DESCRIPTION JP2009184839A

Silica nanosheet, its manufacturing method, and organic solvent dispersion of silica nanosheet

[0001]

The present invention relates to a silica nanosheet and a method for producing the same, and further to an organic solvent dispersion of a silica nanosheet.

[0002]

In a narrow sense, a silica nanosheet is a single layer of siloxane that has been oxidized to two-dimensionally expand Si-O-Si bonds, and each Si atom is thought to be bonded to a hydroxyl group or a hydrogen atom. Theoretically, the thickness of a silica nanosheet is about 0.6 nm, and although there is no restriction on the extent of the surface direction, the length usually extends 100 times or more as large as the thickness.

[0003]

As a method for preparing such silica nanosheets, Japanese Patent Application Laid-Open No. 2006-49729 (Patent Document 1) discloses a method in which concentrated hydrochloric acid is added to a layered silicon compound (e.g., CaSi₂, YbSi₂) to cause a reaction, by-products (e.g., CaCl₂, YbCl₂) are removed by washing to extract a hydrogen-type layered compound (e.g., Weiss-type siloxene: Si₆H₃(OH)₃.HCl), this hydrogen-type layered compound is added to an aqueous solution containing a surfactant (e.g., sodium dodecyl sulfate, tetrabutylammonium) and adjusted to a pH of 5 or less, and the aqueous solution is shaken for a predetermined time (e.g., 10 days).

The silica nanosheet obtained by this method is dispersed in water, and in Patent Document 1, this aqueous dispersion of silica nanosheets is used as it is as a coating liquid containing silica.

[0004]

On the other hand, silica microparticles, which have traditionally been used as inorganic fillers, etc., are often dispersed in an organic solvent when mixed with an organic polymer, and even when added to an aqueous solution, such as when mixed with a hydrophilic polymer, the surface of the silica microparticles may be coated with an organic polymer, and in this case, too, they are often dispersed in an organic solvent.

For this reason, there has been a demand for silica nanosheets dispersed in organic solvents.

[0005]

However, when preparing an organic solvent dispersion from an aqueous dispersion of silica nanosheets, if water is removed from the aqueous dispersion of silica nanosheets by drying or the like, the silica nanosheets aggregate, and these aggregates are difficult to redisperse in the organic solvent. Therefore, it has been practically difficult to convert an aqueous dispersion of silica nanosheets into an organic solvent dispersion.

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[0006]

The present invention has been made in consideration of the problems associated with the above-mentioned conventional techniques, and aims to provide a method for producing silica nanosheets that can produce silica nanosheets that can be dispersed in organic solvents.

[0007]

As a result of extensive research to achieve the above-mentioned objective, the inventors discovered that silica nanosheets that can be dispersed in an organic solvent can be formed by mixing and stirring layered siloxene obtained by reacting monocalcium disilicide with concentrated hydrochloric acid with an organic solvent, thereby completing the present invention.

[0008]

In other words, the method for producing silica nanosheets of the present invention is a method characterized by including a step of reacting monocalcium disilicide with concentrated hydrochloric acid to form layered siloxene, and a step of mixing and stirring the layered siloxene with an organic solvent to form silica nanosheets in the organic solvent.

Furthermore, the silica nanosheet of the present invention is obtained by such a production method and is dispersible in an organic solvent.

[0009]

The organic solvent is preferably one containing dimethyl sulfoxide and/or N,N-dimethylformamide, more preferably one containing dimethyl sulfoxide and/or N,N-dimethylformamide as a main component, and particularly preferably dimethyl sulfoxide and/or N,N-dimethylformamide.

[0010]

In addition, the organic solvent dispersion of silica nanosheets of the present invention is characterized in that it is obtained by mixing and stirring a layered siloxane formed by reacting monocalcium disilicide with concentrated hydrochloric acid with an organic solvent, and forming silica nanosheets in the organic solvent.

