Notice

DESCRIPTION CN103531323A

Preparation method of surfactant-free magnetic liquid

无表面活性剂磁性液体的制备方法

[0001]

Technical Field

技术领域

[0002]

This invention belongs to the field of materials technology, specifically relating to a method for preparing surfactant-free magnetic liquids.

本发明属于材料技术领域，具体涉及无表面活性剂磁性液体的制备方法。

[0003]

Background Technology

背景技术

[0004]

Magnetic liquids are colloidal suspensions composed of magnetic nanoparticles (mostly iron oxide nanoparticles) dispersed as the magnetic phase in a non-magnetic carrier liquid. They are liquid functional materials whose physical properties—such as optical properties and viscosity characteristics—can be controlled by an external magnetic field, but they do not have the remanent magnetization effect found in solid magnetic materials.

磁性液体是磁性纳米微粒（多采用氧化铁纳米微粒）作为磁性相分散于非磁性载液中 构成的胶体悬浮液，是其物理性质——如光学性质、粘度特性等，可由外磁场调控的液态 功能材料，无固体磁性材料所具有的剩磁效应。

To avoid sedimentation and separation of particles in the carrier liquid due to gravity, the particle size of magnetic nanoparticles in magnetic liquids is limited to about 10 nm.

为避免在载液中微粒由于重力作用而产生 的沉降分离，磁性液体中的磁性纳米微粒的粒径限制在10nm左右。

To prevent magnetic nanoparticles from agglomerating due to van der Waals forces and magnetostatic interactions, magnetic nanoparticles are usually encapsulated with surfactants. The steric forces generated by the long-chain molecules of the surfactants overcome the tendency of the particles to agglomerate.

为避免磁性纳米微粒由 于范德瓦耳斯力和静磁相互作用产生的微粒团聚，磁性微粒通常需包裹表面活性剂，通过 表面活性剂长链分子产生的空间位力克服微粒的团聚趋势。

This type of magnetic liquid is called a surfactant-based magnetic liquid. The response rate of the field effect of this magnetic fluid will be affected by the surfactant, whose particles have a hydrodynamic particle size larger than their inherent physical particle size. Furthermore, the dispersed particles can be placed in an acidic base liquid to adsorb hydrogen ions on their surface, forming charged particles. The electrostatic repulsion generated by the like charge overcomes the aggregation between particles. This type of magnetic liquid is called an ionic or double-layer magnetic liquid. In ionic magnetic fluids, the hydrodynamic particle size is the same as the physical particle size. Therefore, for ionic and surfactant-type magnetic liquids composed of magnetic nanoparticles with the same chemical composition and physical particle size, the former has a faster field-induced response than the latter. To prevent iron oxide particles from being dissolved by acid, iron oxide particles in ionic magnetic liquids are usually treated with ferric nitrate to form a protective layer on the surface that resists acid corrosion, with nitric acid aqueous solution used as the dispersion medium.

这种磁性液体称之为表面活性 剂型磁性液体。 这种磁性液体的场致效应的响应速度将受表面活性剂的影响，其微粒的流 体力学粒径大于其固有的物理粒径。 此外，可分散微粒于酸性基液中使其微粒表面吸附氢 离子而形成带电微粒，依靠同种电荷产生的静电排斥作用克服微粒间的团聚。 这种磁性液 体称之为离子型或双电偶层型磁性液体。 在离子型磁性液体中，流体力学粒径与物理粒径 是相同的。 因此对于化学组成和物理粒径相同的磁性纳米微粒构成的离子型与表面活化剂 型磁性液体，前

者的场致响应速度快于后者。 为避免氧化铁微粒为酸所溶解，通常离子型 磁性液体中的氧化铁微粒需采用硝酸铁处理以形成表面抗酸蚀的保护层，用硝酸水溶液作 为分散介质载液。

[0005]

Summary of the Invention

发明内容

[0006]

The technical problem solved by this invention is to provide a method for preparing a magnetic liquid without the use of surfactants.

