

Nano core-shell silica micro-sphere, increasing transmission and anti-reflective composite coating solution and preparations and applications thereof

5 FIELD OF THE INVENTION

The invention relates to a technical field of nano core-shell materials, in particular to an anti-reflective coating solution of glass, as well as preparations and applications thereof.

BACKGROUND OF THE INVENTION

Solar battery packaging glass is used in the solar photovoltaic power generation. In the solar photovoltaic power generation, the better the light transmittance of solar batter packaging glass is, the higher the energy conversion efficiency will be. In the prior art, in order to improve the light transmittance of the solar battery packaging glass, anti-reflection film was plated onto the surface of the solar battery packaging glass to reduce reflection loss of the sunlight, and improve light utilization rate of solar cell module, so as to improve the energy conversion efficiency of solar photovoltaic power generation.

The Silica granular film prepared by nano silica sol is the early type of anti-reflection film, which is consisted of high porous loose structure that accumulated by nano silica granular in the size of dozens to hundreds of nanometers. In other words, it is a structure accumulated by spherical particles, and has a good permeability performance. The mechanical strength of this kind of film is very low, which means the film can be easily wiped out because the chemical bond between nano silica granular and the surface of glass is few. What's more, because of the large surface roughness of the film prepared, dust or organic dirt can easily trapped into low-lying area and difficult to handle, namely, it has poor dirt resistance performance. There is high demands on the mechanical strength and dirt resistance performance of the film, because the solar packaging glass are used outdoors, which often encounter all sorts of rain and snow, hail, wind, car exhaust and other environmental conditions.

As to the requirements for the mechanical strength performance of the film, the existing technology generally take the sol-gel method, using silicate ester as raw materials, preparing silica polymers under the acid catalyst conditions. The polymer film has a good mechanical strength, but has a high dense and low porosity, a higher refractive index and a poor anti-reflection

performance. In order to improve the porosity and the transparent property, a certain amount of organic pore forming agents (such as organic polymers or high-molecular resin etc.) is usually mixed in the silica polymer, removing the organic pore forming agent by calcining under high temperature (above 5 500°C) to form a honeycomb structural film, so as to significantly increase the porosity and transmittance of the film.

SUMMARY OF THE INVENTION

However, in the existing technology, silica anti-reflection film prepared by mixing organic pore forming agents still has the problem of poor dirt resistance performance. Because silica polymers and organic pore forming agents are uniformly mixed before the calcination, potholes inevitably exist on the surface of film for the calcination of organic pore forming agent. As a result, pores opened to atmosphere are formed. The more the organic pore forming agents added, the higher the light transmittance rate would be. But mechanical strength of the film would decrease, and hollows on the film surface would become bigger and much more, which would cause contradictions among increasing light transmittance, and maintaining high dirt resistance performance and high mechanical strength.

In order to solve the above mentioned problems, this invention provides the following technical solutions.

15 A nano core-shell silica micro-sphere, wherein the nano core-shell silica micro-sphere is obtained by a preparation method comprising the following steps:

(1) preparation of polystyrene core by emulsifier-free emulsion polymerization: putting an amino-containing or a quaternized co-monomer and water in a reaction vessel, adding styrene, then heating the mixture up to 20 50-85°C, preferably 70°C under the protection of nitrogen gas, and dropwise adding an initiator aqueous solution to react, and whereby obtaining a cationic polystyrene emulsion;

(2) preparation of a silica coated polystyrene core-shell structured micro- 25 sphere emulsion: mixing the cationic polystyrene emulsion used as a hard template with a solvent, then adding a silicon source material under conditions of stirring at 15-35°C, preferably at room temperature to react and obtaining the silica coated polystyrene nano core-shell structured micro-sphere emulsion.

Preferably, in the above mentioned nano core-shell silica micro-sphere, wherein, said co-monomer is an amino-containing vinyl monomer and / or a quaternized ammonium vinyl monomer; preferably, said the quaternized ammonium vinyl monomer is selected from one or more of the group consisting of acryloyloxyethyl trimethoxy ammonium chloride, methacryloyloxyethyl trimethyl ammonium chloride, (meta)acrylamino propyl trimethyl ammonium chloride, or diallyl dimethyl ammonium chloride ; said amino-contained vinyl monomer is selected from one or more of the group consisting of dimethylamino ethyl (meta)acrylate, diethylamino ethyl (meta)acrylate or diisopropylamino ethyl (meta)acrylate.

Preferably, in the above mentioned nano core-shell silica micro-sphere, wherein, said silicon source material is selected from one or more of the group consisting of tetramethoxysilane, tetraethoxysilane, methyl trimethoxy silane, methyl triethoxysilane, vinyl trimethoxy silane, vinyl triethoxy silane, γ -mercaptopropyl trimethoxy silane, γ -aminopropyl triethoxy silane, γ -glycidoxy propyl trimethoxy silane or γ -(methacryloxy) propyl trimethoxy silane.

Preferably, in the above mentioned nano core-shell silica micro-sphere, wherein, the initiator is potassium persulfate or 2,2' -Azobis(2-methylpropionamidine) hydrochloride.

Preferably, in the above mentioned nano core-shell silica micro-sphere, wherein, in step (1), a mass ratio of the co-monomer to the styrene monomer is (0.5-4) : (10-20) .

Preferably, in the above mentioned nano core-shell silica micro-sphere, wherein, in step (1), a mass ratio of the co-monomer, the styrene monomer, the initiator and the water in the total system is 0.5-4% of the co-monomer, 10-20% of the styrene monomer , 0.1-1% of the initiator and 75-89.4% of the water , respectively.

Preferably, in the above mentioned nano core-shell silica micro-sphere,

wherein, in step (2), the amount of solvent is based on the standard of diluting the cationic polystyrene emulsion to a solid content of 1-20 mass%.

Preferably, in the above mentioned nano core-shell silica micro-sphere, wherein, in step (2), a mass ratio of solid content in the polystyrene emulsion to the added silicon source material is 10-30%.

Preferably, in the above mentioned nano core-shell silica micro-sphere, wherein, in step (2), the solvent is selected from one or more of the group consisting of water, methanol, ethanol, ethylene glycol, n-propyl alcohol, isopropyl alcohol, propylene glycol, glycerol, n-butyl alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol ether, propylene glycol butyl ether, tripropylene glycol monomethyl ether or tripropylene glycol monoether.

Preferably, in the above mentioned nano core-shell silica micro-sphere, wherein, the co-monomer is an amino-containing vinyl monomer, an acid is needed for protonation treatment to the vinyl monomer before step (1), the acid used is selected from an inorganic acids or an organic acids.

Preferably, in the above mentioned nano core-shell silica micro-sphere, wherein, said the inorganic acid is hydrochloric acid, sulfuric acid, nitric acid or phosphoric acid, and the organic acid is acetic acid, citric acid or oxalic acid; preferably, the required amount of inorganic acid based on calculation by monoacid is that the molar ratio of acid to the amino group contained in the amino-containing vinyl monomers is 50-100%.

Preferably, in the above mentioned nano core-shell silica micro-sphere, wherein in step (1), after adding styrene, stirring the obtained mixture at 150-500rpm, preferably 200-450rpm.

Preferably, in the above mentioned nano core-shell silica micro-sphere, wherein in step (1), adding the initiator at the speed of 0.1-2mL/min drop by drop, preferably at 0.5-1.5mL/min.

In addition, the present invention provides a composited coating solution

containing silica alumina sol doped by nano core-shell silica micro-sphere, characterized in that the coating solution is composited by any one of the above mentioned sol of the nano core-shell silica micro-sphere of claim 1 to 13 with a hydroxyl-containing silica alumina sol material.

5 Preferably, in the above mentioned composited coating solution, wherein, calculated by weight percentage, the volume ratio of the hydroxyl-containing silica alumina sol to nano core-shell silica micro-sphere sol is 1: (1-10), preferably 1: (4-10).

10 Preferably, in the above mentioned composited coating solution, wherein, the hydroxyl-containing silica alumina sol material is obtained by reaction of materials containing water, acid catalyst, solvent, aluminum salt and silicon source material, wherein, relative to 1 mL of silicon source material, the mass of aluminum salt is 0.025-0.1g, preferably 0.055-0.1g.

15 Preferably, in the above mentioned composited coating solution, wherein, relative to 1 mL of silicon source material, the content of solvent is 1-20mL, the content of water is 0.1-1mL, and the content of catalyst is 0.01-0.1mL.

20 Preferably, in the above mentioned composited coating solution, wherein, said catalyst is selected from the group consisting of one or more of hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, acetic acid, citric acid and oxalic acid.

