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PDA modification and properties of α -AlH₃

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We present a novel surface coating to resolve the stability of α -AlH₃. Inspired by the strong chemical adhesion of mussels, the polymerization of dopamine was first introduced to coat α -AlH₃ through simple situ polymerization. The α -AlH₃ was used as a substrate. In-depth characterizations confirmed the formation of polydopamine (PDA) on the α -AlH₃ surface. The coated α -AlH₃ sample was characterized by X-ray diffraction X-ray photoelectron spectrometry and Scanning Electron Microscope. The results show that a strong PDA film is formed on the surface of α -AlH₃, and PDA@ α -AlH₃ retains its primary morphology. The crystal form of α -AlH₃ does not change after coating with PDA. The XPS analysis results show that N1 s appears on the material after coating with PDA, indicating that polydopamine is formed on the surface of α -AlH₃. The moisture absorption tests show that the moisture absorption rate of α -AlH₃ is greatly reduced after being coated with PDA. The excellent intact ability of PDA prevents α -AlH₃ from reacting with water in air. The thermal stability of α -AlH₃ before and after coating was analyzed by DSC. This work demonstrates the successful applications of dopamine chemistry to α -AlH₃, thereby providing a potential method for metastable materials.

AlH₃ is a solid-state hydrogen storage, hydrogen provider and reducing agent. Combined with Ammonium dinitramide (ADN), it becomes a high energy material often used for aerospace and missile industry^{1–4}. Theoretical studies have shown that the specific impulse value of AlH₃ is higher in solid, liquid and solid–liquid propellants than Al^{5–7}. AlH₃ is a special compound. It has at least seven different crystalline structures depending on the synthesis conditions: α , β , γ , δ , ϵ and ζ . Among them, α -AlH₃ is the best-studied crystalline^{8–12}. However, α -AlH₃ has a small enthalpy of formation and is in a metastable state. Hence, the problem related to stability remains unresolved^{13–16}.

To date, various researchers in the worldwide have been tackling this problem in improving the stability of AlH₃, including surface passivation, surface coating and doping with other substrates^{17–24}. In spite of this, the appropriate coating material and the novel coating technique for coating α -AlH₃ should be explored.

Dopamine is a biological neurotransmitter that widely exists in living organisms²⁵. The use of dopamine solution through the oxidation-polymerization of monomers has provided a facile and versatile method for modifying the surfaces of solid materials, which has led to the development of bioinspired PDA for the successful modification of various substrates, including metals, metals with native oxide surfaces, ceramics, semiconductors, carbon materials, and synthetic polymers. PDA-mediated chemistry could provide a general method for the fabrication of numerous multifunctional substrates with specific properties^{26–30}. Dopamine chemistry is a straightforward and versatile coating strategy that may open a door for the surface processing of α -AlH₃. However, few works have reported the use of PDA coating on α -AlH₃.

Herein, we report a general and facile approach to the coating of α -AlH₃, which is bioinspired through the in situ polymerization of dopamine. To the best of our knowledge, this is the first report about the application of dopamine chemistry to α -AlH₃. First, dopamine was added to the phosphate buffer saline (PBS). The as-prepared α -AlH₃ then underwent dopamine polymerization through immersion in a freshly prepared dopamine solution, with stirring at 200 rpm for 4 h³⁰. A simple scatter of α -AlH₃ in an aqueous dopamine solution can lead to the spontaneous deposition of PDA film. The stability of α -AlH₃ is significantly improved through the PDA coating. The present work potentially provides a new method for the modification of metastable.

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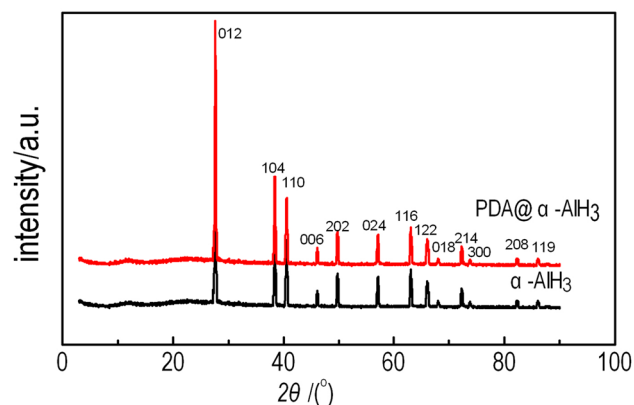


Figure 1. XRD patterns of PDA@ α -AlH₃ and α -AlH₃.