本发明解决的技术问题是提供一种不用表面活性剂的磁性液体的制备方法。

[0007]

The technical solution of this invention is a method for preparing surfactant-free magnetic liquids, comprising the following steps:

本发明的技术方案是无表面活性剂磁性液体的制备方法，包括如下步骤：

[0008]

a. Preparation of iron oxide nanoparticle dispersion: A basic iron hydroxide-based precursor was prepared by chemical precipitation in an alkaline medium. The precursor was washed until the pH of the solution was 7-8 to obtain the precursor. The precursor was then treated in

a ferrous chloride solution, and after washing, dehydration, and drying, iron oxide nanoparticles were obtained.

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a、氧化铁纳米微粒分散相的制备：在碱性介质中通过化学沉淀法制备碱式氢氧化铁基 前驱体，清洗至溶液pH值为7～8，得到前驱体；在氯化亚铁溶液中对前驱体进行处理，清 洗、脱水、干燥后可获得氧化铁纳米微粒；

[0009]

b. Preparation of the dispersion medium carrier: A mixture of glycerol and water is used as the dispersion medium carrier, and nitric acid is added to adjust the concentration of the acidic dispersion medium;

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b、分散介质载液的制备：甘油—水的混合液作为分散介质载液，加入硝酸以调控酸性 分散介质的浓度；

[0010]

c. Synthesis of Magnetic Fluid: Iron oxide nanoparticles, serving as the dispersed phase, were mixed with a dispersion medium, serving as the carrier liquid, under stirring. After natural aging for 10 days, a chemically stable magnetic fluid was obtained. The ratio of the dispersed phase to the dispersion medium was expressed as the volume fraction of the dispersed phase.

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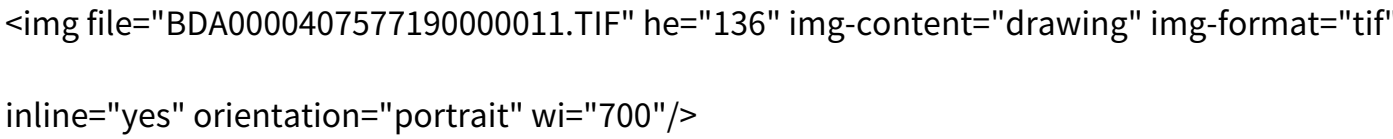
c、磁性液体的合成：在搅拌状态下，将作为分散相的氧化铁纳米微粒与作为载液的分 散介质混合，自然老化10天后得到化学性质稳定的磁性液体；分散相与分散介质的比例由 分散相体积分数表示：



[0011]

Wherein, Φv is 0.0001 to 0.025.

其中，Φv为0.0001～0.025。

[0012]

Preferably, Φv is 0.02.

优选的，Φv为0.02。

[0013]

The volume ratio of glycerol to water is 10-95:90-5.

其中，所述的甘油：水的体积比为10～95：90～5。

[0014]

The most preferred embodiment is that the volume ratio of glycerol to water is 60:40.

最优选，所述的甘油：水的体积比为60：40。

[0015]

In step a, the treatment of the precursor in the ferrous chloride solution is as follows: using a 0.5 mol concentration ferrous chloride solution as the treatment liquid, the volume ratio of the precursor to the treatment liquid is 1:5, heating the treatment liquid to boiling, then pouring the precursor into the treatment liquid with stirring, keeping it boiling for 30 minutes

and then stopping heating, and cooling until iron oxide nanoparticles gradually precipitate out.

其中，步骤a中所述的在氯化亚铁溶液中对前驱体进行处理即：以0.5摩尔浓度氯化亚 铁溶液作为处理液，前驱体与处理液的体积比为1：5，加热处理液至沸腾，然后在搅拌下 将前驱体倒入处理液中，保持沸腾30分钟停止加热，冷却至氧化铁纳米微粒逐渐析出。

[0016]

In step a, the cleaning and dehydration refer to: cleaning the iron oxide nanoparticles with distilled water and then dehydrating them with acetone.