25 Preferably, in the above mentioned nano core-shell silica micro-sphere or the composited coating solution, wherein said silicon source material added in the preparation of nano core-shell silica micro-sphere and hydroxyl-containing silica alumina sol is selected from one or more of tetramethoxysilane, tetraethoxysilane, methyl trimethoxy silane, methyl triethoxysilane, vinyl trimethoxy silane, vinyl triethoxy silane, gamma-mercaptopropyl trimethoxy silane, gamma-aminopropyl triethoxy silane, gamma-glycidoxy propyl trimethoxy silane or gamma -(methacryloyloxy) propyl trimethoxy silane .

The present invention also provides a preparation method of nano core-shell silica micro-sphere, which is characterized in that the nano core-shell silica micro-sphere is obtained by a preparation method comprising the following steps :

5 (1) preparation of polystyrene core by polymerization of emulsifier-free emulsion polymerization: putting an amino-containing or a quaternized co-monomer and water in a reaction vessel, adding styrene, then heating the mixture up to 50-85°C, preferably 70°C under the protection of nitrogen, dropwise adding an aqueous initiator solution to react, and whereby
10 obtaining a cationic polystyrene emulsion;

 (2) preparations of a silica coated polystyrene core-shell structured micro-sphere emulsion: mixing the cationic polystyrene emulsion used as a hard template with a solvent, then adding a silicon source material under conditions of stirring at 15-35°C, preferably at room temperature to react, and
15 obtaining the silica coated polystyrene core-shell structured micro-sphere emulsion.

 In addition, the present invention also provides a preparation method of the composited coating solution containing any one of the above-mentioned silica alumina sol doped by nano core-shell silica micro-sphere, wherein, the
20 composited coating solution containing silica alumina sol and nano core-shell silica micro-sphere is obtained by compositing any one of the above-mentioned sol of nano core-shell silica micro-sphere with hydroxyl-containing silica alumina sol materials.

 The present invention also provides an application of any one of the
25 above-mentioned sol of nano core-shell silica micro-sphere and any one of the above-mentioned composited coating solution containing silica alumina sol doped by nano core-shell silica micro-sphere in the preparation of anti-reflection film in the surface of photovoltaic glass, optical devices or solar device.

The present invention also provides a silica alumina sol, which is characterized in that the silica alumina sol is obtained by reaction of materials containing water, acid used as a catalyst, solvent, aluminum salt and silicon source material, wherein, relative to 1 mL of silicon source material, the mass of aluminum salt is 0.025-0.1g; preferably, relative to 1 mL of silicon source material, the content of solvent is 1-20mL, the content of water is 0.1-1mL, the content of catalyst is 0.01-0.1mL.

The present invention also provides an anti-reflection film, which is obtained by coating any one of the above-mentioned composited coating solution to a glass substrate, with anyone coating method of spraying, dipping, pulling, roller coating, spin coating, flow coating and brush coating , followed by drying and baking-curing at 80-250°C, and tempering at 500-700°C .

An ultra white glass anti-reflective coating solution is prepared in the invention through doping and compositing of the nano core-shell structured silica micro-sphere with silicon aluminum sol. The coating solution is plated on the surface of ultra white solar glass, and the organic nucleus in the nano core-shell silica micro-sphere of the film are burnt out to form nano silica hollow nanosphere after solidifying and tempering. In this method, holes are placed inside of particles instead of the network of silica dioxide, so as to ensure higher transmittance which can be over 94.5%, higher porosity (the porosity of the film can be up to 0.2-0.5 calculated according to the refractive index data of the membrane), higher mechanical strength and dense surface, further to achieve the goal of increasing the light transmittance and maintaining better dirt resistance performance, solving the contradictions among the increasing light transmittance, and maintaining good dirt resistance performance and high mechanical strength. Moreover, the anti-reflection film has high film hardness by firmly attaching to the glass substrate. Due to the dense surface which can prevent corrosion of vapor, it has good weatherability and high industrial application value.

EMBODIMENT

In recent years, in order to prepare anti-reflective coating solution for photovoltaic glass, the nano-SiO₂ hollow micro-sphere is often used, because it has good properties including large specific surface area, high internal porosity, good transparency, high thermal stability, non-toxic and so on. Nano-silica hollow micro-sphere is growing concerning as a novel functional material, and is widely used in a filling material, a catalytic material, a optoelectronic material, a medical sustained-release material, a coating material and other fields.

However, the method of the present invention and the prior art for preparing an increased permeability and anti-reflection film of hollow nano-silica micro-sphere has fundamentally differences in the coating process and the silicon source. In the present invention, the nano core-shell structured silica dispersion liquid is prepared using the cationic polystyrene emulsion as a template, then combined with the silica alumina sol to prepare anti-reflective coating solution, and an anti-reflection film is obtained by toughened treatment. The anti-reflection film with hollow structure is prepared by simple one-step process, and raw materials used in the present invention are easy to obtain.

Preferably, the present invention provided nano core-shell silica micro-sphere and preparation methods thereof, silica alumina sol and preparation methods thereof, and anti-reflective coating solution prepared by compositing the nano core-shell silica micro-sphere with silica alumina sol as described below.

1. A method for preparing nano core-shell silica micro-sphere, including the following steps:

(1) A polystyrene core is prepared by emulsifier-free emulsion polymerization. A certain amount of co-monomer and water are weighted and put in a 250mL volume of four-necked flask, styrene is added under

mechanical stirring and stirred for 30-50 minutes at a speed of 150-500rpm, preferably 200-450rpm, and 250rpm is the best. The mixture is heated up to 50-85 °C, preferably 70 °C under the protection of nitrogen gas, and an aqueous solution containing initiator is dropwise added at a speed of 0.1-2.0mL/min, preferably 0.5-1.5mL/min, 0.5mL/min is the best. A stable cationic polystyrene emulsion with different particle sizes is obtained after reacting for 20-28h, preferably 24h. Preferably, the average particle size of the polystyrene emulsion is 100-300nm, and 100-220nm is better, and the solid mass content is 10-25%.

Wherein, the water added to the four-necked flask can be purified water like deionized water, can also be water containing some organic solvent, such as ethanol, acetone and so on, the amount of the organic solvent can be about 10% by weight at most.

Wherein, the co-monomer can be quaternized vinyl monomer, such as acryloyloxyethyl trimethoxy ammonium chloride, methacryloyloxyethyl trimethyl ammonium chloride, (meta)acrylamido propyl trimethyl ammonium chloride, diallyl dimethyl ammonium chloride and so on; and can also be amino-containing vinyl monomer, such as dimethylamino ethyl (meta)acrylate, diethylamino ethyl (meta)acrylate, diisopropylamino ethyl (meta)acrylate and so on. If the amino-containing vinyl monomer is used, an acid will be needed for protonation treatment before polymerization, and the acid includes inorganic acid and organic acid. The inorganic acid can be hydrochloric acid, sulfuric acid, nitric acid or phosphoric acid, the organic acid can be acetic acid, citric acid or oxalic acid etc.. When the acid is monoacid, the molar ratio of acid to amino group contained in the amino-containing vinyl monomers is 50-100%. When the acid is diprotic acid, the amount of acid would be reduced by half correspondingly.

Wherein, the initiator is preferably KPS (potassium persulfate) or 2,2'-Azobis (2-methylpropionamidine)hydrochloride.

Wherein, the inventors found that temperature and mass ratio of the co-monomer to styrene are important factors to the particle size of cationic polystyrene emulsion prepared in the present invention, which will affect the final porosity of coating film for glass. Preferably, the mass ratio of the co-monomer to styrene is (0.5-4) :(10-20).

Wherein, in the preferably process of polymerization, the polymerization temperature is 50-85°C, preferably 70°C, the mass ratio of co-monomer, styrene monomer, initiator and water in the total system is 0.5-4% of the co-monomer, 10-20% of the styrene monomer, 0.1-1% of the initiator and 75-89.4% of water.

(2) A certain amount of the above-mentioned cationic polystyrene emulsion and solvent are mixed well, and the amount of the solvent is based on the aim to make the polystyrene cationic emulsion diluting to a solid content of preferably 5-15 mass% (to be diluted slightly or undiluted); then, a silicon source material is dropwise added while stirring at 15-35°C, preferably at room temperature, so that the mass ratio of the solid content in the polystyrene emulsion to the silicon source material is to be 10-30%, preferably 15-30%. Then a silica coated polystyrene nano core-shell structured micro-sphere emulsion is obtained after reacting for 3-5h. Wherein, after drying of the emulsion, the solid content of the nano core-shell silica micro-sphere is measured to be 3-30% by weight, preferably 10-25%.

Wherein, the silicon source material is preferably selected from one or more of tetramethoxysilane, tetraethoxysilane, methyl trimethoxy silane, methyl triethoxysilane, vinyl trimethoxy silane, vinyl triethoxy silane, γ -mercaptopropyl trimethoxy silane, γ -aminopropyl triethoxy silane, γ -glycidyl ether oxygen propyl trimethoxy silane or γ -(methacryloyloxy) propyl trimethoxy silane. The solvent is selected from one or more of water, methanol, ethanol, ethylene glycol, n-propyl alcohol, isopropyl alcohol, propylene glycol, glycerol, n-butyl alcohol, ethylene glycol monomethyl ether,

ethylene glycol monoethyl ether, dipropylene glycol methyl ether, propylene glycol dimethyl ether, tripropylene glycol monomethyl ether or tripropylene glycol monoether.