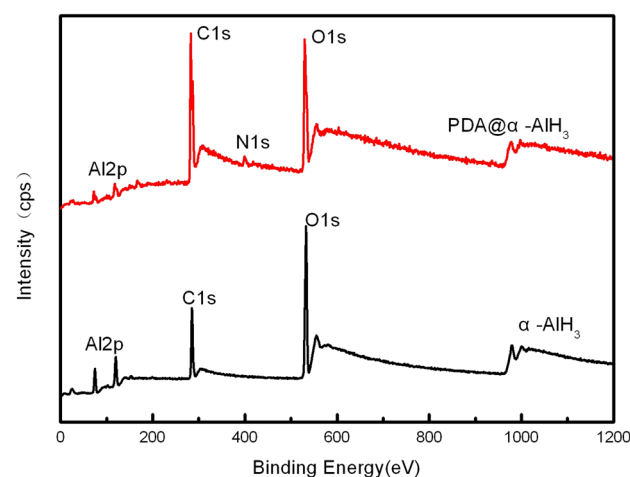


Figure 2. XPS patterns of α -AlH₃ and PDA@ α -AlH₃.

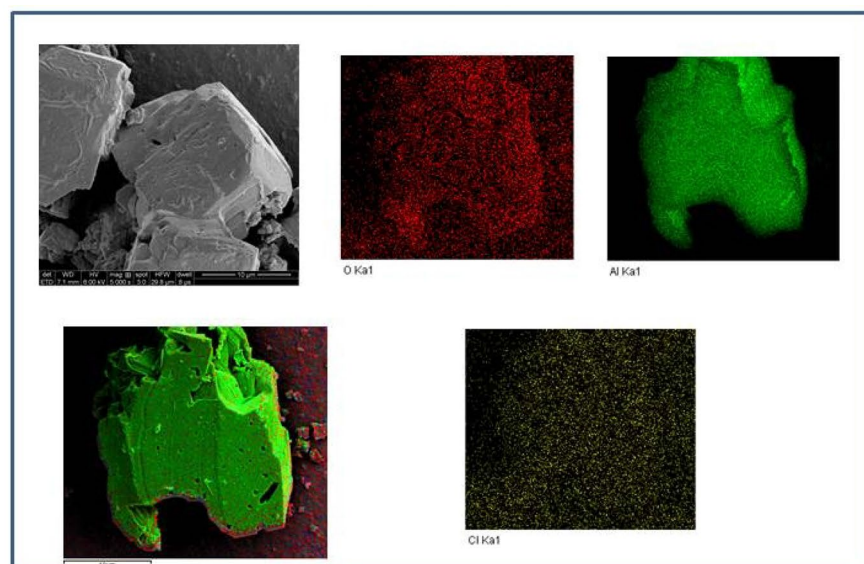
Sample	Al2p/%	C1 s/%	O1 s/%	N1 s/%
α -AlH ₃	43.25	18.17	38.58	0
PDA@ α -AlH ₃	21.27	52.37	22.83	3.53

Table 1. XPS testing results of XPS of α -AlH₃ and PDA@ α -AlH₃.

