

Preparation of in-situ surface-modified nanosilica and its application in separating oil from water

Kai Liu, Nan Zheng, Xiaohong Li, Zhijun Zhang

Key Laboratory of Ministry of Education for Special Functional Materials, Henan University, Kaifeng 475001, Henan, People's Republic of China

E-mail: liukai19870403@yahoo.com.cn

Published in Micro & Nano Letters; Received on 18th November 2012; Revised on 19th December 2012; Accepted on 19th December 2012

A report is presented on the preparation of surface-functionalised nanosilica from silicon tetrachloride (SiCl_4 , one of the major by-products in the polycrystalline silicon industry) by in-situ surface modification in aqueous solution. The approach uses both SiCl_4 and sodium metasilicate as the silicon sources to generate nanosilica, whereas the proportion of sodium metasilicate and SiCl_4 is adjusted to control the pH value of the reaction system. In this way, desired SiO_2 nanoparticles were in-situ surface-modified by hexamethyldisilazane as soon as they were generated in the reaction solution, which makes it feasible to prevent the severe aggregation of nanosilica that often happens during the hydrolytic process. The obtained nanosilica with uniform particle size distribution (mean diameter 35–40 nm) shows superhydrophobicity (a water contact angle of 165°) and excellent organic dispersibility. Thanks to the low cost of raw materials as well as the superhydrophobicity and lipophilicity of as-prepared nanosilica, its application for improving the selective penetration of oil is primarily investigated. The result shows that quartz sand modified by as-prepared nanosilica can separate diesel oil from water successfully, which could be significant for improving crude oil recovery efficiency.

1. Introduction: Silicon tetrachloride (SiCl_4) is one of the major by-products in the polycrystalline silicon industry, but it causes serious environmental pollution as an expensive form of hazardous and irritant wastes [1]. Particularly, SiCl_4 is decomposed into toxic gaseous hydrogen chloride upon exposure to damp air, causing serious threats to people's health. Therefore use of by-product SiCl_4 as a silicon source for preparing superhydrophobic nanosilica is essential in preventing environmental pollution caused by SiCl_4 and in creating products with high added value [2].

Two main methods are currently available for dealing with SiCl_4 . One is hydrogenation of SiCl_4 under high temperature and high pressure yielding trichlorosilane [3]. Another is hydrolysis of SiCl_4 vapour in a flame of hydrogen and oxygen (at high temperature of 1400–1800°C) yielding fumed silica with high added value [4, 5]. The above two routes, however, are less cost-effective, because they rely on high energy consumption reactions to produce the pyrogenic products. Thus it is essential to seek more efficient alternative routes for dealing with by-product SiCl_4 . Heley *et al.* [6, 7] have tried to prepare silica via hydrolysis of SiCl_4 under alkaline conditions, however nanosized silica obtained by this method aggregates severely and possesses poor dispersibility, showing no value to industry.

Bearing those perspectives in mind, in the present research we have established a novel method to synthesise surface-modified nanosilica by in-situ surface modification in aqueous solution. With the established route, SiCl_4 is added dropwise to sodium metasilicate solution yielding nanosilica, and hexamethyldisilazane (HMDS) is also introduced into the reaction system to prevent nascent nanosilica from agglomeration, since the $-(\text{CH}_3)_3$ groups of the hydrolysed products of HMDS can be bonded to the surface of nanosilica resulting in increased inter-particulate repulsion. The present route is more convenient and cost-effective than the above-mentioned hydrogenation route and hydrolysis route for fabricating nanosilica from SiCl_4 , and it can be well adopted to prepare surface-functionalised nanosilica with superior hydrophobicity and organic dispersibility. This Letter reports the preparation of surface-functionalised nanosilica and its application in the separation of diesel oil from water.