其中，步骤a中所述的清洗、脱水是指：用蒸馏水清洗氧化铁纳米微粒，然后用丙酮 脱水。

[0017]

Wherein, the concentration of nitric acid in the dispersion medium is mol/L, where Z_b is the valence of the anion in the carrier dispersion medium, ρ_s is the density of the nanoparticle dispersion phase in g/cm³, M_{ws} is the molecular weight of the nanoparticle dispersion phase, and Φv is the volume fraction of the dispersion phase.

其中，分散介质中的硝酸浓度为 摩尔/升，式中Z _b 是载液分散介 质中的酸根离子的化合价，ρ _s 为纳米微粒分散相的密度g/cm ³ ，M _{ws} 为纳米微粒分散相的分 子量；Φv分散相体积分数。

[0018]

This invention proposes a method for preparing an ionic magnetic liquid composed of iron oxide magnetic nanoparticles without the use of surfactants.

本发明提出了不用表面活性剂，由氧化铁磁性纳米微粒构成的离子型磁性液体制备方 法。

In the method for preparing ionic magnetic liquid proposed in this invention, the iron oxide magnetic nanoparticles do not need to be treated with ferric nitrate to form an acid-resistant layer. Instead, the microparticles form an acid-resistant surface layer during the preparation process.

在本发明提出的离子型磁性液体制备方法中，氧化铁磁性纳米颗粒不需经硝酸铁处理 形成抗酸蚀层，取而代之的是微粒在制备过程中即形成抗酸蚀表面层。

The magnetic liquid prepared by this method contains magnetic nanoparticles without long-chain surfactant coatings, which results in less material consumption, simplified synthesis process, and faster field-induced response compared to conventional surfactant-based magnetic liquids.

由本方法制备的磁 性液体，其中的磁性纳米微粒没有长链的表面活化剂包裹，以致与通常的表面活化剂型磁 性液体相比以致与通常的表面活化剂型磁性液体相比不但耗用的材料较少，简化了合成工艺步骤，并具有较快的场致响应速度。

[0019]

Attached Figure Description

附图说明

[0020]

Figure 1 shows a transmission electron microscope image of the magnetic nanoparticles.

图1为磁性纳米微粒的透射电子显微镜图。

[0021]

Figure 2 shows the specific magnetization curves of the magnetic nanoparticles.

图2为磁性纳米微粒的比磁化曲线。

The horizontal axis in the figure represents the magnetic field strength, and the vertical axis represents the specific magnetization.

图中的横坐标为磁场强度，纵坐标为比磁化强度。

[0022]

Figure 3 shows the specific magnetization curve of the magnetic liquid in Example 1.

图3实施例1中磁性液体的比磁化曲线。

[0023]

Figure 4 shows the specific magnetization curve of the magnetic fluid in Example 2.

图4实施例2中磁性液体的比磁化曲线。

[0024]

Figure 5 shows the specific magnetization curve of the magnetic liquid in Example 3.

图5实施例3中磁性液体的比磁化曲线。

[0025]

Detailed Implementation

具体实施方式

[0026]

The method for preparing the surfactant-free magnetic liquid of the present invention includes the following steps:

本发明无表面活性剂磁性液体的制备方法包括如下步骤：

[0027]

a. Preparation of iron oxide nanoparticle dispersion: A basic iron hydroxide-based precursor was prepared by chemical precipitation in an alkaline medium. The precursor was washed until the pH of the solution was 7-8 to obtain the precursor. The precursor was then treated in a ferrous chloride solution, and after washing, dehydration, and drying, iron oxide nanoparticles were obtained.