[0011]

The reason why the method for producing a silica nanosheet of the present invention makes it possible to disperse a silica nanosheet in an organic solvent is not entirely clear, but the present inventors speculate as follows. That is, it is presumed that organic solvents have a higher affinity for siloxene than water and therefore easily penetrate between the layers of layered siloxene, which is favorable for delamination. It is presumed that the monolayer of siloxene thus exfoliated is oxidized by oxygen in the air, organic solvent molecules, and moisture to form silica nanosheets. Furthermore, as shown in Figure 1, the silica nanosheets in the organic solvent are mainly covered with organic solvent molecules, which have a lower affinity for silanol groups than water molecules, and it is presumed that this makes it possible to easily replace the dispersion medium or apply desired substances.

[0012]

On the other hand, when forming silica nanosheets using water, large ions are inserted between the layers of layered siloxene, which is then swollen, and then mechanical vibration is applied to cause delamination.

At the same time, siloxene is oxidized to form silica nanosheets. However, as shown in FIG. 4, the silica nanosheet in the aqueous solution is mainly covered with water molecules, and it is presumed that these water molecules are coordinated to the silanol groups. When converting such an aqueous dispersion of silica nanosheets into an organic solvent dispersion, a process is required to remove water from the aqueous dispersion by drying or the like. However, at this time, a dehydration condensation reaction occurs between silanol groups via the coordinated water molecules, forming silica gel, which is presumably why it becomes difficult to convert the aqueous dispersion of silica nanosheets into an organic solvent dispersion. In addition, such a dehydration condensation reaction is thought to occur during the production of silica nanosheets, and it is presumed that silica gel is also formed during the production of silica nanosheets, resulting in a low yield of silica nanosheets.

[0013]

According to the present invention, a silica nanosheet that can be dispersed in an organic solvent can be obtained.

Furthermore, it becomes possible to produce silica nanosheets with a much higher yield than when prepared in an aqueous solution.

[0014]

The present invention will be described in detail below based on preferred embodiments thereof.

The method for producing silica nanosheets of the present invention is characterized by comprising the steps of reacting monocalcium disilicide with concentrated hydrochloric acid to form layered siloxene, and mixing and stirring the layered siloxene with an organic solvent to form silica nanosheets in the organic solvent.

In the present invention, concentrated hydrochloric acid means one having a concentration of 30% by mass or more, and the higher the concentration, the more preferable it is.

[0015]

The silica nanosheet obtained by the manufacturing method of the present invention is preferably a single-layered one, but the silica nanosheet of the present invention also includes a single-layered silica nanosheet having two or several layers (preferably 2 to 5 layers) stacked thereon, and a mixture thereof.

Two or more layers of single-layer silica nanosheets stacked on top of each other, as well as mixtures thereof, can form transparent organic solvent dispersions and can be handled essentially in the same way as single-layer silica nanosheets.

[0016]

(Layered siloxene formation step) In the method for producing a silica nanosheet of the present invention, first, monocalcium disilicide and concentrated hydrochloric acid are mixed and stirred to form layered siloxene (Weiss type siloxene).

The resulting layered siloxene is preferably washed several times with an organic solvent such as acetone as necessary to remove by-products (CaCl₂) and the like.

If necessary, the organic solvent remaining between the layered siloxene particles after washing may be removed by drying or the like.

[0017]

The monocalcium disilicide (hereinafter referred to as "CaSi₂") is preferably pulverized as necessary. The particle size of the pulverized CaSi₂ is not particularly limited, but is preferably 2 mm or less from the viewpoint of shortening the reaction time.

[0018]

The mixing ratio of CaSi₂ and concentrated hydrochloric acid is preferably such that the mass of concentrated hydrochloric acid is 20 times or more the mass of CaSi₂. If the mixing ratio is less than the lower limit, the yield of layered siloxene tends to decrease. The temperature during mixing and stirring in this step is preferably 0 to 50 ° C, and more preferably 10 to 30 ° C. If the temperature during mixing and stirring is lower than the above lower limit, the reaction rate tends to decrease. On the other hand, if the temperature exceeds the above upper limit, many interlayer Si-O-Si bonds are formed in the layered siloxene, making delamination difficult and tending to reduce the yield of silica nanosheets. In the above temperature range, the reaction rate tends to increase, so that a higher temperature during mixing and stirring is preferred. In addition, the stirring speed and the stirring time are not particularly limited, and can be set appropriately depending on the amounts of CaSi₂ and concentrated hydrochloric acid, etc.