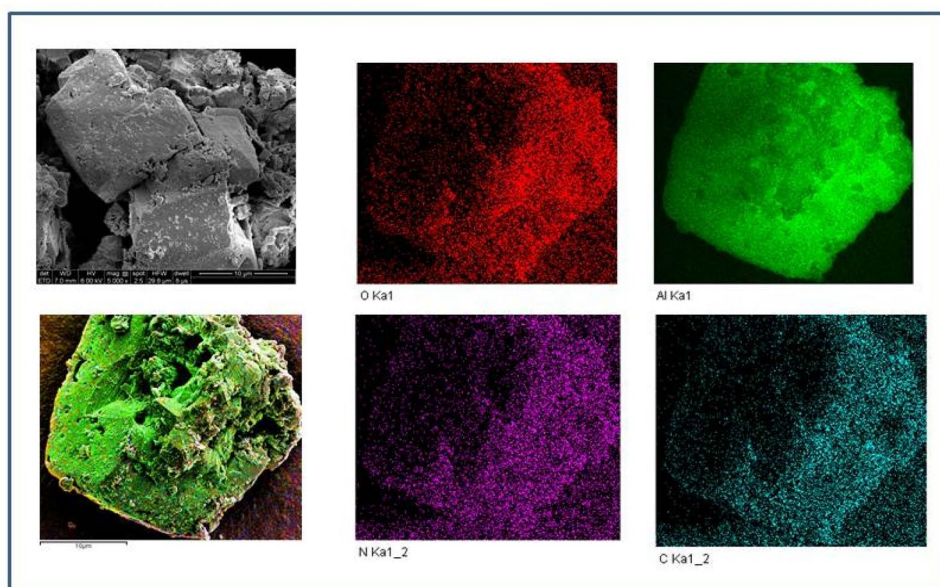
Results and discussion

The PDA@ α -AlH₃ composite and α -AlH₃ were subjected to XRD analysis, and the results are shown in Fig. 1. Figure 1 shows that the characteristic peaks of the PDA was amorphous without the characteristic diffraction peak of PDA. composite material appear at $2\theta = 27.84^\circ, 38.58^\circ, 40.72^\circ, 46.1^\circ, 49.96^\circ, 57.26^\circ, 63.26^\circ, 66.26^\circ, 68.14^\circ, 72.48^\circ, 73.84^\circ, 82.52^\circ, 86.16^\circ$, corresponding to the (012), (104), (006), (202), (024), (116), (122), (018), (214), (300), (208) and (119) planes of α -AlH₃ (JCPDF 23-0761), respectively. The position of the diffraction peak of the PDA@ α -AlH₃ complex is basically the same as the characteristic diffraction peak of α -AlH₃. It shows that the position of the characteristic diffraction peak remains unchanged before and after the modification, indicating that α -AlH₃ has good crystallization performance and PDA was amorphous without the characteristic diffraction peak of PDA. Observed changes in the relative peak intensities are attributed to the decrease of particle crystallinity and the increased scattering power caused by the coated PDA¹⁸.

The surface compositions of PDA@ α -AlH₃ and α -AlH₃ were analyzed by photoelectron spectroscopy (XPS), and the results are shown in Fig. 2 and Table 1. Figure 2 shows that the element types on the surface of α -AlH₃ before and after coating changed. The surface elements of α -AlH₃ before coating only contain three elements: C, Al, and O. After coating, the surface elements of PDA@ α -AlH₃ contained not only three elements: C, Al, and O but also the characteristic N element peak of the polydopamine film. These observations indicate that the surface of α -AlH₃ was successfully coated with a polydopamine film. However, the intensity of the peaks



(a)



(b)

Figure 3. SEM and EDS mapping images of α -AlH₃ and PDA@ α -AlH₃ collected from different location distributions, (a) α -AlH₃, (b) PDA@ α -AlH₃.

has changed. The intensity of the C1 s peak is significantly increased, indicating that the intensity of the O1 s peak and Al2p corresponding to the carbon element in the PDA coated on the surface of α -AlH₃ is significantly reduced. At the same time, it can be seen more specifically from Table 1 that the content of C1 s increased from 18.17% to 52.37%, and the corresponding contents of O and Al were reduced. From Table 1, the content of O1 s is reduced from 38.58% to 22.83%, the content of Al2p is reduced from 43.25% to 21.27%, and the content of N1 s is characteristic of a polydopamine film at 3.53%, indicating that the surface of α -AlH₃ is coated with PDA.

To further study the influence of PDA on the micromorphology of α -AlH₃, the morphology analysis results of PDA@ α -AlH₃ and α -AlH₃ by SEM are shown in Fig. 3. Figure 3 shows the SEM images and atomic distribution as determined by the EDS mapping images of two samples obtained from different locations. Figure 3a is the SEM and EDS-mapping image of α -AlH₃. It has a cubic morphology of polycrystalline irregularity, with a particle size of approximately 10 μ m, a relatively smooth surface, and relatively sharp edges and corners. There is a superpositional phenomenon between the particles. Figure 3b is the SEM and EDS mapping image of PDA@ α -AlH₃. It is a cube with less regularity, with a particle size of approximately 10 μ m. The surface is relatively uneven and is attached to polydopamine particles, indicating that PDA is evenly coated on the α -AlH₃ surface. It is clear that

Elements	Al	O	Cl	N	C
Sample α -AlH ₃ mass %	87.22	12.49	0.29	n.d	n.d
Sample α -AlH ₃ atomic %	80.39	19.41	0.21	n.d	n.d
Sample PDA@ α -AlH ₃ mass %	77.20	7.73	n.d	1.56	13.51
Sample PDA@ α -AlH ₃ atomic %	62.47	10.54	n.d	2.44	24.55

Table 2. Elemental analysis of α -AlH₃ and PDA@ α -AlH₃ samples by EDS, n.d., not detected.