2. Preparation of silica alumina sol, including steps as follows:

5 (1) A certain volume of solvent is added to a three-necked flask, the deionized water and acid are uniformly mixed slowly added to the three-necked flask while stirring at 15-35°C, preferably at room temperature, and continued stirring for 20-50min, preferably 30min to obtain liquid A;

10 (2) A certain mass of aluminum salt and a certain volume of silicon source material are added to the above-mentioned liquid A respectively while stirring at 15-35°C, preferably at room temperature. The mixture is heated up to 40-80°C and continued stirring for 0.5-5h, then stopped stirring. Aging for 1-5d at 25-80°C, a silica alumina sol with a solid content of 2-25 mass% is obtained after cooling(the residual solid content after heating and drying at
15 150°C for 2h). In the processes of preparing silica alumina sol, the amount ratio of solvent, deionized water, acid used as a catalyst, aluminum salt and silicon source material by volume or weight are 1-20(mL): 0.1-1(mL): 0.01-0.1(mL) : 0.025-0.1(g): 1(mL), preferably 1-20(mL): 0.1-1(mL): 0.01-0.1(mL) : 0.055-0.1(g): 1(mL).

20 Wherein, in the present invention, the silicon source material is selected from one or more of tetramethoxysilane, tetraethoxysilane, methyl trimethoxy silane, methyl triethoxysilane, vinyl trimethoxy silane, vinyl triethoxy silane, γ -mercaptopropyl trimethoxy silane, γ -aminopropyl triethoxy silane, γ -glycidyl ether oxygen propyl trimethoxy silane or γ -(methacryloyloxy)
25 propyl trimethoxy silane. The silicon source material mentioned above can not only be used in the preparation of silica coated polystyrene core-shell structured micro-sphere emulsion, but also in the preparation of silica alumina sol. The acid is selected from one or more of hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, acetic acid, citric acid or oxalic acid. The

solvent is selected from one or more of methanol, ethanol, ethylene glycol, n-propyl alcohol, isopropyl alcohol, propylene glycol, glycerol, n-butyl alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monomethyl ether, di-propylene glycol methyl ether, propylene glycol dimethyl ether, tripropylene glycol monomethyl ether or tripropylene glycol monoether. The aluminum salt is selected from one or more of aluminum nitrate, aluminum chloride, aluminum phosphate, aluminum formate, aluminum acetate, aluminum propionate, dialkyl aluminum chloride, alkyl aluminum dichloride, trialkyl aluminum trichloride, aluminum isopropoxide or aluminum acetylacetonate.

3. Preparations of photovoltaic glass coating solution, including steps as follows:

A certain amount of the above-mentioned nano core-shell silica micro-sphere emulsion is added to a three-necked flask, and the silica alumina sol prepared above is added to the three-necked flask or to a three-necked flask containing the nano core-shell silica micro-sphere emulsion prepared in step 1 while stirring at 15-35°C, preferably at room temperature. The mixture is continued stirring for 0.5-4h, then stop stirring. An anti-reflection film coating solution containing nano core-shell structure nucleated by polystyrene and coated by silica (sometimes, PS @ SiO₂ is used to represent the structure) is obtained.

Wherein, the volume ratio of the above-mentioned hydroxyl-enriched silica sol to the nano core-shell silica micro-sphere sol emulsion is 1: (1-10), preferably 1: (4-10).

4. Preparation methods for solar photovoltaic battery package glass

Any coating method of spraying, dipping, pulling, roller coating, spin coating, flow coating and brush coating is used to overlay the anti-reflective coating solution containing PS@SiO₂ nano core-structure to a clean and dry solar photovoltaic battery package glass substrate, followed by baking and

curing at 80-250°C when the surface is dried, then tempering at 500-700°C for 3-5min, so that a finished product of the solar photovoltaic battery package glass is obtained.

Cationic polystyrene emulsion prepared by emulsifier-free emulsion polymerization in the present invention is different from methods of preparing silica hollow micro-sphere in prior art of Chinese Patent Application CN200710025530.1. It is dispersion polymerization not emulsifier-free emulsion polymerization used in patent application of CN200710025530.1. Ammonia water was used as a catalyst in the process of dispersion polymerization, which may cause the core-shell structure become not smooth nor compact. In addition, the method of the present invention is essentially making the negatively charged silica pre-polymer deposited on the surface of the cationic polystyrene template. The negatively charged silica pre-polymer can be quickly captured by the template because of the positively charged surface of the template particles, thereby depositing a layer of silicon dioxide on the surface of the template to form core-shell structured silica nano-particles. Moreover, when compositing with silica-alumina sol can further improve the weatherability of the film formed by silica coated polystyrene coating solution.

Comparing the methods for preparing core-shell silica micro-sphere in the present invention with the disclosed Chinese Patent Application of 201510312827.0 (Title of Invention: "Silica magnesium aluminum sol and core-shell silica spheres coating solution, preparations and applications thereof"), polystyrene used in Patent Application of 201510312827.0 is covered with amphoteric substance of PVP which interacting with silica particles to make the silica deposit on the surface of the polymer, realizing silica coated polystyrene. In that method, the interaction force between PVP and silica particles is weak, and ammonia water used as a catalyst also cause rapid hydrolysis of silicon source material condensation to form silica nano-

particles, causing the silicon dioxide layer is nano silica particles, thus resulting in the silicon layer is rough, not smooth nor compact, or even incomplete, the hollow structure can easily be broken after calcination, finally resulting in poor dirt resistance and poor weatherability. In order to overcome these shortcomings, after tireless intensive studies, inventors of this invention found that using cationic polystyrene as a template to prepare nano core-shell silica micro-sphere, the method has two advantages: (1) the cationic polystyrene emulsion itself has weak acid property which can catalyze the gentle hydrolysis and condensation of the silicon source material to synthesize chainlike or network silica pre-polymer instead of silica particles, so that a smooth and dense silicon layer can be formed on the surface of polystyrene, and the hollow structure is stable after calcination; (2) whether the hydrolyzate of silicon material can effectively self-assemble coating on the surface of template depends on the electrostatic attraction between the hydrolyzate and the template. Only if the electrostatic attraction is strong enough to effectively realize the hydrolyzate of silicon source material self-assembly on the template surface, and effectively reduce or even prevent the hydrolyzate from self-assembling into nuclei. Since the silicon source hydrolyzate is negatively charged, so using cationic template is beneficial to achieve silica coated pre-polymer.

That is to say, advantages of the present invention include place the holes inside the particles not in the network of silica dioxide, which not only ensure high porosity and mechanical strength of the film, but also form a dense surface of the film, achieving the goals of increasing transmittance and maintaining better dirt resistance performance, solving contradictions among increasing transmittance, maintaining good dirt resistance and high mechanical strength. In addition, the anti-reflection film can be firmly attached to the glass substrate, have high hardness, and have good barrier effect on vapor corrosion because the dense surface, so that the film has better

weatherability, and has industrial application value.

The following specific examples illustrate the preparation methods for nano core-shell silica and anti-reflection film composited of silica alumina sol and the nano core-shell silica.

5 **Example 1**

1. A preparation of nano core-shell silica micro-sphere sol

(1) The polystyrene core being prepared by emulsifier-free emulsion polymerization. Acryloyloxyethyl trimethoxy ammonium chloride used as co-monomer was weighted and put in a 250mL volume of four-necked flask together with 100mL of water. Styrene was added under mechanical stirring and stirred for 30 minutes at a speed of 150rpm. The mixture was heated up to 50 °C under the protection of nitrogen gas, and an initiator of KPS (potassium persulfate) aqueous solution was added dropwise at a speed of 2.0mL/min. A stable cationic polystyrene emulsion having an average particle size of 270 nm was obtained after reacting for 20h, with a solid mass content of 10%.

Wherein, the mass percentage of the said co-monomer, styrene monomer, initiator and water in the entire system was 0.5% of the co-monomer, 10% of the styrene, 0.1% of the initiator, and 89.4% of water, respectively.

Wherein, the particle size of polystyrene particles in the above-mentioned polystyrene emulsion was tested by Zeta ZS90 laser particle size analyzer manufactured by the Malvern Company, and the same as the method was used for determining particle size in the following examples.

(2) The above-mentioned cationic polystyrene emulsion and a solvent of methanol were mixed well and the polystyrene emulsion was diluted to a solid content of 5 mass%. Then a silicon source material of tetramethoxysilane was added dropwise while stirring at 15°C, making the mass ratio of solid content in the polystyrene emulsion to the mass of silicon source material to be 10%. A silica coated polystyrene nano core-shell

structured micro-sphere emulsion was obtained after reacting for 3h.