[0019]

(Silica Nanosheet Forming Step) The layered siloxene obtained in the layered siloxene forming step is mixed with an organic solvent and stirred to cause delamination of the layered siloxene. It is believed that the exfoliated siloxene is then oxidized by oxygen in the air, organic solvent molecules, and moisture contained in the organic solvent to form silica nanosheets.

[0020]

Preferred organic solvents used in this step include dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), N,N-diethylformamide, N,N-dimethylacetamide, N,N-diethylacetamide, acetonitrile, methyl isobutyl ketone (MIBK), toluene, chloroform, and 1,3-dimethyl-2-imidazolidinone. These organic solvents may be used alone or in combination of two or more kinds. Among these organic solvents, those containing DMSO and/or DMF are more preferred from the viewpoint of achieving a higher yield of silica nanosheets, those containing DMSO and/or DMF as the main component are even more preferred, and DMSO and/or DMF are particularly preferred.

In addition, in the method for producing silica nanosheets of the present invention, the organic solvent may contain water, but in that case, the water content is preferably 40 mass% or less, and more preferably 20 mass% or less, from the viewpoint of increasing the yield of silica nanosheets.

[0021]

The mixing ratio of the layered siloxene to the organic solvent is preferably such that the mass of the organic solvent is at least 5 times the mass of the layered siloxene.

If the mixing ratio is less than the above lower limit, the yield of silica nanosheets tends to decrease.

[0022]

As a stirring method, any common stirring method that provides a shear rate of 1 sec^{— 1} or more at any position in the mixture of layered siloxene and organic solvent can be used, but a method in which inorganic beads made of zirconia or alumina (preferably with a diameter of about 2 mm) are added to the mixture and stirred using a roller pot mill or a stirring blade made of fluororesin is preferred.

When inorganic beads having a diameter of 2 mm are used, the amount of the inorganic beads added is preferably 5 to 100 times, and more preferably 15 to 20 times, the mass of the layered siloxene, in the case of zirconia beads, for example.

The stirring speed is preferably in the range of 3 to 150 rpm, and more preferably in the range of 80 to 120 rpm.

In the method for producing silica nanosheets of the present invention, the yield of silica nanosheets is improved by stirring, but if the stirring speed falls below the above-mentioned lower limit, the effect of improving the yield of silica nanosheets by stirring tends to decrease, while if the stirring speed exceeds the above-mentioned upper limit, frictional heat tends to make it difficult to control the reaction temperature.

In addition, in the manufacturing method of the present invention, a continuous mixer with a shear rate of 1 sec (NER 15) or more can also be used.

[0023]

The temperature during mixing and stirring in this step is preferably 10 to 70 ° C, and more preferably 10 to 25 ° C.

However, the temperature must be equal to or higher than the melting point of the organic solvent used (for example, 19 ° C. or higher in the case of DMSO).

If the temperature during mixing and stirring is below the above lower limit, the delamination rate tends to decrease, whereas if it exceeds the above upper limit, a condensation reaction of the produced silica nanosheets occurs, resulting in the formation of precipitates such as silica gel, and the actual yield of silica nanosheets tends to decrease.

[0024]

The stirring time in this step is preferably from 4 to 100 hours, more preferably from 8 to 20 hours.

If the stirring time is shorter than the above lower limit, the amount of silica nanosheets produced will be small and the yield of silica nanosheets will tend to decrease; on the other hand, if the stirring time is longer than the above upper limit, the production efficiency of silica nanosheets (production amount per unit time) will decrease and a condensation reaction will occur of the produced silica nanosheets, resulting in the formation of precipitates such as silica gel and a decrease in the actual yield of silica nanosheets.

[0025]

(Purification Step) The solution containing the silica nanosheets (dispersion of the silica nanosheets in an organic solvent) obtained in the silica nanosheet formation step may contain solid impurities such as unreacted layered siloxene and by-products.

In this step, it is preferable to remove these solid impurities by a known separation and purification method such as centrifugation or suction filtration, if necessary.

