METHOD FOR SILANE COUPLING AGENT COMPOUNDING MODIFICATION AND DISPERSING OPTIMIZATION FOR PHOTOVOLTAIC-GRADE SUBMICRON SILICA MICRO-POWDER

Field of the Invention

[0001] The present application relates to the technical field of surface modification and dispersion of inorganic non-metallic materials, specifically to a method for silane coupling agent compounding modification and dispersing optimization for photovoltaic-grade submicron silica micro-powder.

Background to the Invention

[0002] With the increasing requirements for high-purity, high-performance silicon-based materials in the photovoltaic industry, photovoltaic-grade submicron silica micro-powder is widely used as a key filler in encapsulants, thermal interface materials, and battery backsheets. To improve its compatibility and dispersion stability in the organic matrices, silane coupling agents are often used for the surface modification thereof. However, prior silane coupling agents still have significant shortcomings in the compounding modification and dispersing optimization for photovoltaic-grade submicron silica micro-powder, making it difficult to simultaneously achieve a high grafting efficiency, an excellent dispersibility, and a long-term storage stability, thus limiting its application performance in high-end photovoltaic materials.

[0003] The patent with the publication number CN105419675B, entitled "SILANE COUPLING AGENT AND APPLICATION THEREOF" (authorized publication date: May 8, 2018), discloses a multifunctional silane coupling agent with a general structure, which contains multiple active groups such as epoxy groups, amino groups and mercapto groups in its molecule, is suitable for sealant systems and can improve the adhesion performance to low surface energy or porous materials. This technical solution is not specifically designed for the surface characteristics of inorganic micro-powders (especially submicron silica micro-powders), and its consideration regarding the aspects of dispersion stability of the powder is limited; and the structure of the coupling agent also fails to fully account for the stringent requirements of photovoltaic-grade materials, such as restrictions on metal ion impurities and sensitivity to moisture, and does not involve compounding modification processes or dispersing optimization means, furthermore its improvement effect on the agglomeration problem of silica micro-powder in non-polar or weakly polar systems is limited, thus making it challenging to meet the comprehensive requirements of photovoltaic encapsulation materials for high filling, high transparency and long-term reliability.

[0004] The patent with the publication number CN118834234B, entitled "SILANE COUPLING AGENT AND SILANE SURFACE TREATING AGENT" (authorized publication date: September 26, 2025), proposes a novel silane coupling agent containing an alicyclic structure, which is used to enhance the protective capability of metal substrates. In terms of structure, the coupling agent introduces C5-C20 alicyclic groups to enhance hydrophobicity and film-forming properties, however, its application scenarios focuses on metal surface treatment and does not address the surface modification of inorganic powders (especially submicron-scale silica micro-powder); and simultaneously, the solution thereof does not provide compounding modification strategies for powders with high specific surface areas (such as multi-functional group synergy, gradient coating, or solvent-additive synergistic dispersion systems), offering a limited improvement to the re-agglomeration problem of silica micro-powder in resin matrices caused by van der Waals forces. In addition, its formulation system does not fully consider the stringent control requirements for trace impurities such as sodium, iron, and chlorine in photovoltaic materials, posing a potential risk of introducing contamination and potentially affecting the long-term reliability of photovoltaic modules.

[0005] The above analysis shows that although the prior silane coupling agent technique has achieved certain results in specific fields (such as sealants, metal corrosion protection, or rubber reinforcement), however, in terms of the special modification of photovoltaic-grade submicron silica micro-powder, the following shortcomings are commonly observed.

[0006] (1) There is a lack of customized molecular design targeting the high specific surface area and surface hydroxyl density of submicron silica micro-powder.

[0007] (2) There is no establishment of a synergistic process for compounding modification and high-efficiency dispersion.

[0008] (3) There is neglect of the special requirements of photovoltaic materials for an ultra-low impurity content and a long-term environmental stability.

[0009] (4) Modification with a single silane coupling agent cannot balance compatibility and dispersion stability. For example, epoxy-based silanes offer a good compatibility but suffer from a low steric hindrance, while amino silanes that exhibit a strong adhesion but have an insufficient hydrophobicity.

[0010] Therefore, it is necessary to develop a method for silane coupling agent compounding modification and dispersing optimization for photovoltaic-grade submicron silica micro-powder, so as to realize the integration of a high grafting rate, an excellent dispersion stability and a material purity, thereby supporting the industrialization requirements of next-generation high-performance photovoltaic encapsulation materials.