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a、氧化铁纳米微粒分散相的制备：在碱性介质中通过化学沉淀法制备碱式氢氧化铁基 前驱体，清洗至溶液pH值为7～8，得到前驱体；在氯化亚铁溶液中对前驱体进行处理，清 洗、脱水、干燥后可获得氧化铁纳米微粒；

[0028]

b. Preparation of the dispersion medium carrier: A mixture of glycerol and water is used as the dispersion medium carrier, and nitric acid is added to adjust the concentration of the acidic dispersion medium;

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b、分散介质载液的制备：甘油—水的混合液作为分散介质载液，加入硝酸以调控酸性 分散介质的浓度；

[0029]

c. Synthesis of Magnetic Fluid: Iron oxide nanoparticles, serving as the dispersed phase, are mixed with a dispersion medium, serving as the carrier liquid, under stirring. After natural aging for 10 days, a chemically stable magnetic fluid is obtained. The ratio of the dispersed phase to the dispersion medium is expressed as the volume fraction of the dispersed phase.

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c、磁性液体的合成：在搅拌状态下，将作为分散相的氧化铁纳米微粒与作为载液的分 散介质混合，自然老化10天后得到化学性质稳定的磁性液体；分散相与分散介质的比例由 分散相体积分数表示：

[0030]

Wherein, Φv is 0.0001 to 0.025.

其中，Φv为0.0001～0.025。

[0031]

Preferably, Φv is 0.02.

优选的，Φv为0.02。

[0032]

The volume ratio of glycerol to water is 10-95:90-5.

其中，所述的甘油：水的体积比为10～95：90～5。

[0033]

The most preferred embodiment is that the volume ratio of glycerol to water is 60:40.

最优选，所述的甘油：水的体积比为60：40。

[0034]

In step a, the treatment of the precursor in the ferrous chloride solution is as follows: using a 0.5 mol concentration ferrous chloride solution as the treatment liquid, the volume ratio of the precursor to the treatment liquid is 1:5, heating the treatment liquid to boiling, then pouring the precursor into the treatment liquid with stirring, keeping it boiling for 30 minutes and then stopping heating, and cooling until iron oxide nanoparticles gradually precipitate out.

其中，步骤a中所述的在氯化亚铁溶液中对前驱体进行处理即：以0.5摩尔浓度氯化亚 铁溶液作为处理液，前驱体与处理液的体积比为1：5，加热处理液至沸腾，然后在搅拌下 将前驱体倒入处理液中，保持沸腾30分钟停止加热，冷却至氧化铁纳米微粒逐渐析出。

[0035]

In step a, the cleaning and dehydration refer to: cleaning the iron oxide nanoparticles with distilled water and then dehydrating them with acetone.

其中，步骤a中所述的清洗、脱水是指：用蒸馏水清洗氧化铁纳米微粒，然后用丙酮 脱水。

[0036]

Wherein, the concentration of nitric acid in the dispersion medium is mol/L, where Z_b is the valence of the anion in the carrier dispersion medium, ρ_s is the density of the nanoparticle dispersion phase in g/cm³, M_{ws} is the molecular weight of the nanoparticle dispersion phase, and Φv is the volume fraction of the dispersion phase.

其中，分散介质中的硝酸浓度为 摩尔/升，式中Z _b 是载液分散介 质中的酸根离子的化合价，ρ _s 为纳米微粒分散相的密度g/cm ³ ，M _{ws} 为纳米微粒分散相的分 子量；Φv分散相体积分数。

[0037]

In this invention, if Φv < 0.0001, the field-induced properties of the magnetic liquid are very weak, and it loses the characteristics of a magnetic functional material; if Φv > 0.025, the particles in the magnetic liquid may precipitate.

本发明中，若Φv<0.0001，则磁性液体的场致性质非常弱，失去磁功能材料的特征；若 Φv>0.025，则磁性液体中的微粒可能出现沉淀。

Research has shown that magnetic fluids with a Φv of 0.02 exhibit better performance.

经过研究发现，在Φv为0.02磁性液体的性 能较好。

[0038]

In this invention, the inventors discovered through multiple experiments that when the volume ratio of glycerol to water is 10-95:90-5, the resulting magnetic liquid exhibits better performance.

本发明中，发明人通过多次试验发现甘油：水的体积比为10～95：90～5时，所得到 的磁性液体的性能较好。

In particular, the optimal ratio of glycerol to water is 60:40.