After heating and drying for 2 hours at 150°C, the residual solid content of the nano core-shell silica microsphere was measured to be about 16% by weight.

5 2. A preparation method for hydroxyl-enriched silica sol

(1) A solvent of 100mL of methanol was added to a three-necked flask, deionized water and a catalyst of nitric acid were uniformly mixed and were slowly added to the three-necked flask while stirring at 15°C, and continued stirring for 30min to obtain liquid A;

10 (2) An aluminum salt of aluminum nitrate and a silicon source material of tetraethoxysilane were added to the liquid A respectively under conditions of stirring at 15°C. The solution was heated up to 40°C and continued stirring for 0.5h, then stopped stirring. Aging for one day at 25°C, a hydroxyl-enriched silica alumina sol with a determined solid content of 15% by weight
15 was obtained after cooling down (the residual solid content after heating and drying for 2h at 150°C).

In the above-mentioned process of preparing of hydroxyl-enriched silica sol, the dosage proportion of the solvent, the deionized water, the acid, the aluminum salt, and the alkoxy silane was 1mL: 0.1mL: 0.01mL: 0.025g: 1mL.

20 3. A preparations of photovoltaic glass coating solution

The above-mentioned 100mL of hydroxyl-enriched silica alumina sol was added to a three-necked flask, nano core-shell silica micro-sphere sol prepared in step 1 was added to the three-necked flask under conditions of stirring at 15°C, and continued stirring for 0.5h, then stopped stirring. An
25 anti-reflective film coating solution 1# containing PS@ SiO₂ nano core-shell structure was obtained.

Wherein, the volume ratio of the above-mentioned hydroxyl-enriched silica sol to the nano core-shell silica micro-sphere sol was 1: 1.

4. Performance evaluations of the coating solution

(1) Determining light transmittance of the coating film

The coating solution # 1 was rolled onto a ultra-white solar glass (3.2mm thick patterned glass) with a light transmittance of 92.01%. A transparent coating with film thickness of 150nm was obtained after baking-curing at 200°C when the surface became dry, and toughening treatment for 4min at 650°C with the glass . The light transmittance was 94.63% measured by air floating bench spectral transmittance measurement system AOPTEK GST-3 of Beijing Aobo Tai Technology Co., Ltd. by referencing standard ISO9050.

The change result of visible light transmittance before and after coating is increased by 2.62%.

Specifically, the said "light transmittance" and "transmittance" in all examples were intended to mean the average transmittance T_E measured within the range of 380nm to 1100nm, and the calculation formula is shown as follows:

$$T_E = \frac{\sum_{\lambda=380}^{\lambda=1100} \tau(\lambda) S_i \Delta \lambda}{\sum_{\lambda=380}^{\lambda=1100} S_i \Delta \lambda}$$

In the formula,

S_λ : Relative spectral distribution of AM1.5 solar light;

$\Delta \lambda$: wavelength interval , nm;

$\tau(\lambda)$: actual measured solar light spectrum transmittance of samples

(2) Determining porosity of the coating film

The refractive index of glass coating was 1.38 measured by film thickness meter of Filmetrics F20-UV, calculated by the formula of $n_p^2 = n_1^2 p + n_2^2 (1-p)$ (wherein, n_p refers to refractive index of film, n_1 and n_2 are refractive indexes of porous material (air) and dense material(pure SiO₂ quartz glass) respectively, n_1 is 1, n_2 is 1.5; p refers to porosity of film) to get the porosity. Film thickness meter of Filmetrics F20-UV can measure

thickness and refractive index based on the principles of optical interference. The porosity was calculated to be about 0.27 according to the film refractive index data measured.

(3) Determining dirt resistance performance of film

5 Rapid test was carried out using Scotch 610-1PK tape manufactured by the 3M Company. And the method included adhering the 3M tape to the surface of the coating film, squeezing hard, and tearing the tape at a degree of 90° vertical to the film surface. According to the shallow or heavy marks remained on film surface, 1-5 grade was rated respectively, wherein grade 1
10 means no marks, grade 2 means slight marks, grade 3 means obvious marks, grade 4 means residual white marks, grade 5 means degumming. The higher the grade is, it means the worse the dirt resistance performance is, and grade below 3 is qualified.

The test result was grade 3, namely qualified.

15 (4) Determining the pencil hardness performance of the film

The pencil hardness of the coating film was determined according to the Chinese national standard GB/T6739, wherein the load was 750g, and the result was 3H hardness, namely $\geq H$, so the film reached the requirement of national standard.

20 (5) After the salt fog resistance test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules ”), constant temperature and humidity test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules ”), outdoor exposure test(referencing standard IEC61215), UV test(referencing standard JC/T2170-2013 “Anti-Reflective
25 film glass for photovoltaic modules”), friction test(referencing standard EN1096-2), acid resistance test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules”), and wet freezing test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules”) conducted on the coating film, the changes of light

transmittance were determined according to the method mentioned above. The measured conditions, methods and results were summarized in table 1-2, and the test equipments and models thereof used in each performance index were shown in table 1-1:

5 Table 1-1 Test Equipments foreach performance of the coating film

Serial Number	Performance Index	Device Model
1	Salt fog resistance test	SO2/YWXQ-750B
2	Constant temperature and humidity test	SEWTH-Z-100UHS
3	Outdoor exposure test	
4	UV test	UV-3422
5	Friction test	903/2
6	Acid resistance test	
7	Wet freezing test	WK10'/60-175
8	Transmittance	BTG-5

Table 1-2 Test results for each performance of the coating film

Test Project	Criterion for judgement		Test conditions	Test results	Single evaluation
	Test conditions	Changes of transmittance			
salt fog resistance test	Conditions:(50±5)g/L NaCl, time: 96h	$\Delta T \leq 0.8\%$	96h	$\Delta T = -0.03\%$ qualified	P
constant temperature and humidity test	Temperature: 85°C, humidity: 85%RH,	$\Delta T \leq 0.8\%$	1000h	$\Delta T = 0.32\%$ qualified	P

	time: 1000h				
outdoor exposure test	Total irradiation: 60kwh/m ² , time: 600h	$\Delta T \leq 0.8\%$	600h	$\Delta T = 0.13\%$ qualified	P
UV test	Total irradiation: 15kwh/m ² , time: 720h	$\Delta T \leq 0.8\%$	720h	$\Delta T = 0.07\%$ qualified	P
friction test	500 cycles	$\Delta T \leq 0.8\%$	500 cycles	$\Delta T = 0.02\%$ qualified	P
acid resistance test	Concentration: 1 mol/L HCl , time: 24h	$\Delta T \leq 0.8\%$	24h	$\Delta T = 0.16\%$ qualified	P
wet freezing test	Temperature: - 40 °C / +85 °C , 85%RH, 10 cycles	$\Delta T \leq 0.8\%$	10 cycles	$\Delta T = 0.64\%$ qualified	P

The above test results showed that after coating the coating solution prepared by methods of the present invention onto a glass, the light transmittance of the film was improved, dirt resistance performance was good, and the hardness is high, and acid resistance, friction resistance, weatherability and other performances were excellent.

Example 2

1. A Preparation of nano core-shell silica micro-sphere sol

(1) The polystyrene core being prepared by emulsifier-free emulsion polymerization. Dimethylamino ethyl methacrylate used as co-monomer was weighted and put in a 250mL volume of four-necked flask together with 100mL of water, and an equimolar acetic acid was added in the same mole as

thedimethylamino ethyl methacrylate. Styrene was added under mechanical stirring and stirred for 30 minutes at a speed of 200rpm. The mixture was heated up to 85°C under the protection of nitrogen gas, and an initiator of KPS aqueous solution was added dropwise at a speed of 1.5mL/min. A stable
5 cationic polystyrene emulsion having an average particle size of 220 nm was obtained after reacting for 28h, with a solid mass content of 23.5%.

Wherein, the mass percentage of the said co-monomer, styrene monomer, initiator and water in the entire system was 4% of the copolymer monomer, 20% of the styrene, 1% of the initiator, and 75% of water, respectively.

10 (2) The above-mentioned cationic polystyrene emulsion and a solvent of ethanol were mixed well and the polystyrene emulsion was diluted to a solid content of 8% by weight. Then a silicon source material of methyl trimethoxy silane was added dropwise while stirring at 35°C, making the mass ratio of solid content in the polystyrene emulsion to the mass of silicon source
15 material to be 30%. A silica coated polystyrene nano core-shell structured micro-sphere emulsion was obtained after reacting for 5h.

After heating and drying for 2 hours at 150°C, the residual solid content of the nano core-shell silica microsphere was measured to be about 16% by weight.