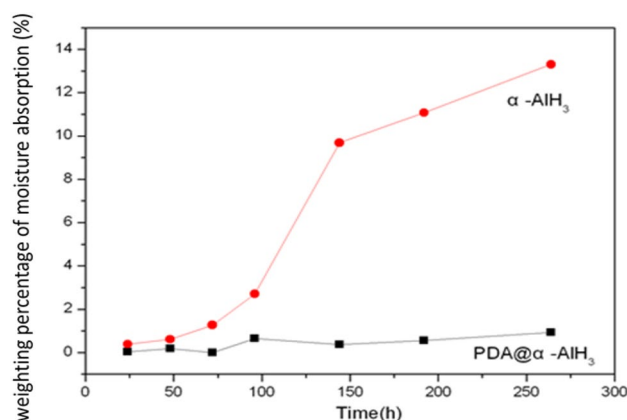


Figure 4. The moisture absorption curves of α -AlH₃ and PDA@ α -AlH₃.

the elements of α -AlH₃ determined by EDS mapping are different in terms of their composition and distribution. EDS mapping shows that the Al shown in green is full of coverage because Al is the major element present in α -AlH₃. The O distribution is shown in red patches and dots. The Cl distribution is shown in yellow patches and dots. This shows that some Cl minerals included in α -AlH₃ have been unremoved by cleaning.

After coating, the elements of PDA@ α -AlH₃ contained not only Al and O but also the characteristic N and C elements of polydopamine. The C distribution is shown in blue patches and dots. The N distribution is shown in purple patches and dots. The composition of samples determined by EDS is given in Table 1. As seen from Table 2, the C atomic percentage was increased by 24.55%, and when the N atomic percentage was increased by 2.44%, α -AlH₃ was coated by PDA, showing a significant enrichment of the C and N contents. At the same time, the Al and the O atomic percentages were decreased by 7.88% and 8.87%, respectively.

Some studies have shown that dopamine first undergoes oxidation to dopaminequinone under alkaline conditions, followed by intramolecular cyclization via 1,4 Michael-type addition to yield leu-codopaminechrome. Leucodopaminechrome further undergoes oxidation and rearrangement to form 5,6-dihydroxyindole, which is easily oxidized to 5,6-indolequinone^{28,29}. These two reaction products are capable of undergoing branching reactions, leading to the formation of multiple isomers of dimers and higher oligomers, which self-assemble through the reverse dismutation reaction between catechol and o-quinone to yield the cross-linked polymer³⁰. A number of supramolecular interactions, including π -stacking, charge transfer, and hydrogen bonding, have been shown to be the prominent features of the polymer's structures³⁰. In addition, with the increasing time, the coverage of PDA on the α -AlH₃ surface increases due to conjugation of PDA aggregates on the surface, accompanying by the growth of PDA aggregates, which result in the deposition of PDA particles onto α -AlH₃ surface. Therefore, compact and uniform PDA coating on α -AlH₃ was possibly due to these factors. Firstly, under ambient conditions, polydopamine was prone to diffusion on organic α -AlH₃ surfaces through noncovalent binding interaction such as hydrogen bonding, or π - π stacking to yield an effective adhesion layer; secondly, reactions between catechol in dopamine molecule and oxidation product o-quinone yielded the cross-linked polymers; thirdly, the cross-linked polymers can further assemble to PDA aggregates and deposit on the α -AlH₃ surfaces, resulting in the PDA layers.

To study whether a small amount of coating agent PDA can slow down the moisture absorption of α -AlH₃, the moisture absorption rates of PDA@ α -AlH₃ and α -AlH₃ were tested. The water contact angles of PDA@ α -AlH₃ and α -AlH₃ are measured. These results are shown in Fig. 4. The results show that at room temperature and 93% relative humidity, the moisture absorption rate of α -AlH₃ coated with PDA is significantly lower than that of α -AlH₃. With increasing time, the moisture absorption rate of uncoated α -AlH₃ increases rapidly with storage time and reaches the equilibrium point of moisture absorption after 12 days, which is as high as 13.3%. The moisture absorption rate of α -AlH₃ after being coated with PDA is only 0.5%, which shows that the polydopamine film on the surface plays an important role in isolating moisture in the air.