Statement of Invention

[0011] The purpose of the present application is to provide a method for silane coupling agent compounding modification and dispersing optimization for photovoltaic-grade submicron silica micro-powder, so as to solve the problems above-mentioned in the background art.

[0012] To achieve the above purposes, the present application provides the following technical solution: a method for silane coupling agent compounding modification and dispersing optimization for photovoltaic-grade submicron silica micro-powder, including the following steps:

[0013] drying the photovoltaic-grade submicron silica micro-powder at 105–115°C for 2-4 h under an inert atmosphere, cooling to a room temperature, and then placing in a high-shear mixing reactor, where the surface hydroxyl content index of the photovoltaic-grade submicron silica micro-powder is 1.5–3.0 mmol/g;

[0014] where the specific inert gas (such as nitrogen gas or argon gas) should have a gas purity of ≥99.999% to prevent trace amounts of oxygen gas or moisture from affecting the surface condition of the powder; and the drying temperature of 105-115°C is further refined into a staged heating: room temperature → 80°C (1 h) →110°C (2-3 h) to reduce powder agglomeration;

[0015] adding the first silane coupling agent solution and the second silane coupling agent solution sequentially, where after the first silane coupling agent is reacted for 1.5-2.5 h, the second silane coupling agent is added; and after the first silane coupling agent is reacted completely and the temperature is lowered to 70°C, the second silane coupling agent is added;

[0016] then adding a dispersion additive solution and continuing stirring at 2000-4000 rpm and 70-90°C for 1.0-2.0 h;

[0017] removing the solvent through a reduced-pressure distillation after the reaction is completed, drying the obtained solid in a vacuum drying oven at 60°C for 6-12 h to obtain a modified silica micro-powder;

[0018] where the first silane coupling agent is 3-(2,3-epoxypropoxy)propyltrimethoxysilane, the solution thereof is prepared by mixing the coupling agent with anhydrous ethanol at a mass ratio of 1:(8-12), and the pH is adjusted to 4.0-4.5 with glacial acetic acid;

[0019] the second silane coupling agent is N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, the solution thereof is prepared by mixing the coupling agent with anhydrous isopropanol at a mass ratio of 1:(10–15), and diluting with deionized water to a solid content of 3-5 wt%;

[0020] the dispersion additive is polyether-modified polysiloxane, and the solution thereof is prepared by mixing the additive with anhydrous n-hexane at a mass ratio of 1:(20–30); and

[0021] the photovoltaic-grade submicron silica micro-powder has a particle size D50 of 0.3–0.8 μm, a specific surface area of 15–25 m^2/g, and sodium, iron, and chloride ion contents each less than 1 ppm.

[0022] Preferably, the addition amount of the first silane coupling agent solution accounts for 1.5-3.0 wt% of the mass of the silica micro-powder, and the addition means is to add dropwise to the reaction system at a constant rate by a metering pump within 10-15 min, and the system temperature is maintained at 65±2°C during the dropwise addition process.

[0023] Preferably, the addition amount of the second silane coupling agent solution accounts for 0.8-1.5 wt% of the mass of silica micro-powder. After the reaction of the first silane coupling agent is completed and the temperature is cooled to 70°C, the second silane coupling agent solution is injected into the reactor in the form of a spray through the bottom feed port, where the spray has a pressure of 0.2–0.4 Mpa, and the atomization particle size is regulated within the range of 20–50 μm.

[0024] Preferably, the high-shear mixing reactor is equipped with a double-layer jacketed temperature control system, where the inner layer is a reaction chamber and the outer layer is charged with thermal oil for temperature regulation; and three layer of serrated dispersion discs are installed inside the reaction chamber. The upper disc is 5 cm away from the liquid level, the middle disc is located at the center of the liquid level, and the lower disc is 3 cm away from the bottom; and the spacing between adjacent discs is equal, and the rotating shaft is installed vertically.

[0025] Preferably, the reduced-pressure distillation is carried out in a rotary evaporator until no condensate is produced, where a water bath temperature is 50-60°C, a vacuum degree is -0.095 to -0.098 MPa, and a distillation time is 40–60 min.

[0026] Preferably, the vacuum drying oven is equipped with a porous stainless steel tray inside, where the tray has a pore diameter of 0.5 mm and a porosity of 40%, and a paving thickness of the silica micro-powder is not more than 5 mm. During the drying process, the material is turned over once every 2 h. The turning-over is carried out by the means of pulse purging with clean nitrogen gas at an air pressure of 0.1 MPa, each purging lasts for 10 s, and the purging is carried out 3 times in total.

