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Mingna QIN
Xi'an Institute of Modern Chemistry
Wang TANG
Xi'an Institute of Modern Chemistry
Yajie CHEN
Xi'an Institute of Modern Chemistry
Wei WANG
Xi'an Institute of Modern Chemistry
Yan ZhANG
Fujian Normal University of Technology
Tao GUO
Xi'an Institute of Modern Chemistry
Qiang SHI (qmn5158@163.com)
Xi'an Institute of Modern Chemistry

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Study on Surface Structure Characterization and Stability of α-AlH_3 coated with PW

Mingna QIN[1], Wang TANG [1], Ya-jie CHEN [1], Wei WANG [1], Yan ZHANG [2], Tao GUO [1]✉, Qiang SHI[1]✉,

(1. Xi'an Institute of Modern Chemistry, Xi'an 710065,Shaanxi;2. Fujian Normal University of Technology, Fuzhou, Fujian 350007)

✉Corresponding author e-mail: qmn5158sina.com, qmn5158@163.com

Abstract: Alpha-aluminum hydride (a-AlH_3) is usually metastable due to the small enthalpy of formation, poor stability, high chemical activity, sensitive to moisture, easy to combine with water in the air. In order to inhibit the hygroscopicity of α-AlH_3 and improve its storage and stability, PW (paraffin wax) is selected as the coating material, and the solvent-non-solvent method is used to coat the surface of α-AlH_3. The structure and topography of α-AlH_3 before and after coating are characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffractometer (XRD), X-ray electron spectroscopy (XPS), elemental analysis, and scanning electron microscopy (SEM). The results show that PW forms a uniform and complete coating layer on the surface of α-AlH_3, and the crystal structure and morphology of the α-AlH_3 samples after the coating are not changed, and the moisture absorption weight gain rate is reduced from 12% before the coating to 0.8%, and the hygroscopicity is greatly reduced. Furthermore, the a-AlH_3 coated by PW also shows excellent performance in resisting water erosion, and the hydrophobic angle increases from 27° to 98° after the PW is coated on the a-AlH_3 surface. This research provides a easy method for the safe application of a-AlH_3 in the field of solid propellants

Keywords: α-AlH_3; PW； solvent-non-solvent; hygroscopicity

Alpha-aluminum hydride (a-AlH_3) is a solid-state hydrogen storage with a high hydrogen content, its relative molecular mass is 30.0, the density is 1.48 g/cm^3, the hydrogen content is as high as 10.08%, its hydrogen storage density is 148 g/L, which is twice that of liquid hydrogen (70.8 g/L). and it is less toxic, has a higher combustion calorific value than aluminum powder, and is an ideal solid propellant fuel [1-5].

High-energy propellants consisting of AlH_3, ammonium dinitroamide (ADN), and energetic binders are reported to be typical high-energy, low-characteristic signal, and clean solid propellants, with a standard theoretical specific impulse of up to 294 s, which is 20% to 30% higher than standard propellants (butylhydroxy solid propellants) [6-10].

AlH_3 is a special compound. It has at least seven different crystalline structures depending on the synthesis conditions: α α, β γ δ ε and ζ. Among them, the most stable and the only one that has application value in solid propellant formulations [11-15]. However, a-AlH_3 is usually metastable due to the small enthalpy of formation, poor stability, high chemical activity, sensitive to moisture, easy to combine with water in the air, resulting in AlH_3 will decompose and release hydrogen, directly affecting the storage safety and application safety of AlH_3, limiting its application in high-energy propellants. In order to further expand the application of a-AlH_3 in the field of propellants, the problem of hygroscopicity of α-AlH_3 must be solved [16-20].

At present, researchers have carried out lots of research work on improving the stability of a-AlH_3, reducing water absorption and optimal compatibility. The main methods include surface passivation method, ion doping method and surface coating method [21-25]. The surface coating method has attracted much attention in recent years. Because, it does not destroy the chemical reactivity of a-AlH_3. It contains a two-phase interface on the surface and changes the surface state of a-AlH_3[21-26].