20 2. A Preparation method for hydroxyl-enriched silica sol

(1) A solvent of 100mL of ethylene glycol monoethyl ether was added to a three-necked flask, the deionized water and a catalyst of sulphuric acid were uniformly mixed and were slowly added to the three-necked flask while stirring at 35°C, and continued stirring for 20min to obtain liquid A;

25 (2) An aluminum salt of aluminum nitrate and an alkoxy silane of methyl trimethoxy silane were added to the above-mentioned liquid A respectively under conditions of stirring at 35°C. The solution was heated up to 80°C and continued stirring for 5h, then stopped stirring. Aging for three days at 75°C, a hydroxyl-enriched silica alumina sol with a determined solid

content of 2.5% by weight was obtained after cooling down (the residual solids content after heating and drying for 2h at 150°C).

In the above-mentioned process of preparing hydroxyl-enriched silica sol, the dosage proportion of the solvent, the deionized water, the acid, the aluminum salt and the alkoxysilane was 20mL: 1mL: 0.08mL: 0.085g: 1mL.

3. A preparation of photovoltaic glass coating solution

The above-mentioned 100mL of hydroxyl-enriched silica alumina sol was added to a three-necked flask, nano core-shell silica micro-sphere sol prepared in step 1 was added to the three-necked flask under conditions of stirring at 35°C, and continued stirring for 3h, then stopped stirring. An anti-reflective film coating solution 2# containing PS @ SiO₂ nano core-shell structure was obtained.

Wherein, the volume ratio of the above-mentioned hydroxyl-enriched silica sol to the nano core-shell silica micro-sphere sol was 1: 8.

4. Performance evaluation of the coating solution

(1) Determining light transmittance of the coating film

The coating solution 2# was rolled onto a ultra-white solar glass (3.2mm thick patterned glass) with a light transmittance of 92.01%. A transparent coating with film thickness of 150nm was obtained after baking-curing at 200°C when the surface became dry, and toughening treatment for 4min at 650°C with the glass. The light transmittance was 94.79% measured by air floating bench spectral transmittance measurement system AOPTeK GST-3 of Beijing Aobo Tai Technology Co., Ltd. by referencing standard ISO9050.

The change result of visible light transmittance before and after coating is increased by 2.78%.

(2) Determining porosity of the coating film

The refractive index of glass coating was 1.35 measured by film thickness meter of Filmetrics F20-UV, calculated by the formula of $n_p^2 = n_1^2 p + n_2^2 (1 - p)$ (the same as the example 1) to get the porosity. Film

thickness meter of Filmetrics F20-UV can measure thickness and refractive index based on the principles of optical interference. The porosity was calculated to be about 0.34 according to the film refractive index data measured.

5 (3) Determining dirt resistance performance of the film

Rapid test was carried out using Scotch 610-1PK tape manufactured by 3M Company. And the method included adhering the 3M tape to the surface of the coating film, squeezing hard, and tearing the tape at a degree of 90° vertical to the film surface. According to the shallow or heavy marks
10 remained on film surface, 1-5 grade was rated respectively, wherein grade 1 means no marks, grade 2 means slight marks, grade 3 means obvious marks, grade 4 means residual white marks, grade 5 means degumming. The higher the grade is, it means the worse the dirt resistance performance is, and grade below 3 is qualified.

15 The test result was grade 3, namely qualified.

(4) Determining the pencil hardness performance of the film

The pencil hardness of the coating film was determined according to the Chinese national standard GB/T6739, wherein the load was 750g, and the result was 2H hardness, namely $\geq H$, so the film reached the requirement of
20 national standard.

(5) After the salt fog resistance test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules ”), constant temperature and humidity test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules ”), outdoor exposure test(referencing standard
25 IEC61215), UV test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules”), friction test(referencing standard EN1096-2), acid resistance test (referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules”), and wet freezing test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for

photovoltaic modules”) conducted on the coating film, the changes of light transmittance were determined according to the above mentioned method. The measured conditions, methods and results were summarized in table 2(The test equipments used in this example were the same as example 1, and the text equipments used in all the following examples were the same as the example 1).

Table 2 Test results for each performance of the coating film

Test Project	Criterion for judgement		Test conditions	Test results	Single evaluation
	Test conditions	Changes of transmittance			
salt fog resistance test	conditions: (50±5) g/L NaCl , time:96h	$\Delta T \leq 0.8\%$	96h	$\Delta T = 0.67\%$ qualified	P
constant temperature and humidity test	Temperature: 85℃, humidity: 85%RH, time: 1000h	$\Delta T \leq 0.8\%$	1000h	$\Delta T = 0.13\%$ qualified	P
outdoor exposure test	Total irradiation: 60kwh/m ² , time: 600h	$\Delta T \leq 0.8\%$	600h	$\Delta T = 0.24\%$ qualified	P
UV test	Total irradiation: 15kwh/m ² , time:720h	$\Delta T \leq 0.8\%$	720h	$\Delta T = 0.07\%$ qualified	P
friction test	500 cycles	$\Delta T \leq 0.8\%$	500 cycles	$\Delta T = 0.31\%$ qualified	P
acid	Concentration: 1mol/L	$\Delta T \leq 0.8\%$	24h	$\Delta T = 0.11\%$	P

resistance test	HCl , time:24h			qualified	
wet freezing test	Temperature: -40℃ /+85℃, 85%RH, 10 cycles	$\Delta T \leq 0.8\%$	10 cycles	$\Delta T = 0.09\%$ qualified	P

The above test results showed that after coating the coating solution prepared by methods of the present invention onto a glass, the light transmittance of the film was improved, dirt resistance performance was good, and the hardness is high, and acid resistance, friction resistance, weatherability and other performance were excellent.

Example 3

1. A preparation of nano core-shell silica micro-sphere sol

(1) The polystyrene core being prepared by emulsifier-free emulsion polymerization. Methacryloyloxyethyl trimethyl ammonium chloride used as co-monomer was weighted and put in a 250mL volume of four-necked flask together with 100mL of water. Styrene was added under mechanical stirring and stirred for 50 minutes at a speed of 250rpm. The mixture was heated up to 70℃ under the protection of nitrogen gas, and an initiator of 2,2'-Azobis(2-methylpropionamidine)hydrochloride aqueous solution was added dropwise at a speed of 0.5mL/min. A stable cationic polystyrene emulsion having an average particle size of 150 nm was obtained after reacting for 24h, with a solid mass content of 17%.

Wherein, the mass percentage of the said co-monomer, styrene monomer, initiator and water in the entire system was 2.5% of co-monomer, 15% of the styrene, 0.6% of the initiator, and 81.9% of water, respectively.

(2) The above-mentioned cationic polystyrene emulsion and a solvent of isopropyl alcohol were mixed well and the polystyrene emulsion was diluted to a solid content of 12% by weight. Then a silicon source material of

tetraethoxysilane was added dropwise while stirring at 25°C, making the mass ratio of solid content in the polystyrene emulsion to the mass of the silicon source material to be 15%. A silica coated polystyrene nano core-shell structured micro-sphere emulsion was obtained after reacting for 3h.

5 After heating and drying for 2 hours at 150°C, the residual solid content of the nano core-shell silica microsphere was measured to be about 20% by weight.

2. A preparation method for hydroxyl-enriched silica sol

10 (1) A solvent of 100mL of isopropyl alcohol was added to a three-necked flask, deionized water and a catalyst of hydrochloric acid were uniformly mixed and were slowly added to the three-necked flask while stirring at 35°C, and continued stirring for 30min to obtain liquid A.

15 (2) An aluminum salt of aluminum isopropoxide and an alkoxysilane of tetraethoxysilane were added to the above-mentioned liquid A respectively under conditions of stirring at 35°C. The solution was heated up to 50°C and continued stirring for 3h, then stopped stirring. Aging for three days at 80°C, a hydroxyl-enriched silica alumina sol with a determined solid content of 4% by weight was obtained after cooling down (the residual solid content after heating and drying for 2h at 150°C for 2h).

20 In the above-mentioned process of preparing hydroxyl-enriched silica sol, the dosage proportion of the solvent, the deionized water, the acid, the aluminum salt and the alkoxysilane was 10mL: 0.5mL: 0.05mL: 0.075g: 1mL.

3. A preparation of photovoltaic glass coating solution

25 The above-mentioned 100mL of hydroxyl-enriched silica alumina sol was added to a three-necked flask, nano core-shell silica micro-sphere sol prepared in step 1 was slowly added to the three-necked flask under conditions of stirring at 30°C, and continued stirring for 1h, then stopped stirring. An anti-reflective film coating solution 3# containing PS @ SiO₂ nano core-shell structure was obtained.

Wherein, the volume ratio of the above-mentioned hydroxyl-enriched silica alumina sol to the nano core-shell silica micro-sphere sol was 1: 4.