[0027] Preferably, the anhydrous ethanol, anhydrous isopropanol, and anhydrous n-hexane are subjected to a molecular sieve dehydration treatment before use and are filtered through a 0.22 μm polytetrafluoroethylene membrane. The contents of sodium, iron, and other metal ions and chloride ions are all below 0.1ppb confirmed by an ICP-MS detection.

[0028] Preferably, the polyether-modified polysiloxane has a number average molecular weight of 2000–4000, and an HLB value of 8-10, where the polyether chain segments thereof are copolymerized from ethylene oxide and propylene oxide in a molar ratio of 3:1, and the end-capping group is methyl.

[0029] Preferably, the reaction chamber of the high-shear mixing reactor is made of 316L stainless steel, and the inner wall is subjected to an electrolytic polishing treatment to a surface roughness Ra≤0.4 μm.

[0030] For a modified photovoltaic-grade submicron silica micro-powder, the surface thereof is grafted with a compound coating layer of 3-(2,3-epoxypropoxy)propyltrimethoxysilane and N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, where the coating rate is 5-10 wt%, a sodium/iron/chloride ion content is ≤0.5 ppm, and a dispersion uniformity in EVA is ≤5 μm (agglomerate particle size).

[0031] A method for silane coupling agent compounding modification and dispersing optimization for photovoltaic-grade submicron silica micro-powder is provided, which is used in the preparation of highly-filled composite materials for photovoltaic encapsulants, thermal interface materials or battery backsheets, where when the highly-filled composite materials are used for photovoltaic encapsulants, the yellowing index of the encapsulated parts is ≤1.0 (after 1000h aging), and when the highly-filled composite materials are used for the thermal interface material, the thermal conductivity is ≥1.8 W/(m·K).

[0032] Compared with the prior art, the beneficial effects of the present application are achieved by the method for silane coupling agent compounding modification and dispersing optimization for photovoltaic-grade submicron silica micro-powder, which are as follows:

[0033] the present application constructs a compound organic coating layer with chemical activity, steric stability, and ultra-low impurity characteristics on the surface of submicron silica micro-powder by precisely regulating the molecular type, addition order, reaction conditions, and dispersion additive structure of the silane coupling agent, achieving molecular-level dispersion and strong interfacial bonding in a highly filled EVA system, and ultimately achieving a comprehensive performance target of a high light transmittance, a high thermal stability, and a long-term environmental reliability; and the above-mentioned process parameters and material selections do not exist in isolation, but rather form an integrated technical solution with mutual coupling and synergistic interaction, jointly constituting the core technical path to overcome the bottleneck in the application of photovoltaic-grade silica micro-powder in high-end encapsulation materials.

Brief Description of the Drawings

[0034] FIG. 1 is a schematic view of the modification production process of the silica micro-powder.

Detailed Description

[0035] The technical solutions in the embodiments of the present application have been clearly and completely described. Obviously, the described embodiments are only some embodiments of the present application, and not all embodiments. Based on the embodiments of the present application, all other embodiments obtained by those skilled in the art without creative effort fall within the scope of protection of the present application.

[0036] The present application provides a technical solution: a method for silane coupling agent compounding modification and dispersing optimization for photovoltaic-grade submicron silica micro-powder, including the following steps:

[0037] drying the photovoltaic-grade submicron silica micro-powder at 105-115°C for 2-4 h under an inert atmosphere, cooling to a room temperature, and then placing in a high-shear mixing reactor;

[0038] adding the first silane coupling agent solution and the second silane coupling agent solution sequentially, where the first silane coupling agent was reacted for 1.5-2.5

h, then the second silane coupling agent was added; and after the first silane coupling agent was reacted completely and the temperature was lowered to 70°C, the second silane coupling agent was added;

[0039] where the addition amount of glacial acetic acid to the first silane coupling agent solution needed to be quantified (e.g., 0.5-1.0 wt% of the mass of coupling agent) to avoid affecting the reactive activation of the epoxy groups due to the pH adjustment deviations; and the addition amount of deionized water of the second silane coupling agent solution should specify the calculation method (e.g., X% based on the total mass of the mixed system of the coupling agent and anhydrous isopropanol) to ensure that the solid content was accurately controlled within the range of 3-5 wt%;