Paraffin wax is not only a hydrophobic material, but also a commonly desensitizers used in explosives[28]. Due to the hydrophobicity of PW materials, AlH_3 can be avoided to directly contact with air and improve the wet stability of α-AlH_3. Due to the blunt nature of paraffin wax , it can also reduce the sensitivity of AlH_3. Therefore, the wet stability and the sensitivity of α-AlH_3 could be effectively improved, which will promote the application of α-AlH3 in high-energy solid propellants.

Results and discussion

The structural characterization of α-AlH_3 and α-AlH_3 coated by PW were characterized by XRD. The results were shown in Figure 1. As can be seen from Figure 1, the characteristic diffraction peaks of α-AlH_3 [11-15] appeared at 2θ=27.84°, 38.58°, 40.72°, 46.1°, 49.96°, 57.26°, 63.26°, 68.14°, 72.48°, 73.84°, 73.84°, which were consistent with the (012),(111), (110), (006), (202), (024), (116) and (122) planes of a-AlH3(JCPDS 23-0761), respectively. Compared to a-AlH_3, no new diraction peaks appeared for the a-AlH_3 coated by PW ,which indicates that the organic layer coated on the surface of a-AlH_3 did not change the physical phase structure of a-AlH_3 .Observed changes in the relative peak intensities are attributed to the decrease of particle crystallinity and the increased scattering power caused by the coated PW.

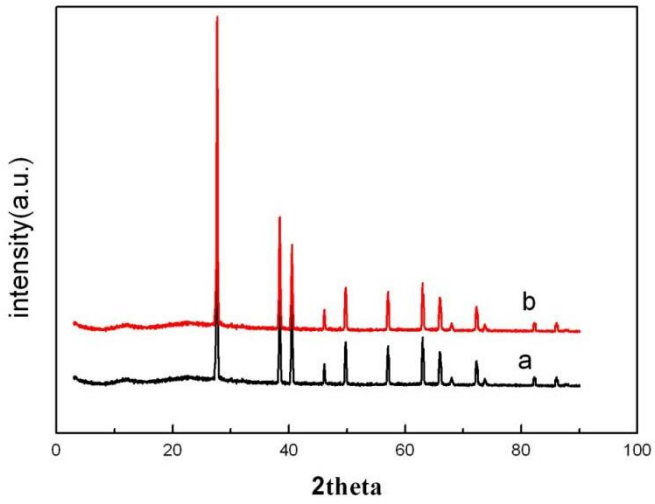


Figure 1 XRD patterns of α-AlH_3（a）and α-AlH_3 coated by PW（b）

The FT-IR spectra of PW, a-AlH_3, and the a-AlH_3 coated by PW were displayed in Figure 2. The FT-IR spectra showed that PW exhibited C-H bonds at 2918 cm^{-1} 2849 cm^{-1} 1473 cm^{-1} and 729cm^{-1}. The C-H bonds at 2918 cm^{-1} and 2849 cm^{-1} are the telescopic vibration absorption peaks of the C-H bond of -CH_2- and -CH_3. The C-H bond at 1473 cm^{-1} is the bending vibration absorption peak of -CH_2- and -CH_3, C-H bond at 729 cm^{-1} is the C-H bending vibration absorption peak outside the bond surface. The FT-IR spectra showed that a-AlH_3 exhibited Al-H bonds at 1719 cm^{-1}, 866 cm^{-1} and 672 cm^{-1} which were attributed to the Al–H bond stretching absorption vibration peak, the Al–H bond out-of-plane bending vibration absorption peak and the Al–H bond in-plane bending vibration absorption peak, respectively. After coating by PW, the characteristic peaks of PW at 2918 cm^{-1} and 2849 cm^{-1} are shown in the FT-IR spectra of the a-AlH3 coated by PW, while the characteristic peaks of a-AlH_3 at 1719 cm^{-1}, 866 cm^{-1}, and 672 cm^{-1} did not change significantly, indicating that the surface of a-AlH_3 was coated with the organic layer.