Thermal stability is a key performance factor for novel materials. To investigate the thermal stability of the samples before and after modification, the thermal performance was determined by DSC. The test results of the samples are displayed in Fig. 5. The characteristic parameters are summarized in Table 3. As shown in Fig. 5,

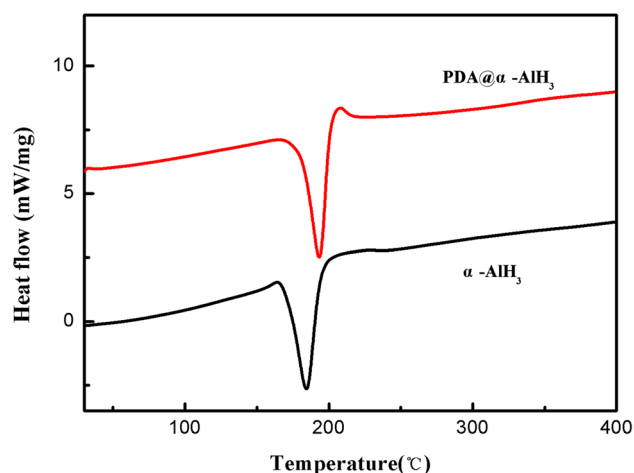


Figure 5. The DSC curves of α -AlH₃ and PDA@ α -AlH₃.

Sample	Endothermic peak			
	T _o /°C	T _p /°C	T _e /°C	ΔH /Jg ⁻¹
α -AlH ₃	166.2	181.2	204.1	405.1
PDA/ α -AlH ₃	177.1	191.1	210.2	418.6

Table 3. Thermal analysis data of α -AlH₃ and PDA@ α -AlH₃. T_o: onset temperature; T_p: peak temperature of thermal profile; T_e: end temperature; ΔH : total energy for endothermic profile.

No.	Sample	Storage time/d	Percent hydrogen/%		Decomposition rate/%
			Initial	windup	
#1	α -AlH ₃	365	9.745	9.632	1.16
#2	PDA/ α -AlH ₃	365	9.136	9.126	0.11
#3	PDA/ α -AlH ₃	365	9.095	9.089	0.07
#4	PDA/ α -AlH ₃	365	9.235	9.215	0.22

Table 4. The H element content of α -AlH₃ and PDA@ α -AlH₃ stored at room temperature.

the DSC curve of α -AlH₃ exhibits a single endothermic desorption process starting at and peaking at 181.2 °C, which is in accordance with the endothermic reaction being attributed to the dehydrogenation of α -AlH₃. However, the thermal decomposition temperature of PDA@ α -AlH₃ is 191.1 °C, indicating that the thermal stability of α -AlH₃ is greatly improved after PDA modification, which is due to the formation of organic PDA to improve its heat resistance. These results clearly demonstrate that PDA@ α -AlH₃ completely decomposed into Al is more difficult than pure α -AlH₃.

According to the relevant literature, AlH₃ will slowly decompose to hydrogen at room temperature. For this reason, the prepared samples are naturally placed in a desiccator, and after a period of time, the hydrogen content is tested, and the decomposition rate is indirectly calculated through the change in hydrogen content. The test results of samples α -AlH₃ and PDA@ α -AlH₃ are shown in Table 4. Table 4 shows that the hydrogen content of the product is reduced due to the decomposition of. The initial hydrogen content of sample #1 is 9.745%. From the initial hydrogen content data of #2, #3 and #4, we can see that there are varying degrees of reduction in hydrogen about α -AlH₃ modified by PDA. However, from the perspective of decomposition rate, the decomposition rate of α -AlH₃ is the highest, and the decomposition rate is reduced after modification by PDA. The decomposition of PDA@ α -AlH₃ may be slowed due to the formation of the organic polymer PDA. The more organic content there was, the lower the decomposition rate.

To investigate the influence of PDA on the sensitivity of α -AlH₃, different batches of prepared PDA@ α -AlH₃ samples were numbered, and the impact, friction and electrostatic sensitivity were tested to study the influence of PDA on the sensitivity of α -AlH₃. The impact sensitivity was conducted according to the GJB772A-97 standard method 601.1. The friction sensitivity was conducted according to the GJB772A-97 standard method 602.1. The electrostatic sensitivity was evaluated according to the GJB5891.27-2006.¹⁸ The test results are shown in the Table 5.