[0040] subsequently adding the dispersion additive solution, and continuing stirring at 2000-4000 rpm and 70-90 °C for 1.0-2.0 h;

[0041] removing the solvent by reduced-pressure distillation after the reaction was completed, drying the obtained solid in a vacuum drying oven at 60°C for 6-12 h to obtain the modified silica micro-powder;

[0042] where the first silane coupling agent was 3-(2,3-epoxypropoxy)propyltrimethoxysilane, and the solution thereof was prepared by mixing the coupling agent with anhydrous ethanol at a mass ratio of 1:(8-12), and the pH was adjusted to 4.0-4.5 with glacial acetic acid;

[0043] the second silane coupling agent was N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, the solution thereof was prepared by mixing the coupling agent with anhydrous isopropanol at a mass ratio of 1:(10-15), and then diluting with deionized water to a solid content of 3-5 wt%;

[0044] the dispersion additive was polyether-modified polysiloxane, and the solution thereof was prepared by mixing the additive with anhydrous n-hexane at a mass ratio of 1:(20–30); and

[0045] the photovoltaic-grade submicron silica micro-powder had a particle size D50 of 0.3–0.8 μm, a specific surface area of 15–25 m²/g, and sodium, iron, and chloride ion contents less than 1 ppm.

[0046] Further, the addition amount of the first silane coupling agent solution accounted for 1.5–3.0 wt% of the mass of the silica micro-powder, the solution was added dropwise into the reaction system at a constant rate by a metering pump within 10-15 min, and the system temperature was maintained at 65±2°C during the dropwise addition process.

[0047] Further, the addition amount of the second silane coupling agent solution accounted for 0.8–1.5 wt% of the mass of silica micro-powder. After the reaction of the first silane coupling agent was completed and the temperature was cooled to 70°C, the second silane coupling agent solution was injected into the reactor in the form of a spray through the bottom feed port, where the spray had a pressure of 0.2-0.4 MPa and the atomization particle size was regulated within the range of 20-50 μm.

[0048] During the process of spray-injecting the second silane coupling agent, the spraying time was 5-10 min, and the spraying was coordinately controlled with the stirring; and the rotation speed was maintained at 4500 rpm during the spraying to avoid agglomeration caused by excessively high concentrations of local coupling agent.

[0049] Further, the high-shear mixing reactor was equipped with a double-layer jacketed temperature control system, where the inner layer was a reaction chamber, and the outer layer was charged with thermal oil for temperature regulation; and three layer of serrated dispersion discs were installed inside the reaction chamber. The upper disc was 5 cm away from the liquid level, the middle disc was located at the center of the liquid level, and the lower disc was 3 cm away from the bottom; and the spacing between adjacent discs was equal, and the rotating shaft was installed vertically.

[0050] The stirring rotation speed of the high-shear mixing reactor was refined in stages: the speed was 3000-4000 rpm (focusing on uniform dispersion) when adding the first silane coupling agent; the rotation speed was increased to 4000-5000 rpm (enhancing the contact between the spray coupling agent and the powder) after adding the second silane coupling agent; and the speed was reduced to 2000-3000 rpm (avoiding the coating layer from being damaged by excessive shearing) after adding the dispersion additive.

[0051] Impurity control requirements for silane coupling agents and dispersion additive: the sodium, iron, and chloride ion content thereof should be below 0.5 ppb, and the detection method was ICP-MS, forming a full-chain of impurity control.

[0052] Further, the reduced-pressure distillation was carried out in a rotary evaporator until no more condensate was produced, where a water bath temperature was 50–60°C, a vacuum degree was -0.095 to -0.098 MPa, and a distillation time was 40–60 min.

[0053] Further, the vacuum drying oven was equipped with a porous stainless steel tray inside, where the tray had a pore diameter of 0.5 mm and a porosity of 40%, and a paving thickness of the silica micro-powder was not more than 5 mm. During the drying process, pulse purging by nitrogen gas was performed 3 times every 2 h (with an interval of 30 s) at an air pressure of 0.1 MPa for the turning-over, where each purging lasted for 10 s, and the entire cycle was repeated 3 times in total.

[0054] Cooling means for dried powder: naturally cooling to a room temperature under vacuum state to avoid contact with air and moisture absorption.

[0055] Further, the anhydrous ethanol, anhydrous isopropanol, and anhydrous n-hexane were subjected to molecular sieve dehydration treatment before use and were filtered through a 0.22 μm polytetrafluoroethylene membrane. The metal ion content was confirmed by ICP-MS detection, where the contents of sodium, iron, and other metal ions and chloride ions were all below 0.1 ppb.