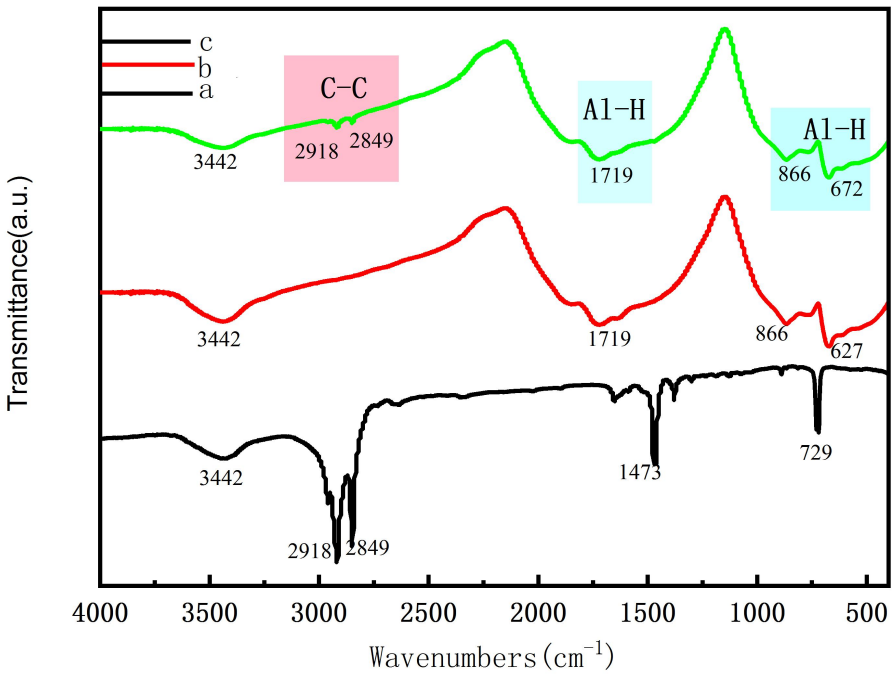


Figure 2 The FT-IR spectra of PW（a）α-AlH_3（b）and α-AlH_3 coated by PW （c）

The surface components of α-AlH_3 and α-AlH_3 coated by PW were analyzed using photo electron spectroscopy (XPS), and the results are shown in Figure 2 and Table 1. As can be seen from Figure 3, the types of elements on the surface of α-AlH3 before and after the coating have not changed, and they are all C, Al, and O elements. However, the intensity of the peaks has changed to varying degrees, and the strength of the C1s peak has been significantly enhanced, indicating that the carbon element in the PW coated on the surface of α-AlH_3 is caused, and the corresponding strength of O1s peak and Al2p is significantly reduced. At the same time, from Table 1, we can also see more specifically that the content of C1s elements increased from 41.00% to 56.23%, and the corresponding O elements and Al elements decreased, corresponding to Table 1 O1s from 30.38% to 27.52%, Al2p from 27.45% to 15.18%, indicating that the surface of α-AlH3 is coated with PW.

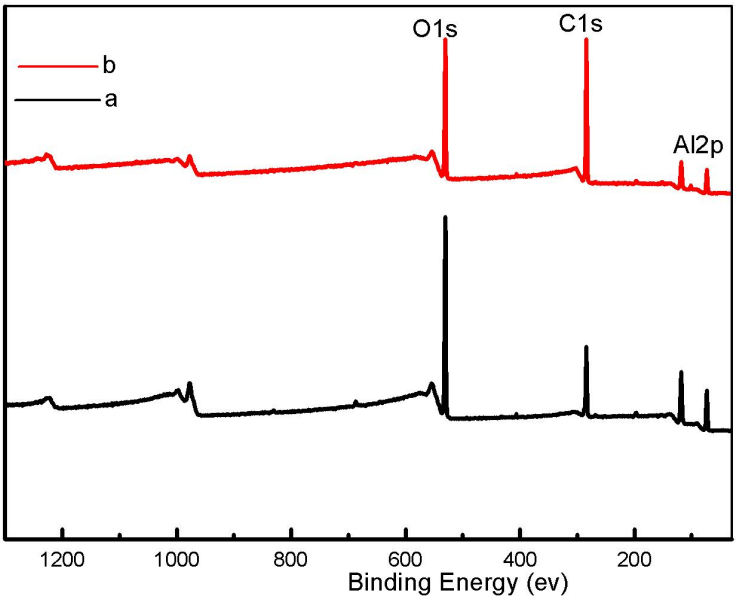


Figure 3 XPS patterns of α-AlH_3（a）and α-AlH_3 coated by PW（b）

samples	Al2p/%	C1s/%	O1s/%
α-AlH_3	27.45	41.00	30.38
α-AlH_3 coated by PW	15.18	56.23	27.52