For example, a transparent organic solvent dispersion of silica nanosheets can be obtained by subjecting the solution containing the silica nanosheets obtained in the silica nanosheet formation process to centrifugation (3,500 rpm x 20 minutes) to recover the supernatant, or by subjecting the solution to suction filtration (using a 5 μm membrane filter) to recover the filtrate.

The conditions for centrifugation and suction filtration are not limited to the above conditions, and can be set appropriately.

[0026]

(Coupling treatment process) In the method for producing silica nanosheets of the present invention, it is preferable to add a coupling agent to the obtained organic solvent dispersion of silica nanosheets (preferably purified) and subject the dispersion to a heat treatment to react the silica nanosheets with the coupling agent.

This makes it possible to stably disperse the silica nanosheets in the organic solvent for a longer period of time without causing aggregation.

The coupling agent is not particularly limited, but a silane coupling agent having an alkoxysilyl group in the molecule is preferred.

[0027]

The silica nanosheet obtained by the manufacturing method of the present invention is composed mainly of silicon and oxygen, and is a thin flake having a length of 100 nm or more in the planar direction and a thickness of 1 nm or less.

The silica nanosheets can usually be obtained in a state of being dispersed in an organic solvent, and this organic solvent dispersion of the silica nanosheets can be easily subjected to solvent replacement depending on the purpose and application.

Examples of the organic solvent used for the solvent replacement include those exemplified in the silica nanosheet formation step.

Furthermore, the solvent replacement is not limited to between organic solvents, and it is also possible to replace the solvent with water.

[0028]

The present invention will be described in more detail below based on examples and comparative examples, but the present invention is not limited to the following examples.

[0029]

Example 1 24.4 g of CaSi₂ (a reagent manufactured by Soekawa Rikagaku Co., Ltd.) was pulverized so as to pass through a sieve with 1.4 mm openings.

Half of this ground CaSi₂ (12.2 g) and 500 ml of concentrated hydrochloric acid (a reagent manufactured by Wako Pure Chemical Industries, Ltd.) were placed in a 1000 ml conical beaker and stirred with a magnetic stirrer in a water bath kept at 10 to 15 ° C. for 40 minutes.

As a result, a solution containing a yellow-green bulky solid (Wyeth type siloxene) was obtained.

This solution was immediately suction filtered using a membrane filter with a pore size of 5 μ m, and the filter cake (Wyeth type siloxane) was washed by mixing with acetone and filtering.

This acetone wash was repeated three times.

The remaining ground CaSi_NER18 (12.2 g) was similarly treated with concentrated hydrochloric acid, washed three times with acetone, and then mixed with the above filter cake.

[0030]

85.4 g of this acetone-containing filter cake (Wyeth-type siloxane) was placed in a 1000 ml separable flask, and 365 g of dimethyl sulfoxide (a reagent manufactured by Wako Pure Chemical Industries, Ltd., hereinafter abbreviated as "DMSO") and 500 g of zirconia beads having a diameter of 2 mm were added. This mixture was stirred at room temperature (20 to 23 ° C.) for 15 hours using a stirring blade made of fluororesin (rotation speed: 120 rpm).

After stirring was completed, the mixture was a cloudy brown liquid.

This mixture was subjected to centrifugation (3,500 rpm x 20 minutes) to remove the muddy matter, and the supernatant was subjected to suction filtration using a membrane filter with a pore size of 5 μm to recover the filtrate, thereby obtaining 163 g of a pale yellow, transparent solution containing silica nanosheets (DMSO dispersion of silica nanosheets).

[0031]

Thermogravimetric analysis was performed on this pale yellow, transparent solution (heated in air from 25 ° C to 1000 ° C at a heating rate of 10 ° C/min). The silica nanosheet content calculated from the ash content was 0.50 mass% (Table 1). In addition, the yield relative to the theoretical value of the amount of silica nanosheets produced calculated from the amounts of raw materials (hereinafter referred to as "yield of silica nanosheets") was 12% (Table 1).