尤其，在甘油：水的体积比为60：40时，达到最佳。

[0039]

Example 1: Preparation of magnetic liquid using the method of the present invention

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实施例1采用本发明方法制备磁性液体

[0040]

Preparation of iron oxide nanoparticles in the first step

第一步氧化铁纳米微粒的制备

[0041]

(1) Precursor preparation

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(1)前驱体制备

[0042]

Ferric chloride and nickel nitrate were used as raw materials, and their aqueous solutions were mixed in a molar ratio of 2:1 for iron to nickel.

以三氯化铁和硝酸镍为原料，按铁与镍的摩尔比为2：1的比例选取两者的水溶液进行 混合。

Pour 10 times the volume of a 0.7 mol sodium hydroxide solution into a ferric chloride-nickel nitrate mixture, then heat to boiling. After boiling for 5 minutes, stop heating and allow to cool naturally to room temperature.

将10倍体积的0.7摩尔浓度的氢氧化钠溶液倒入三氯化铁-硝酸镍混合液中，然后加 热至沸腾，沸腾5分钟后停止加热，自然冷却至室温。

During the cooling process, the precursor gradually precipitates out.

冷却过程中前驱体逐渐沉淀析出。

[0043]

A 0.01 mol concentration aqueous solution of nitric acid was used as the cleaning solution.

用0.01摩尔浓度的硝酸水溶液作为清洗液。

Mix the precipitate and the washing solution at a volume ratio of 1:5, stir thoroughly, and then separate by centrifugation. Repeat this step 3 times.

按沉淀物与清洗液的体积比为1：5进行混 合，充分搅拌后经离心机分离，重复此步骤3次。

[0044]

(2) Preparation of magnetic nanoparticles

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(2)磁性纳米微粒的制备

[0045]

A 0.5 mol concentration ferrous chloride solution was used as the treatment solution.

以0.5摩尔浓度氯化亚铁溶液作为处理液。

Select an appropriate amount of treatment solution with a volume ratio of precursor to treatment solution of 1:5, heat the treatment solution to boiling, then pour the precursor into the treatment solution while stirring, keep boiling for 30 minutes and then stop heating.

根据前驱体与处理液的体积比为1:5选取适 量的处理液，加热处理液至沸腾，然后在搅拌下将前驱体倒入处理液中，保持沸腾30分钟 停止加热。

As the air cools to room temperature, nanoparticles gradually precipitate out.

自然冷却至室温，冷却过程中纳米微粒逐渐析出。

[0046]

The precipitate was washed twice with distilled water and then dehydrated three times with acetone.

用蒸馏水清洗沉淀物二次，然后用丙酮脱水三次。

The dehydrated precipitate was placed in a silica gel desiccator, and after 24 hours, dry and anhydrous magnetic nanoparticle powder was obtained.

脱水后的沉淀物放入硅胶干燥器中， 二十四小时后得到干燥无水的磁性纳米微粒粉体。

[0047]

The transmission electron microscope image of the prepared magnetic nanoparticles is shown in Figure 1, and the specific magnetization curve is shown in Figure 2.

所制备的磁性纳米微粒的透射电子显微镜象如图1所示，比磁化曲线如图2所示。

[0048]

Step 2: Preparation of the dispersion medium

第二步分散介质的制备

[0049]

The dispersion medium carrier liquid was prepared with a glycerol to water ratio of 10:90.

按甘油与水的比例为10：90配置分散介质载液。

Prepare a magnetic liquid with Φ_v = 0.02 and a nitric acid concentration of 4.46 × 10⁻² mol/L.

配制Φ _v =0.02的磁性液体，硝酸浓度 为4.46×10 ⁻² 摩尔/升。

[0050]

Step 3: Synthesis of Magnetic Liquid

第三步磁性液体合成

[0051]

The magnetic nanoparticle powder and carrier liquid were selected according to a volume ratio of 2:98.

按磁性纳米微粒粉体与载液的体积比为2：98的比例选取纳米微粒粉体和载液。

A magnetic liquid with a particle volume fraction Φ_v of 0.02 was synthesized by dispersing nanoparticle powder in a carrier liquid.