Table1：Testing results of XPS of α-AlH_3 andα-AlH_3 coated by PW

The SEM images were used to observe the microscopic appearance and particle size distribution of both a-AlH_3 and the a-AlH_3 coated by PW. The topography and elemental distribution of α-AlH_3 and the a-AlH_3 coated by PW were shown in Figure 4a and 4b. As can be seen from the topography analysis of Figure 4a and Figure 4b in Figure 4, the topography of α-AlH_3 before and after coating has not changed significantly, it is a cube, the particle size is about 10~25 μ m, and the coating material does not change the crystal morphology of α-AlH_3, which is consistent with the conclusion that the crystal form of the above XRD analysis has not changed. As can be seen from the distribution of elements in Figure 4a and 4b, It is clear that the elements of α-AlH_3 determined by EDS mapping are different in terms of their composition and distribution. EDS mapping in Figure 4a shows that the Al shown in red is full of coverage Because Al element is the major element present in α-AlH_3. The O element distribution is shown in red patches and dots are mainly the O

elements in the oxide layer of Al_2O_3 formed by passivation treatment on the surface of α-AlH_3, After coating, the elements of the α-AlH_3 coated by PW not only contained Al and O but also the characteristic C elements of PW. The C distribution is shown in green full of coverage,which are consistent with the above XPS analysis of the element types.