[0032]

Next, 3.2 g of a silane coupling agent (manufactured by Chisso Corporation, product name "Sila Ace S510") was mixed with 20 g of an ethanol solution containing 0.2 mass % acetic acid (a reagent manufactured by Wako Pure Chemical Industries, Ltd.) and 20 mass % water, and the mixture was allowed to stand for 5 minutes. This solution was mixed with 163 g of the DMSO dispersion of silica nanosheets, placed in a 500 ml beaker, and heat-treated in a hot air oven at 110 ° C. for 1.5 hours without covering it. After the heat treatment, the mixed solution was pale yellow and transparent, and its mass was 132 g. When this mixed solution was allowed to stand for one month, no precipitation was formed, and it was confirmed that the silica nanosheets were stably dispersed in the organic solvent for a long period of time.

[0033]

A portion of this mixed solution was collected, vacuum dried, and then observed with a transmission electron microscope (TEM) and subjected to fluorescent X-ray elemental analysis (EDX). 2A and 2B show TEM photographs of the obtained silica nanosheets. FIG. 3 shows the fluorescent X-ray spectrum of the obtained silica nanosheet. As is clear from the TEM photograph shown in FIG. 2A, the obtained silica nanosheets were flakes having a length of 100 nm or more in the planar direction. In addition, it was presumed that the light-colored portion of the silica nanosheet portion in FIG. 2B was a single layer (theoretical value: 0.65 nm). Furthermore, as is clear from the EDX results shown in FIG. 3, it was confirmed that the main components of the obtained silica nanosheet were silicon and oxygen.

[0034]

Example 2 The ground CaSi_NER19 (12.0 g) obtained in the same manner as in Example 1 was treated with 500 ml of concentrated hydrochloric acid in the same manner as in Example 1, and washed three times with acetone to recover a filter cake. The filter cake was dried at room temperature using a vacuum dryer to obtain a Wyeth type siloxene. A 50 ml glass container was charged with 0.5 g of the Wyeth type siloxene, 10 g of an organic solvent (N,N-dimethylformamide (DMF), N,N-diethylformamide, N,N-dimethylacetamide, N,N-diethylacetamide, acetonitrile, methyl isobutyl ketone (MIBK), toluene, chloroform, or 1,3-dimethyl-2-imidazolidinone), and 60 g of zirconia beads having a diameter of 2 mm, and then sealed. The mixture was stirred using a roller mill (rotation speed: 15 rpm) at room temperature (20 to 23 ° C.) for 20 hours. After stirring, the mixture was suction filtered using a membrane filter with a pore size of 5 μm to recover the filtrate, and a pale yellow transparent solution containing silica nanosheets (dispersions of silica nanosheets in various organic solvents) was obtained. This pale yellow, transparent solution was subjected to thermogravimetric analysis in the same manner as in Example 1 to determine the content and yield of silica nanosheets. The results are shown in Table 1.

[0035]

Example 3 The ground CaSi_NER20 (4.0 g) obtained in the same manner as in Example 1 was treated with 400 ml of concentrated hydrochloric acid in the same manner as in Example 1, and washed three times with acetone to recover a filter cake (Wyeth type siloxane). In a 50 ml glass container were placed 1.0 g of the Wyeth type siloxene containing acetone, 10 g of DMSO (water content: 0 mass%, 10 mass%, 20 mass%, or 40 mass%), and 60 g of zirconia beads having a diameter of 2 mm, and the mixture was stirred for 16 hours in the same manner as in Example 1. After stirring, the mixture was suction filtered using a membrane filter having a pore size of 5 μm to recover the filtrate, and a pale yellow transparent solution containing silica nanosheets (DMSO dispersion of silica nanosheets) was obtained. This pale yellow, transparent solution was subjected to thermogravimetric analysis in the same manner as in Example 1 to determine the content of silica nanosheets. The results are shown in Table 2.

[0036]

Comparative Example 1 The ground CaSi_NER21 (2.0 g) obtained in the same manner as in Example 1 was treated with 200 ml of concentrated hydrochloric acid in the same manner as in Example 1, and washed three times with acetone to recover a filter cake. The filter cake was dried at room temperature using a vacuum dryer to obtain a Wyeth type siloxene.

[0037]

This Wyeth type siloxene was mixed with an aqueous solution (pH 3.2) prepared by dissolving 2.71 g of sodium dodecyl sulfate (a reagent manufactured by Wako Pure Chemical Industries, Ltd.) in 800 ml of water, and the mixture was stirred using a magnetic stirrer. The color of the suspension was orange when stirring was started, but after stirring for about 6 days, the color changed to pale yellow. Stirring was continued, and the color turned pale gray 10 days after the start of stirring.