4. Performance evaluations of the coating solution

(1) Determining light transmittance of the coating film

5 The coating solution 3# was rolled onto a ultra-white solar glass (3.2mm thick patterned glass) with a light transmittance of 92.01%. A transparent coating with film thickness of 150nm was obtained after baking-curing at 200°C when the surface became dry, and toughening treatment for 4min at 650°C with the glass. The light transmittance was 95.21% measured by air floating
10 bench spectral transmittance measurement system AOPTEK GST-3 of Beijing Aobo Tai Technology Co., Ltd. by referencing standard ISO9050.

The change result of visible light transmittance before and after coating is increased by 3.2%.

(2) Determining porosity of the coating film

15 The refractive index of glass coating was 1.29 measured by film thickness meter of Filmetrics F20-UV, calculated by the formula of $n_p^2 = n_1^2 p + n_2^2 (1 - p)$ (the same as the example 1) to get the porosity. Film thickness meter of Filmetrics F20-UV can measure thickness and refractive index based on the principles of optical interference. The porosity was
20 calculated to be about 0.47 according to the film refractive index data measured.

(3) Determining dirt resistance performance of the film

Rapid test was carried out using Scotch 610-1PK tape of 3M Company. And the method included adhering the 3M tape to the surface of the coating
25 film, squeezing hard, and tearing the tape at a degree of 90° vertical to the film surface. According to the shallow or heavy marks remained on film surface, 1-5 grade was rated respectively, wherein grade 1 means no marks, grade 2 means slight marks, grade 3 means obvious marks, grade 4 means residual white marks, grade 5 means degumming. The higher the grade is, it

means the worse the dirt resistance performance is, and grade below 3 is qualified.

The test result was grade 1, namely qualified.

(4) Determining the pencil hardness performance of the film

5 The pencil hardness of the coating film was determined according to the Chinese national standard GB/T6739, wherein the load was 750g, and the result was 2H hardness, namely $\geq H$, so the film reached the requirement of national standard.

10 (5) After the salt fog resistance test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules ”), constant temperature and humidity test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules ”), outdoor exposure test (referencing standard IEC61215), UV test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules”), friction test(referencing standard EN1096-2), acid resistance test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules”),and wet freezing test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules”) conducted on the coating film, the changes of light transmittance were determined according to the above mentioned method .

20 The measured conditions, methods and results were summarized in table 3(The test equipments used in this example were the same as example 1, and the test equipments used in all the following examples were the same as the example 1).

Table 3 Test results for each performance of the coating film

Test Project	Criterion for judgement		Test conditions	Test results	Single evaluation
	Test conditions	Changes of transmittance			

salt fog resistance test	conditions: (50±5) g/L NaCl , time:96h	$\Delta T \leq 0.8\%$	96h	$\Delta T = -0.13\%$ qualified	P
constant temperature and humidity test	Temperature: 85°C, humidity: 85%RH, time: 1000h	$\Delta T \leq 0.8\%$	1000h	$\Delta T = 0.18\%$ qualified	P
outdoor exposure test	Total irradiation: 60kwh/m ² , time: 600h	$\Delta T \leq 0.8\%$	600h	$\Delta T = -0.21\%$ qualified	P
UV test	Total irradiation: 15kwh/m ² , time:720h	$\Delta T \leq 0.8\%$	720h	$\Delta T = 0.03\%$ qualified	P
friction test	500 cycles	$\Delta T \leq 0.8\%$	500 cycles	$\Delta T = -0.15\%$ qualified	P
acid resistance test	Concentration:1mol/L HCl , time:24h	$\Delta T \leq 0.8\%$	24h	$\Delta T = 0.08\%$ qualified	P
wet freezing test	Temperature: -40°C /+85°C, 85%RH, 10 cycles	$\Delta T \leq 0.8\%$	10 cycles	$\Delta T = -0.11\%$ qualified	P

The above test results showed that after coating the coating solution prepared by methods of the present invention onto a glass, the light transmittance of the film was improved, dirt resistance performance was good, and the hardness is high , and acid resistance, friction resistance, weatherability and other performances were excellent.

Example 4

1. A preparation of nano core-shell silica micro-sphere sol

(1) The polystyrene core being prepared by emulsifier-free emulsion polymerization. Methacryloyloxyethyl trimethyl ammonium chloride used as
5 co-monomer was weighted and put in a 250mL volume of four-necked flask together with 100mL of water. Styrene was added under mechanical stirring and stirred for 30 minutes at a speed of 300rpm. The mixture was heated up to 65°C under the protection of nitrogen gas, and an initiator of KPS aqueous solution was added drop by drop at a speed of 1mL/min. A stable cationic
10 polystyrene emulsion having an average particle size of 178 nm was obtained after reacting for 20h, with a solid mass content of 15%.

Wherein, the mass percentage of the said co-monomer, styrene monomer, initiator and water in the entire system was 1.5% of the co-monomer, 14% of the styrene, 0.6% of the initiator, and 83.9% of the water, respectively.

15 (2) A silicon source material of tetramethoxysilane was added dropwise into the above-mentioned cationic polystyrene emulsion while stirring at room temperature, making the mass ratio of solid content in the polystyrene emulsion to the mass of the silicon source material to be 20%. A silica coated polystyrene nano core-shell structured micro-sphere emulsion was obtained
20 after reacting for 4h.

After heating and drying for 2 hours at 150°C, the residual solid content of the nano core-shell silica microsphere was measured to be about 25% by weight.

2. A preparation method for hydroxyl-enriched silica sol

25 (1) A solvent of 100mL of ethylene glycol monoethyl ether was added to a three-necked flask, deionized water and a catalyst of citric acid were uniformly mixed and were slowly added to the three-necked flask while stirring at room temperature, and continued stirring for 30min to obtain liquid A;

(2) An aluminum of aluminum propionate and a silicon source material of methyl trimethoxy silane were added to the above-mentioned liquid A respectively under conditions of stirring at room temperature. The solution was heated up to 80°C and continued stirring for 5h, then stopped stirring. Aging for three day at 50°C, a hydroxyl-enriched silica alumina sol with a solid content of 3% by weight was obtained after cooling down (the residual solid content after heating and drying at 150°C for 2h).

In the above-mentioned process of preparing hydroxyl-enriched silica sol, the dosage proportion of the solvent, the deionized water, the acid, the aluminum salt and the alkoxysilane was 15mL: 1mL: 0.07mL: 0.055g: 1mL.

3. A preparation of photovoltaic glass coating solution

The above-mentioned 100mL of hydroxyl-enriched silica alumina sol was added to a three-necked flask, nano core-shell silica micro-sphere sol prepared in step 1 was slowly added to the three-necked flask while stirring at room temperature, and continued stirring for 2h, then stopped stirring. An anti-reflective film coating solution 4# which containing PS @ SiO₂ nano core-shell structure was obtained.

Wherein, the volume ratio of the above-mentioned hydroxyl-enriched silica sol to the nano core-shell silica micro-sphere sol was 1: 8.

4. Performance evaluations of the coating solution

(1) Determining light transmittance of the coating film

The coating solution 4# was rolled onto a ultra-white solar glass (3.2mm thick patterned glass) with a light transmittance of 92.01%. A transparent coating with film thickness of 150nm was obtained after baking-curing at 200°C when the surface became dry, and toughening treatment for 4min at 650°C with the glass. The light transmittance was 95.16% measured by air floating bench spectral transmittance measurement system AOPTEK GST-3 of Beijing Aobo Tai Technology Co., Ltd. by referencing standard ISO9050.

The change result of visible light transmittance before and after coating

is increased by 3.15%.

(2) Determining porosity of the coating film

The refractive index of glass coating was 1.31 measured by film thickness meter of Filmetrics F20-UV, calculated by the formula of $n_p^2 = n_1^2 p + n_2^2 (1 - p)$ (the same as the example 1) to get the porosity. Film thickness meter of Filmetrics F20-UV can measure thickness and refractive index based on the principles of optical interference. The porosity was calculated to be about 0.42 according to the film refractive index data measured.

10 (3) Determining dirt resistance performance of the film

Rapid test was carried out using Scotch 610-1PK tape of the 3M company. And the method included adhering the 3M tape to the surface of the coating film, squeezing hard, and tearing the tape at a degree of 90° vertical to the film surface. According to the shallow or heavy marks remained on film surface, 1-5 grade was rated respectively, wherein grade 1 means no marks, grade 2 means slight marks, grade 3 means obvious marks, grade 4 means residual white marks, grade 5 means degumming. The higher the grade is, it means the worse the dirt resistance performance is, and grade below 3 is qualified.

20 The test result was grade 1, namely qualified.

(4) Determining the pencil hardness performance of the film

The pencil hardness of the coating film was determined according to the Chinese national standard GB/T6739, wherein the load was 750g, and the result was 3H hardness, namely $\geq H$, so the film reached the requirement of national standard.