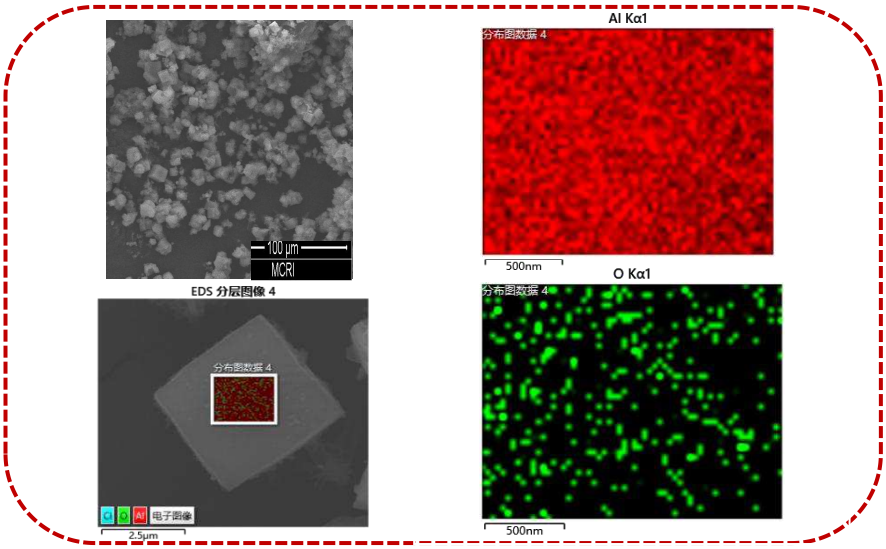


Figure 4a The SEM images of α-AlH_3

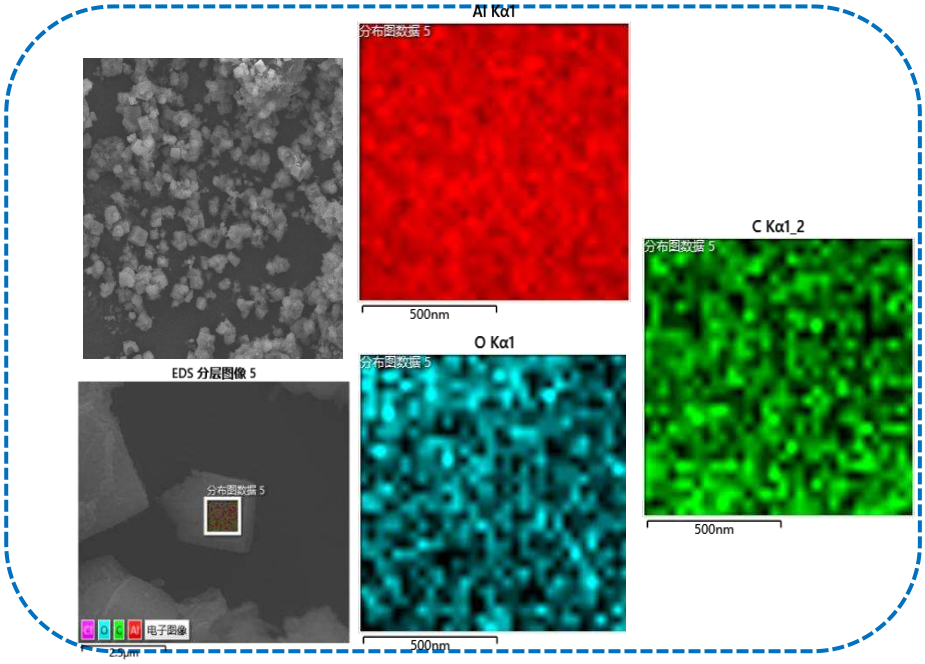


Figure 4b The SEM images of α-AlH_3 coated by PW

The thermal performance of α-AlH_3 and the α-AlH_3 coated by PW were tested using METTLER thermal analyzers, and the results were shown in Figure 5. In Figure 5, the DSC curve of PW has a sharp heat absorption peak at 54 °C, which is the PW melting heat absorption peak. Curve b in Figure 5 is the DSC curve of α-AlH_3, the

DSC curve of α-AlH_3 has a large endothermic peak at 180.38 °C, where the heat absorption peak is α-AlH3 thermal decomposition of the endothermic peak, which is consistent with the previous literature report; in Figure 5, the curve c is α-AlH_3 after PW coating, the DSC curve of α-AlH_3 after couching, the DSC curve of α-AlH3 after PW coating has two obvious endothermic peaks, and there is a small endothermic peak at 54 °C. Here the endothermic peak is the coated layer PW melt heat absorption peak, there is a large heat absorption peak at 180.37 ° C, the absorption peak is the base material α-AlH_3 thermal decomposition heat absorption peak, and compared with the previous heat absorption peak before the coating, the thermal decomposition temperature is slightly increased, and the PW melt heat absorption peak appears, indicating that the surface of the α-AlH_3 is coated with PW, which were consistent with the previous infrared spectral analysis and XPS analysis.