[0038]

The suspension that had been stirred for 10 days was centrifuged (3500 rpm x 20 minutes) and the supernatant was recovered, which was found to be turbid. This supernatant was subjected to suction filtration using a membrane filter having a pore size of 5 μm, and the filtrate was collected to obtain a colorless and transparent aqueous solution containing silica nanosheets (aqueous dispersion of silica nanosheets). This colorless, transparent aqueous solution was concentrated ten-fold using a rotary evaporator to remove water-soluble components. The content of silica nanosheets in the concentrated liquid calculated from the mass of the ash was 0.02 mass%, and the yield was 0.6% (Table 1).

[0039]

Comparative Example 2 20 ml of the concentrated solution containing the silica nanosheet obtained in Comparative Example 1 and 5 ml of an organic solvent (hexane, toluene or chloroform) were placed in a 50 ml glass container and vigorously shaken, and then allowed to stand until the aqueous phase and the oil phase separated. The resulting oil phase was dried, but nothing precipitated when any of the organic solvents was used.

[0040]

Comparative Example 3 When 20 ml of the concentrated solution containing the silica nanosheet obtained in Comparative Example 1 and 0.2 g of an ethanol solution (concentration: 1% by mass) of a silane coupling agent (Sila-Ace S310, S320, S330, or S510 (product name, manufactured by Chisso Corporation)) were placed in a 50 ml glass container and stirred, a flocculent precipitate was formed for each of the silane coupling agents. This flocculant was recovered by centrifugation, mixed with ethanol and centrifuged again to dry the flocculant. 20 ml of methyl isobutyl ketone (MIBK) was added to this flocculent precipitate, and the mixture was stirred and ultrasonically treated, but the flocculent precipitate did not dissolve regardless of which silane coupling agent was used.

[0043]

As is clear from the results shown in Figures 2A, 2B, and 3, it was confirmed that when Wyeth-type siloxene was treated with an organic solvent (Example 1), a silica nanosheet containing silicon and oxygen as main components was formed. Furthermore, as is clear from the results shown in Tables 1 and 2, it was confirmed that the silica nanosheet production method of the present invention using an organic solvent (Examples 1 to 3) significantly improves the yield of silica nanosheets compared to production in an aqueous solution (Comparative Example 1). Furthermore, as is clear from the results shown in Table 2, it was confirmed that the lower the water content of the organic solvent, the higher the content of silica nanosheets, i.e., the higher the yield of silica nanosheets.

[0044]

Moreover, as is clear from the results shown in Comparative Example 2, it was difficult to extract the silica nanosheets in the aqueous solution with an organic solvent. Furthermore, as is clear from the results shown in Comparative Example 3, even when silica nanosheets in an aqueous solution were treated with a silane coupling agent, they aggregated and precipitated, and it was difficult to disperse them in an organic solvent. In other words, it was confirmed that it is difficult to disperse silica nanosheets prepared in an aqueous solution in an organic solvent.

[0045]

As described above, according to the present invention, it is possible to produce a silica nanosheet dispersed in an organic solvent. Furthermore, it becomes possible to produce silica nanosheets with a much higher yield than when prepared in an aqueous solution.

[0046]

Therefore, the method for producing silica nanosheets of the present invention makes it possible to obtain silica nanosheets dispersed in an organic solvent in high yield, and is therefore useful as silica microparticles for use in materials that have organic polymers as a continuous phase, such as paints, adhesives, rubber, and plastic products.

[0047]

FIG. 1 is a schematic diagram showing a state of silica nanosheets dispersed in DMSO.

1 is an electron microscope photograph showing the silica nanosheet obtained in Example 1.

1 is an electron microscope photograph showing the silica nanosheet obtained in Example 1.

1 is a graph showing the fluorescent X-ray spectrum of the silica nanosheet obtained in Example 1.

FIG. 2 is a schematic diagram showing the state change from a silica nanosheet water dispersion to silica gel when a drying treatment is applied to silica nanosheets dispersed in water.