(5) After the salt fog resistance test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules ”), constant temperature and humidity test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules ”), outdoor exposure test(referencing standard

IEC61215), UV test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules”), friction test(referencing standard EN1096-2), acid resistance test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules”), and wet freezing test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules”) conducted on the coating film, the changes of light transmittance were determined according to the above mentioned method. The measured conditions, methods and results were summarized in table 4(The test equipments used in this example were the same as example 1, and the test equipments used in all the following examples were the same as the example 1).

Table 4 Test results for each performance of the coating film

Test Project	Criterion for judgement		Test conditions	Test results	Single evaluation
	Test conditions	Changes of transmittance			
salt fog resistance test	Conditions: (50±5) g/L NaCl, time: 96h	$\Delta T \leq 0.8\%$	96h	$\Delta T = -0.17\%$ qualified	P
constant temperature and humidity test	Temperature: 85℃, humidity: 85%RH, time: 1000h	$\Delta T \leq 0.8\%$	1000h	$\Delta T = -0.33\%$ qualified	P
outdoor exposure test	Total irradiation: 60kwh/m ² , time: 600h	$\Delta T \leq 0.8\%$	600h	$\Delta T = -0.29\%$ qualified	P
UV test	Total irradiation: 15kwh/m ² , time:720h	$\Delta T \leq 0.8\%$	720h	$\Delta T = 0.06\%$ qualified	P

friction test	500 cycles	$\Delta T \leq 0.8\%$	500 cycles	$\Delta T = -0.23\%$ qualified	P
acid resistance test	Concentration: 1mo l/L HCl , time: 24h	$\Delta T \leq 0.8\%$	24h	$\Delta T = 0.05\%$ qualified	P
wet freezing test	Temperature: -40°C / $+85^{\circ}\text{C}$, 85%RH, 10 cycles	$\Delta T \leq 0.8\%$	10 cycles	$\Delta T = -0.13\%$ qualified	P

The above test results showed that after coating the coating solution prepared by methods of the present invention onto a glass, the light transmittance of the film was improved, dirt resistance performance was good, and the hardness is high, and acid resistance, friction resistance, weatherability and other performances were excellent.

Example 5

1. A preparation of nano core-shell silica micro-sphere sol

(1) The polystyrene core being prepared by emulsifier-free emulsion polymerization. Diallyl dimethyl ammonium chloride used as co-monomer was weighted and put in a 250mL volume of four-necked flask together with 100mL of water. Styrene was added under mechanical stirring and stirred for 30 minutes at a speed of 450rpm. The mixture was heated up to 85°C under the protection of nitrogen gas, and an initiator of KPS (potassium persulfate) aqueous solution was added drop by drop at a speed of 0.5mL/min. A stable cationic polystyrene emulsion having an average particle size of 100 nm was obtained after reacting for 28h, with a solid mass content of 24%.

Wherein, the mass percentage of the said co-monomer, styrene monomer, initiator and water in the entire system was 4% of co-monomer, 20% of the styrene, 0.7% of the initiator, and 75.3% of water, respectively.

(2) The above-mentioned cationic polystyrene emulsion and a solvent of

propylene glycol monomethyl ether were mixed well and the polystyrene emulsion was diluted to a solid content of 5% by weight. Then a silicon source material of methyl triethoxysilane was added dropwise while stirring at 35°C, making the mass ratio of solid content in the polystyrene emulsion to the mass of the silicon source material to be 20%. A silica coated polystyrene nano core-shell structured micro-sphere emulsion was obtained after reacting for 3h.

After heating and drying for 2 hours at 150°C, the residual solid content of the nano core-shell silica micro-sphere was measured to be about 10% by weight.

2. A preparation method for hydroxyl-enriched silica sol

(1) A solvent of 100mL of ethylene glycol monoethyl ether was added to a three-necked flask, deionized water and a catalyst of oxalic acid were uniformly mixed and were slowly added to the three-necked flask while stirring at 20°C, and continued stirring for 50min to obtain liquid A;

(2) An aluminum salt of alkyl aluminum dichloride and an alkoxysilane of methyl trimethoxy silane were added to the above-mentioned liquid A respectively under conditions of stirring at 20°C. The solution was heated up to 80°C and continued stirring for 1h, then stopped stirring. Aging for five days at 50°C, a hydroxyl-enriched silica alumina sol with a determined solid content of 5.5% by weight was obtained after cooling down (the residual solid content after heating and drying at 150°C for 2h).

In the above-mentioned process of preparing hydroxyl-enriched silica sol, the dosage proportion of the solvent, the deionized water, the acid, the aluminum salt and the alkoxysilane was 8mL: 1mL: 0.03mL: 0.100g: 1mL.

3. A preparation of photovoltaic glass coating solution

The above-mentioned 100mL of hydroxyl-riched silica alumina sol was added to a three-necked flask, nano core-shell silica micro-sphere sol prepared in step 1 was slowly added to the three-necked flask while stirring at

20°C, and continued stirring for 4h, then stopped stirring. An anti-reflective film coating solution 5# containing PS @ SiO₂ nano core-shell structure was obtained.

Wherein, the volume ratio of the above-mentioned hydroxyl-enriched silica sol to the nano core-shell silica micro-sphere sol was 1: 10.

4. Performance evaluations of the coating solution

(1) Determining light transmittance of the coating film

The coating solution 5# was rolled onto a ultra-white solar glass (3.2mm thick patterned glass) with a light transmittance of 92.01%. A transparent coating with film thickness of 150nm was obtained after baking-curing at 200°C when the surface became dry, and toughening treatment for 4min at 650°C with the glass. The light transmittance was 94.93% measured by air floating bench spectral transmittance measurement system AOPTEK GST-3 of Beijing Aobo Tai Technology Co., Ltd. by referencing standard ISO9050.

The change result of visible light transmittance before and after coating is increased by 2.92%.

(2) Determining porosity of the coating film

The refractive index of glass coating was 1.33 measured by film thickness meter of Filmetrics F20-UV, calculated by the formula of $n_p^2 = n_1^2 p + n_2^2 (1 - p)$ (the same as the example 1) to get the porosity. Film thickness meter of Filmetrics F20-UV can measure thickness and refractive index based on the principles of optical interference. The porosity was calculated to be about 0.38 according to the film refractive index data measured.

(3) Determining dirt resistance performance of the film

Rapid test was carried out using Scotch 610-1PK tape of 3M company. And the method included adhering the 3M tape to the surface of the coating film, squeezing hard, and tearing the tape at a degree of 90° vertical to the film surface. According to the shallow or heavy marks remained on film

surface, 1-5 grade was rated respectively, grade 1 means no marks, grade 2 means slight marks, grade 3 means obvious marks, grade 4 means residual white marks, grade 5 means degumming. The higher the grade is, it means the worse the dirt resistance performance is, and grade below 3 is qualified.

5 The test result was grade 2, namely qualified.

(4) Determining the pencil hardness performance of the film

The pencil hardness of the coating film was determined according to the Chinese national standard GB/T6739, wherein the load was 750g, and the result was 3H hardness, namely $\geq H$, so the film reached the requirement of national standard.

(5) After the salt fog resistance test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules ”), constant temperature and humidity test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules ”), outdoor exposure test(referencing standard IEC61215), UV test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules”), friction test(referencing standard EN1096-2), acid resistance test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules”), and wet freezing test(referencing standard JC/T2170-2013 “Anti-Reflective film glass for photovoltaic modules”) conducted on the coating film, the changes of light transmittance were determined according to the above mentioned method . The measured conditions, methods and results were summarized in table 5 (The test equipments used in this example were the same as example 1, and the test equipments used in all the examples were the same as the example 1).

25 Table 5 Test results for each performance of the coating film

Test Project	Criterion for judgement		Test conditions	Test results	Single evaluation
	Test conditions	Changes of transmittan			

		ce			
salt fog resistance test	conditions: (50±5) g/L NaCl , time:96h	$\Delta T \leq 0.8\%$	96h	$\Delta T = -0.37\%$ qualified	P
constant temperature and humidity test	Temperature: 85°C, humidity: 85%RH, time: 1000h	$\Delta T \leq 0.8\%$	1000h	$\Delta T = -0.51\%$ qualified	P
outdoor exposure test	Total irradiation: 60kwh/m ² , time: 600h	$\Delta T \leq 0.8\%$	600h	$\Delta T = -0.62\%$ qualified	P
UV test	Total irradiation: 15kwh/m ² , time:720h	$\Delta T \leq 0.8\%$	720h	$\Delta T = 0.07\%$ qualified	P
friction test	500 cycles	$\Delta T \leq 0.8\%$	500 cycles	$\Delta T = -0.23\%$ qualified	P
acid resistance test	Concentration:1mol/L HCl , time:24h	$\Delta T \leq 0.8\%$	24h	$\Delta T = 0.11\%$ qualified	P
wet freezing test	Temperature: -40°C /+85°C, 85%RH, 10 cycles	$\Delta T \leq 0.8\%$	10 cycles	$\Delta T = -0.29\%$ qualified	P

The above test results showed that after coating the coating solution prepared by methods of the present invention onto a glass, the light transmittance of the film was improved, dirt resistance performance was good, and the hardness is high, and acid resistance, friction resistance,

weatherability and other performances were excellent.