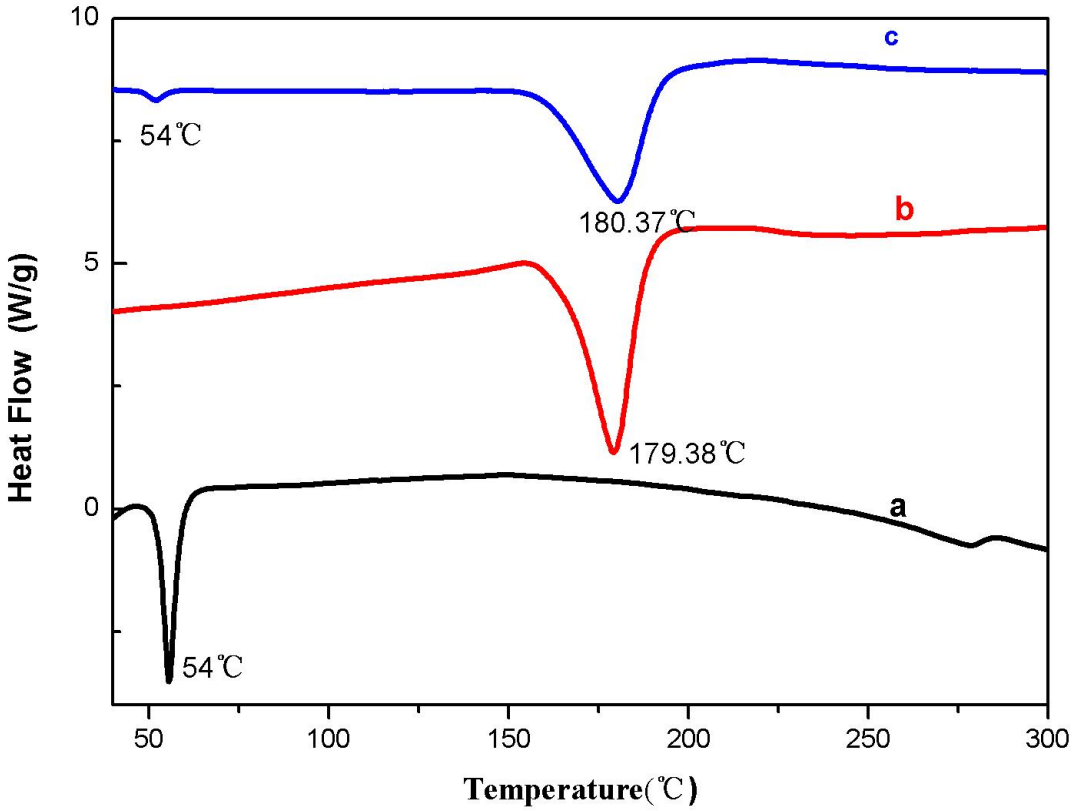


Figure 5 The DSC curves of PW（a),α-AlH_3（b）and α-AlH_3 coated by PW(c)

In order to study whether a small amount of coating agent PW can slow down the moisture absorption performance of α-AlH_3, the contact angle and moisture gain rate of α-AlH_3 and α-AlH_3 coated by PW were tested, and the results were shown in Figure 6.

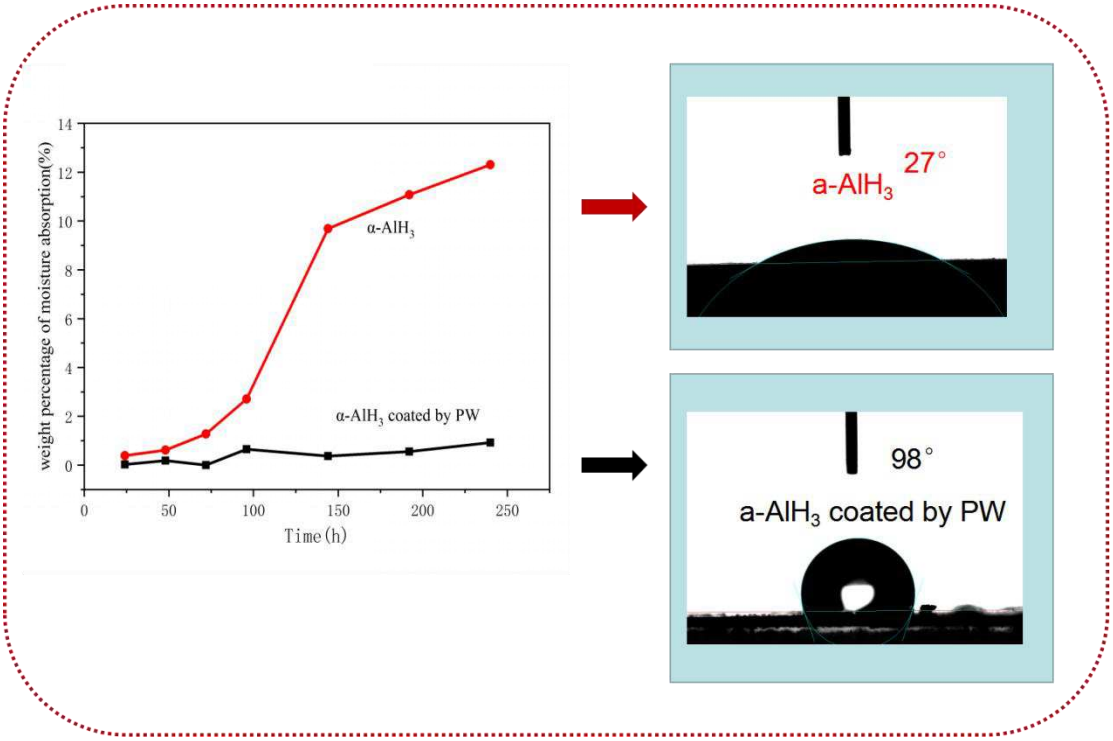


Figure 6 The hygroscopic curves and contact angles of α-AlH_3 and α-AlH_3 coated by PW