将纳米 微粒粉体分散于载液中合成微粒体积分数Φ _v 为0.02的磁性液体。

[0052]

After standing for 10 days, a magnetic liquid was obtained.

静置10天后得到磁性液体。

[0053]

The specific magnetization curve of the synthesized magnetic liquid is shown in Figure 3. Compared with the magnetization curve of the magnetic nanoparticle powder shown in Figure 2, it can be seen that the two have similar shapes. This indicates that the prepared magnetic liquid retains the magnetization properties of the magnetic nanoparticles.

所合成磁性液体比磁化曲线如图3所示，与图2所示的磁性纳米微粒粉体的磁化曲线相 比，可见两者具有相似的形状，由此可知所制备的磁性液体保持了磁性纳米微粒的磁化性质。

Example 2: Preparation of magnetic liquid using the method of the present invention

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实施例2采用本发明方法制备磁性液体

[0054]

Preparation of iron oxide nanoparticles in the first step

第一步氧化铁纳米微粒的制备

[0055]

As in Example 1.

如实施例1。

[0056]

Step 2: Preparation of the dispersion medium

第二步分散介质的制备

[0057]

The dispersion medium carrier liquid was prepared by mixing glycerol and water in a ratio of 60:40.

按甘油与水的比例为60：40配制分散介质载液。

Prepare a magnetic liquid with Φ_v = 0.02 and a nitric acid concentration of 4.46 × 10-² mol/L.

配制Φ _v =0.02的磁性液体，硝酸浓度 为4.46×10- ² 摩尔/升。

[0058]

Step 3: Synthesis of Magnetic Liquid

第三步磁性液体合成

[0059]

The nanoparticles and carrier liquid were selected according to a volume ratio of 2:98.

按磁性纳米微粒粉体与载液的体积比为2：98的比例选取纳米粉体和载液。

A magnetic liquid with a particle volume fraction Φ_v of 0.02 was synthesized by dispersing nanoparticle powder in a carrier liquid.

将纳米微粒 粉体分散于载液中合成微粒体积分数Φ _v 为0.02的磁性液体。

[0060]

After standing for 10 days, a magnetic liquid was obtained.

静置10天后得到磁性液体。

[0061]

The specific magnetization curve of the synthesized magnetic liquid is shown in Figure 4.

所合成磁性液体的比磁化曲线如图4所示。

[0062]

Example 3: Preparation of magnetic liquid using the method of the present invention

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实施例3采用本发明方法制备磁性液体

[0063]

Preparation of iron oxide nanoparticles in the first step

第一步氧化铁纳米微粒的制备

[0064]

As in Example 1.

如实施例1。

[0065]

Step 2: Preparation of the dispersion medium

第二步分散介质的制备

[0066]

The dispersion medium carrier liquid was prepared by mixing glycerol and water in a ratio of 94:6.

按甘油与水的比例为94：6配制分散介质载液。

Prepare a magnetic liquid with Φ_v = 0.02 and a nitric acid concentration of 4.46 × 10⁻² mol/L.

配制Φ _v =0.02的磁性液体，硝酸浓度为 4.46×10 ⁻² 摩尔/升。

[0067]

Step 3: Synthesis of Magnetic Liquid

第三步磁性液体合成

[0068]

The nanoparticles and carrier liquid were selected according to a volume ratio of 2:98.

按磁性纳米微粒粉体与载液的体积比为2：98的比例选取纳米粉体和载液。

A magnetic liquid with a particle volume fraction Φ_v of 0.02 was synthesized by dispersing nanoparticle powder in a carrier liquid.

将纳米微 粒粉体分散于载液中合成微粒体积分数Φ _v 为0.02的磁性液体。

[0069]

After standing for 10 days, a magnetic liquid was obtained.

静置10天后得到磁性液体。

[0070]

The specific magnetization curve of the synthesized magnetic liquid is shown in Figure 5.

所合成磁性液体的比磁化曲线如图5所示。