[0056] Further, the polyether-modified polysiloxane had a number average molecular weight of 2000-4000, and an HLB value of 8-10, where the polyether chain segments were copolymerized from ethylene oxide and propylene oxide in a molar ratio of 3:1, and the end-capping group was methyl.

[0057] Further, the reaction chamber of the high-shear mixing reactor was made of 316L stainless steel, and the inner wall was subjected to an electrolytic polishing treatment to a surface roughness of Ra≤0.4 μm.

[0058] Cleaning procedures for equipment such as high-shear mixing reactors, rotary evaporators, and vacuum drying ovens: cleaning with anhydrous ethanol and purging with nitrogen gas before use to prevent residual impurities in the equipment from contaminating the materials.

[0059] A modified photovoltaic-grade submicron silica micro-powder, the surface thereof was grafted with a compound coating layer of 3-(2,3-epoxypropoxy)propyltrimethoxysilane and N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, where the coating rate was 5-10 wt%, a sodium/iron/chloride ion content was ≤0.5 ppm, and a dispersion uniformity in EVA was ≤5 μm (agglomerate particle size).

[0060] A method for silane coupling agent compounding modification and dispersing optimization for photovoltaic-grade submicron silica micro-powder was provided, which was used in the preparation of highly-filled composite materials for photovoltaic encapsulants, thermal interface materials or battery backsheets, where when the highly-filled composite materials were used for photovoltaic encapsulants, the yellowing index of the encapsulated parts was ≤1.0 (after 1000h aging), and when the highly-filled composite materials were used for the thermal interface material, the thermal conductivity was ≥1.8 W/(m·K).

[0061] Example 1: taking 100g of photovoltaic-grade submicron silica micro-powder with a particle size D50=0.5 μm, a specific surface area of 20 m²/g, and sodium/iron/chloride ion content ≤ 0.8 ppm, drying under a nitrogen gas atmosphere (purity of 99.999%) according to the following procedure: room temperature→80°C (1h)→110°C (3h), cooling to a room temperature, then placing into a high-shear mixing reactor made of 316L stainless steel; preparing the first silane coupling agent solution: mixing 2.0 g of 3-(2,3-epoxypropoxy)propyltrimethoxysilane with 20 g of anhydrous ethanol, adding 0.02 g of glacial acetic acid to adjust the pH to 4.2, and filtering through a 0.22 μm membrane; adding dropwise the solution into the reactor at a constant rate by using a metering pump within 12 min, maintaining the system temperature at 65°C, the stirring rotation speed at 3500rpm, and reacting for 2 h; lowering the temperature to 70°C and preparing the second silane coupling agent solution: mixing 1.0 g of N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane with 12 g of anhydrous isopropanol, adding 3.3 g of deionized water, and diluting to a solid content of 4 wt%, spray-injecting through the bottom feed port at a pressure of 0.3 MPa (atomization particle size of 30 μm), increasing the rotation speed to 4500 rpm, and reacting for 1.5 h; preparing a dispersion additive solution: mixing 0.5 g of polyether-modified polysiloxane (number average molecular weight of 300, HLB=9) with 12.5 g of anhydrous n-hexane, injecting into the reactor, and then heating to 80°C, reducing the rotation speed to 2500 rpm, and stirring for 1.5 h; placing the reaction product in a rotary evaporator, and distilling for 50 min under a water bath of 55°C and a vacuum degree of -0.096 MPa until no condensate was produced; and spreading the solid evenly on a porous stainless steel tray (thickness of 3 mm) and drying in a vacuum drying oven at 60°C for 8 h, purging with 0.1 MPa nitrogen gas pulses three times every 2 h (with 10 s each time, and an interval of 30 s), where the obtained modified silica micro-powder had sodium/iron/chloride ion contents ≤ 0.5 ppm, and when the filling rate in the EVA matrix reached 60%, the light transmittance was ≥ 92%, and no obvious agglomeration was observed after 6 months of storage.

[0062] Although the present application has been described in detail with reference to the foregoing embodiments, those skilled in the art can still modify the technical solutions described in the foregoing embodiments or make equivalent substitutions for some of the technical features. Any modifications, equivalent substitutions, improvements, etc., made within the spirit and principles of the present application should be included within the protection scope of the present application.