The moisture absorption performance of a-AlH_3 and a-AlH_3 coated by PW were tested by the dryer balance method. The a-AlH_3 and a-AlH_3 coated by PW were placed at room temperature and 93% humidity for a long time by weight gain method, and the hygroscopic curve were recorded as shown in Figure 6, and the hygroscopic weight gain rate of a-AlH_3 after 30 days at room temperature was 12%, while the hygroscopic weight gain of the PW coated a-AlH_3 composite was only 0.8% The hygroscopicity weight gain was significantly improved. The hygroscopicity of a-AlH_3 increases significantly over time, and the hygroscopicity of coated by PW initially increased and then remained stable over time . It is speculated that it mainly stems from the close binding of PW to α-AlH_3, which effectively inhibits the reaction of AlH_3 with water vapor. The contact angle of a-AlH_3 is 27 °, The contact angle of α-AlH3 by PW coated is 98 °, PW can be a good moisture and the surrounding environment isolation due to its hydrophopicity. This feature is conducive to the long-term storage and application of a-AlH_3.

To investigate the influence of PW on the sensitivity of α-AlH_3, different batches of prepared α-AlH_3 samples were numbered, and the impact, friction and electrostatic sensitivity were tested to study the influence of PW on the sensitivity of α-AlH_3. The impact sensitivity was conducted according to the GJB772A-97 standard method 601.1[11]. The friction sensitivity was conducted according to the GJB772A-97 standard

method 602.1[11]. The electrostatic sensitivity was evaluted according to the GJB5891.27-2006.[18] The test results are shown in the table 2.

No	sample	Impact sensitivity	Friction sensitivity	Electrostatic sensitivity
#1	α-AlH_3	14%	40% （90°3.92MPa）	V_{50}=10.0kV no fire
#2	α-AlH_3 coated by PW	5%	30% （90°3.92MPa）	V_{50}=10.0kV no fire
#3	α-AlH_3 coated by PW	6%	31% （90°3.92MPa）	V_{50}=10.0kV no fire
#4	α-AlH_3 coated by PW	5%	32% （90°3.92MPa）	V_{50}=10.0kV no fire
#5	α-AlH_3 coated by PW	5%	30% （90°3.92MPa）	V_{50}=10.0kV no fire

Table 2. The sensitivity results of α-AlH_3 and AlH_3 coated by PW

Experimental batch number #1 is α-AlH_3, and experimental batch numbers #2, #3, #4 and #5 are all coated materials. From the above table 2, it can be seen that the α-AlH_3 surface modification material PW has an effect on α-AlH_3. The impact sensitivity and friction sensitivity of α-AlH_3 coated by PW have been reduced to a certain extent. The electrostatic sensitivity has no change. The reason is that PW has a lubricating effect on α-AlH_3. After being modified by PW, it can meet the requirements of later application .

Conclusion

In our research work, the hydrophobic film of PW was firstly successfully formed on the surface of α-AlH_3 by solvent anti-solvent method . The structure and morphology of them were characterized by various characterization methods. The characterization results demonstrate that the physical phase structure of the sample has not changed, the PW layer is completely and effectively covered on the surface of α-AlH_3 . After the modification of α-AlH_3 by PW, the stability of α-AlH_3 coated by PW is significantly higher than that of α-AlH_3 in 93% high humidity environment. The contact angle of *α*-AlH_3 is improved from 27° to 98°. The impact sensitivity and friction sensitivity of α-AlH_3 have also been reduced. This present research provides a simple and effective method for the storage performance of α-AlH_3 and its application in high-energy explosives and solid rocket propellants.

Experimental

Materials

α-AlH_3 was typically synthesized following a wet chemical method. $LiAlH_4$ and $AlCl_3$

react in diethyl ether to produce an alane-ether complex. Then, α-AlH_3 was crystallized from the crystallization solution by removing ether by heating the crystallization solution to a temperature ranging from approximately 80 ℃ to 90 ℃; additionally, the crystallization additive was also added to the crystallization solution. α-AlH_3 was synthesized in our institute. All coating experiments were carried out under an argon atmosphere (ultra-high purity) by using the standard Schlenk techniques. PW was purchased from Aladdin Biochemical Technology Co. Ltd. The other chemicals were commercial, analytical grade and used without further purification

