Excessive oxidative intermediates initially react with the overflowing Zr particles at the interface, as Zr is easily excited in strong oxidizing environments.

The Zr fireball ignites instantaneously as a “hotspot,” igniting the internally highly active pure Zr, forming a fireball in highly oxidative environments.

The Zr fireball ignites instantaneously as a “hotspot,” igniting the intermediates diffused in the space, resulting in a large area of flames.

The generation of intermediates ceases as the applied electrical energy is removed, while the remaining active species are rapidly consumed by the combustion reaction, manifesting as extinguishing macroscopically. The residual heat at the anode interface rapidly
dissipates downward due to the enhanced heat transfer efficiency of the condensed phase caused by Zr, which can promote the termination of the thermal induced decomposition at the interface.

Conclusions
This study presents a novel strategy to simultaneously enhance the combustion characteristics of electrically controlled solid propellant and mitigate the electrostatic hazard of doped Zr. The results demonstrated that the utilization of PVP, containing hydrophilic groups, to encapsulate Zr facilitated the production of Zr@PVP composite particles with low electrostatic sensitivity, which were suitable for one-pot fabrication of fully electrostatically isolated ECSP. Zr promoted the concentrated-rapid exothermic decomposition of the propellant due to the compositional catalytic effect. Additionally, the electrically controlled combustion diagnosis demonstrated the combustion enhancement of Zr on the propellant. We also proposed a mechanism of excited-Zr to form a fireball, serving as a “hot spot” to continuously trigger the diffusion combustion of highly reactive intermediate species.

Author contributions
Z. Wang: Writing – review & editing, Writing – original draft, Investigation, Data curation, Conceptualization. F. Li: Writing – review & editing, Investigation, Formal analysis, Data curation. Q. Zhang: Writing – review & editing, Investigation, Formal analysis. K. Ouyang: Software, Methodology, Formal analysis. R. Shen: Methodology, Conceptualization, Supervision. Y. Ye: Project administration, Supervision. L. T. Deluca: Methodology, Formal analysis. W. Zhang: Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Formal analysis.

Conflicts of interest
There are no conflicts to declare.

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Data Availability Statement

All data generated or analysed during this study are included in this published article [and its supplementary information files].