CLAIMS

1. A nano core-shell silica micro-sphere wherein the nano core-shell silica micro-sphere is obtained by a preparation method comprising the following steps:

(1) preparation of polystyrene core by emulsifier-free emulsion polymerization: putting an amino-containing or quaternized co-monomer and water in a reaction vessel, adding styrene, then heating the mixture up to 50-85°C under the protection of nitrogen gas, and dropwise adding an initiator aqueous solution to react, and whereby obtaining a cationic polystyrene emulsion;

(2) preparation of a silica coated polystyrene core-shell structured micro-sphere emulsion: mixing the cationic polystyrene emulsion used as a hard template with a solvent, then adding a silicon source material under conditions of stirring at 15-35°C to react and obtaining the silica coated polystyrene nano core-shell structured micro-sphere emulsion.

2. The nano core-shell silica micro-sphere according to claim 1, wherein, said co-monomer is an amino-containing vinyl monomer and / or a quaternized vinyl monomer; preferably, said quaternized vinyl monomer is selected from one or more of the group consisting of acryloyloxyethyl trimethoxy ammonium chloride, methacryloyloxyethyl trimethyl ammonium chloride, (meta)acrylamino propyl trimethyl ammonium chloride, or diallyl dimethyl ammonium chloride; said amino-containing vinyl monomer is selected from one or more of the group consisting of dimethylamino ethyl (meta)acrylate, diethylamino ethyl (meta)acrylate or diisopropylamino ethyl (meta)acrylate.

3. The nano core-shell silica micro-sphere according to claim 1 or 2, wherein, said silicon source material is selected from one or more of the

group consisting of tetramethoxysilane, tetraethoxysilane, methyl trimethoxy silane, methyl triethoxysilane, vinyl trimethoxy silane, vinyl triethoxy silane, γ -mercaptopropyl trimethoxy silane, γ -aminopropyl triethoxy silane, γ -glycidooxy propyl trimethoxy silane or γ -(methacryloxy) propyl trimethoxy silane .

4. The nano core-shell silica micro-sphere according to any one of claim 1 to 3, wherein, said initiator is potassium persulfate or 2,2'-azobis(2-methylpropionamidine) hydrochloride.

5. The nano core-shell silica micro-sphere according to any one of claim 1 to 4, wherein, in step (1) , a mass ratio of the co-monomer to the styrene monomer is (0.5-4) : (10-20) .

6. The nano core-shell silica micro-sphere according to any one of claim 1 to 5, wherein, in step (1), a mass ratio of the co-monomer, the styrene monomer, the initiator and the water in the total system is 0.5-4% of the co-monomer, 10-20% of the styrene monomer, 0.1-1% of the initiator and 75-89.4% of the water, respectively.

7. The nano core-shell silica micro-sphere according to any one of claim 1 to 6, wherein, in step (2), the amount of solvent is based on the standard of diluting the cationic polystyrene emulsion to a solid content of 1-20 mass%.

8. The nano core-shell silica micro-sphere according to any one of claim 1 to 7, wherein in step (2), a mass ratio of solid content in the polystyrene emulsion to the added silicon source material is 10-30%.

9. The nano core-shell silica micro-sphere according to any one of claim 1 to 8, wherein, in step (2), the solvent is selected from one or more of the group consisting of water, methanol, ethanol, ethylene glycol, n-propyl alcohol, isopropyl alcohol, propylene glycol, glycerol, n-butyl alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol methyl ether, propylene glycol butyl ether, tripropylene glycol monomethyl ether or tripropylene glycol monoether.

10. The nano core-shell silica micro-sphere according to any one of claim 2 to 9, wherein, when the co-monomer is an amino-containing vinyl monomer, an acid is needed for protonation treatment to the amino-containing vinyl monomer before step (1), and the acid used is selected from an inorganic acid or an organic acid.

11. The nano core-shell silica micro-sphere according to claim 10, wherein, said the inorganic acid is hydrochloric acid, sulfuric acid, nitric acid or phosphoric acid, and the organic acid is acetic acid, citric acid or oxalic acid; preferably, the required amount of inorganic acid based on calculation by monoacid is that the molar ratio of acid to the amino group contained in the amino-containing vinyl monomers is 50-100%.

12. The nano core-shell silica micro-sphere according to any one of claim 1 to 11, wherein, in step (1), after adding styrene, stirring the obtained mixture at 150-500rpm, preferably 200-450rpm.

13. The nano core-shell silica micro-sphere according to any one of claim 1 to 12, wherein, in step (1), dropwise adding the initiator at the speed of 0.1-2mL/min, preferably 0.5-1.5mL/min.

14. A composited coating solution containing silica alumina sol doped by nano core-shell silica micro-sphere, characterized in that the coating solution is composited by a sol of the nano core-shell silica micro-sphere of any one of claim 1 to 13 with a hydroxyl-containing silica alumina sol material.

15. The composited coating solution according to claim 14, wherein, calculated by weight percentage, the volume ratio of the hydroxyl-containing silica alumina sol to nano core-shell silica micro-sphere sol is 1: (1-10), preferably 1: (4-10).

16. The composited coating solution according to claim 14 or 15, wherein, the hydroxyl-containing silica alumina sol material is obtained by reaction of materials containing water, acid catalyst, solvent, aluminum salt

and silicon source material, wherein, relative to 1 mL of silicon source material, the mass of aluminum salt is 0.025-0.1g, preferably 0.055-0.1g.

17. The composited coating solution according to claim 16, wherein, relative to 1 mL of silicon source material, the content of solvent is 1-20mL,
5 the content of water is 0.1-1mL, and the content of catalyst is 0.01-0.1mL.

18. The composited coating solution according to claim 16 or 17, wherein said catalyst is selected from one or more of the group consisting of hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, acetic acid, citric acid and oxalic acid.

10 19. The composited coating solution according to any one of claim 14 to 18, wherein said silicon source material added in the preparation of hydroxyl-containing silica alumina sol is selected from one or more of tetramethoxysilane, tetraethoxysilane, methyl trimethoxy silane, methyl triethoxysilane, vinyl trimethoxy silane, vinyl triethoxy silane, γ - mercaptopropyl trimethoxy silane, γ -aminopropyl triethoxy silane, γ -
15 glycidoxy propyl trimethoxy silane or γ -(methacryloyloxy) propyl trimethoxy silane.

20. A preparation method of nano core-shell silica micro-sphere of any one of claim 1 to 13, is characterized in that the nano core-shell silica micro-
20 sphere is obtained by a preparation method comprising the following steps:

(1) preparation of polystyrene core by emulsifier-free emulsion polymerization: putting an amino-containing or a quaternized co-monomer and water in a reaction vessel, adding styrene, then heating the mixture up to 50-85°C under the protection of nitrogen gas, adding dropwise an initiator
25 aqueous solution to react, and whereby obtaining a cationic polystyrene emulsion;

(2) preparation of a silica coated polystyrene core-shell structured micro-sphere emulsion: mixing the cationic polystyrene emulsion used as a hard template with a solvent, then adding a silicon source material under condition

of stirring at 15-35°C to react and obtaining the silica coated polystyrene nano core-shell structured micro-sphere emulsion.

21. A preparation method of the composited coating solution containing silica alumina sol doped by nano core-shell silica micro-sphere according to any one of claims 14 to 18, wherein, the composited coating solution containing silica alumina sol doped by nano core-shell silica micro-sphere is obtained by compositing a sol of the nano core-shell silica micro-sphere of any one of claim 1 to 13 with a hydroxyl-containing silica alumina sol material.

22. An application of a sol of nano core-shell silica micro-sphere of any one of claims 1 to 13 or the composited coating solution containing silica alumina sol doped by nano core-shell silica micro-sphere sol of any one of claims 14 to 18 for the preparation of increased permeability and anti-reflection film in a surface of photovoltaic glass, optical device or solar device.

23. A silica alumina sol, characterized in that the silica alumina sol is obtained by reaction of materials containing water, acid used as a catalyst, solvent, aluminum salt and silicon source material, wherein, relative to 1 mL of silicon source material, the mass of aluminum salt is 0.025-0.1g; preferably, relative to 1 mL of silicon source material, the content of solvent is 1-20mL, the content of water is 0.1-1mL, the content of catalyst is 0.01-0.1mL.

24. An increased permeability and anti-reflection film, wherein the increased permeability and anti-reflection film is obtained by coating the composited coating solution of any one of claim 14 to 18 to a glass substrate, with any one coating method of spraying, dipping, pulling, roller coating, spin coating, flow coating and brush coating, followed by drying and baking-curing at 80-250°C, and tempering at 500-700°C.