No	sample	Impact sensitivity (%)	Friction sensitivity	Electrostatic sensitivity
#1	α -AlH ₃	14	40% (90°3.92 MPa)	V ₅₀ = 10.0 kV no fire
#2	PDA/ α -AlH ₃	12	44% (90°3.92 MPa)	V ₅₀ = 10.0 kV no fire
#3	PDA/ α -AlH ₃	14	44% (90°3.92 MPa)	V ₅₀ = 10.0 kV no fire
#4	PDA/ α -AlH ₃	14	40% (90°3.92 MPa)	V ₅₀ = 10.0 kV no fire
#5	PDA/ α -AlH ₃	12	40% (90°3.92 MPa)	V ₅₀ = 10.0 kV no fire

Table 5. The sensitivity results of α -AlH₃ and PDA@AlH₃.

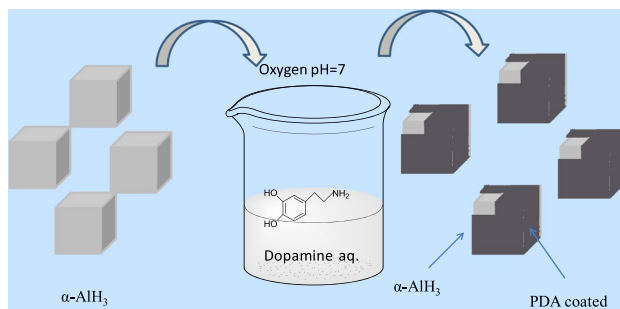


Figure 6. Possible deposition process of PDA@ α -AlH₃.

Experimental batch number #1 is α -AlH₃, and experimental batch numbers #2, #3, #4 and #5 are all PDA-modified materials. From Table 5, it can be seen that the α -AlH₃ surface modification material polydopamine has an effect on α -AlH₃. The impact sensitivity, friction sensitivity and electrostatic sensitivity have little effect. The reason is that PDA did not change the crystal morphology, structure and crystal surface energy of α -AlH₃. After being modified by PDA, it can meet the requirements of later application indexes.

Conclusion

Polydopamine (PDA) was successfully generated on the surface of α -AlH₃ by in situ dopamine (DA) polymerization, and the structure and morphology of the package were characterized by various test methods, such as XRD, XPS and SEM. The results showed that the coating layer was more uniform, the coating effect was better, and the crystal type of the material was not changed. The stability of the PDA@ α -AlH₃ composite at room temperature and 93% high humidity is significantly higher than that of uncoated α -AlH₃. This research provides new ideas for the long-term storage performance of α -AlH₃ and its application in propellants.

Methods and materials

α -AlH₃ was typically synthesized following a wet chemical method. LiAlH₄ and AlCl₃ react in diethyl ether to produce an alane-ether complex. Then, α -AlH₃ was crystallized from the crystallization solution by removing ether by heating the crystallization solution to a temperature ranging from approximately 80 °C to 90 °C; additionally, the crystallization additive was also added to the crystallization solution. α -AlH₃ was synthesized in our institute. Dopamine hydrochloride was purchased from Sigma–Aldrich and used as received. The other chemicals were commercial, analytical grade and used without further purification.

Coating of α -AlH₃ with PDA. A phosphate-buffered saline (PBS pH = 7 ~ 7.5) solution was first prepared after the as-prepared solution and α -AlH₃ was dispersed to the PBS solution, with stirring at 300 rpm for 30 min. Then, dopamine was added to the above suspension, with stirring at 200 rpm for 4 h. During the polymerization process, the color of the solution changed from white to dark brown as a result of dopamine polymerization. The obtained dark brown solution was filtered. The samples were rinsed with distilled water and then dried in a vacuum oven at 60 °C. The entire operation process is shown in Fig. 6.

Hygroscopicity test. Static hygroscopicity refers to the GJB772A-97 method. 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 -AlH₃ and PDA@ α -AlH₃ 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 h, the change in moisture absorption rate was observed, and the moisture absorption rate was calculated as follows:

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

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.

Characterization. Structural characterization of the α - AlH_3 and PDA@ α - AlH_3 samples was performed by powder X-ray diffraction (XRD, DMAX2400 with $Cu K_\alpha$ radiation at $\lambda = 1.5418 \text{ \AA}$). 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 K α radiation (1486.6 eV)). The content of H element was analysed using organic element analyzer. 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 $10 \text{ }^\circ\text{C}/\text{min}$ under an Ar_2 gas flow rate of $70 \text{ ml}/\text{min}$ to prevent oxidation.

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Author contributions

M.Q., B.Y., Q.S. and W.T., led the research study and prepared the manuscript. S.C., T.G., and W.W. characterized the samples under the supervision of Y.Z. and Z.G.. All the authors discussed the results and commented on the manuscript.

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Competing interests

The authors declare no competing interests.

Additional information

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