Coating of α-AlH_3 with PW

The preparation processes of coating of α-AlH_3 with PW is shown in Figure 7. Firstly, α-AlH_3 (1.0 g） was added to a three-mouth flask（250 mL). The absolute（150 ml）was added to the above three-mouth flask（250 mL）. The above three-mouth flask（250 mL）was placed under ultrasonic action for 30 min. Secondly, PW（0.01 g）was dissolved in petroleum ether（20 ml）to give PW petroleum ether solution. At room temperature, the petroleum ether solution of PW was slowly added to the above suspension containing α-AlH_3. After the dropwise addition is completed, the reaction continued for 30min ~ 60min, the mixture is steamed on the rotary evaporator, the solvent is removed to dry to obtain a white powder.[23]

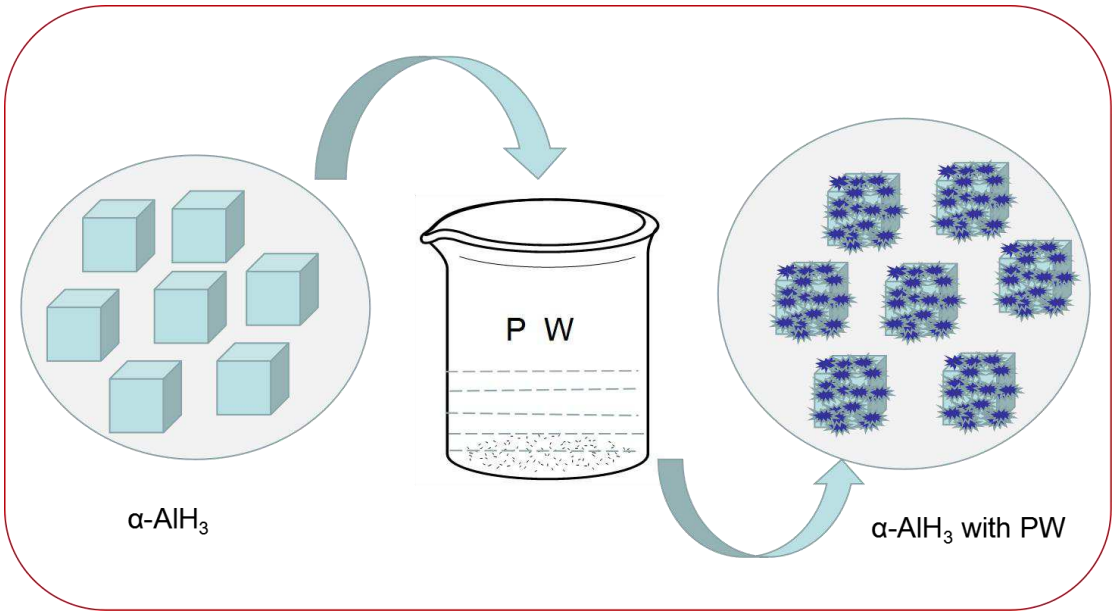


Figure 7. Possible deposition process of α-AlH_3 coated by PW

Materials characterization

Fourier transform infrared spectroscopy (FT-IR) was performed on a US PerkinElmer

instrument to identify the functional groups. The morphology of the samples was examined by field emission scanning electron microscopy (SEM, Quanta600FEG). The surface chemistry was analyzed using X-ray elemental analysis (XPS, Thermo Fisher spectrometer equipped with monochromatic Al Ka radiation (1486.6 eV)).The thermal analysis was studied by DSC (NETZSCH STA 449C). The samples were heated from room temperature to the set temperatures with a heating rate of 10 ℃/min under an Ar_2 gas flow rate of 70 ml/min to prevent oxidation[11].

Hygroscopicity test

Static hygroscopicity refers to the GJB772A-97 method[11]. Place the saturated solution of potassium nitrate in a desiccator. After equilibrium, a hygrometer was used to determine the relative humidity in the desiccator to be 93%. Combine α-AlH_3 and α-AlH_3 coated at the same time. Place it in a dry place, and use a Mettler analytical electronic analytical balance for weighing, with an accuracy of 0.0001. The weight change was recorded every 24 hours, the change in moisture absorption rate was observed, and the moisture absorption rate was calculated as follows:

$$Q = \frac{\nabla \mathrm{G}}{\mathrm{m}} \times 100\%$$

In the formula, Q is the moisture absorption rate, ΔG is the weight gain of the sample after moisture absorption, and m is the initial weight of the sample.[11]

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