2. Experimental

2.1. Preparation of nanosilica: First, 94 g of sodium metasilicate was dissolved in 800 ml of deionised water in a reactor equipped

with two isopiestic dropping funnels and a condenser. Then, 38 g of SiCl_4 was placed into one dropping funnel, and 18 g of HMDS was dissolved in absolute ethanol and placed into another dropping funnel. Upon the dropwise addition of SiCl_4 to the reactor under vigorous stirring at room temperature, SiCl_4 was hydrolysed. The reaction solution appeared turbid when the concentration of SiCl_4 reached a certain value, whereas more and more particles were generated upon continuous addition of SiCl_4 . When SiCl_4 was completely dripped into the reactor, HMDS, the surface modifier, was dropwise added to the reactor still under vigorous stirring, allowing the formation of foam from the aqueous solution. The resultant suspension was heated to 70°C and held there for 4 h, followed by filtering. The filtered cake was washed repeatedly using deionised water until Cl^- could not be detected with aqueous silver nitrate. The as-washed filtered cake was re-dispersed in the mixed solution of deionised water and ethanol (volume ratio 4 : 1) to form an emulsion. The resultant emulsion was spray-dried at an outlet temperature of 140°C, yielding white loose SiO_2 nanoparticles with good flowability.

An unmodified nanosilica sample was prepared in the same manner but in the absence of surface modifier HMDS.

2.2. Characterisation: A JEOL JEM-2100 transmission electron microscope (TEM) was used to observe the morphology of silica particles and estimate their size. Infrared spectra using KBr crystal in a wavenumber range of 400–4000 cm^{-1} were obtained with an AVATAR360 Fourier transform infrared spectrometer (FTIR). The water contact angle of nanosilica film was measured with an optical contact angle meter (DM-500 Drop master model). As-prepared nanosilica was dispersed in toluene. A glass slide was immersed into the resultant toluene solution containing as-prepared nanosilica. The immersed glass slide was lifted out of the toluene solution and dried at ambient condition giving ready-for-use nanosilica film after volatilisation of the toluene.

2.3. Preparation of modified quartz sand: As-prepared surface-modified nanosilica was ultrasonically dispersed in absolute alcohol for 10 min. Then, quartz sand with an average particle diameter of 0.15 mm was immersed in the solution for ~12 h. Upon completion of immersion, the quartz sand was

collected and dried in an oven at 80°C for several hours giving ready-for-use modified quartz sand after the evaporation of alcohol.

3. Results and discussion

3.1. Formation mechanism of nanosilica: Fig. 1 shows the formation mechanism of nanosilica, where Me stands for $-\text{CH}_3$. In-situ surface modification of nanosilica by HMDS is a condensation-like polymerisation process [8, 9], where the hydrolysed products of SiCl_4 and sodium metasilicate act as the monomers and HMDS as the chain terminator. The condensation polymerisation of the hydrolysed products is a process of chain growth, and the surface-modifying process is similar to the chain termination procedure.

First, SiCl_4 is rapidly hydrolysed to produce HCl and $\text{Si}(\text{OH})_4$ [10]. Anhydration among the hydroxyls of $\text{Si}(\text{OH})_4$ provides nuclei for the formation of primary nanosilica, whereas HCl is gradually neutralised by sodium metasilicate. When the pH value of the reaction system reaches about 10, sodium metasilicate is hydrolysed to form silicic acid. Primary nanosilicas' nuclei are continuously coated by silicic acid via condensation at three dimensions, generating nanosilica clusters through bonding among Si and O atoms. As soon as the nanoclusters are formed, trimethylsilyl originated from HMDS reacts rapidly with the hydroxyl of nanosilica, yielding a modifying layer on the surface of the nanoclusters. The trimethylsilyl substitute a mass of active hydroxyl groups of SiO_2 and give rise to a steric hindrance. As a result, nanoscale SiO_2 is prevented from continuously growing up or agglomerating, and the nanosilica particles 'capped' with organic compound are obtained by controlling the reaction conditions [11].

3.2. Structural characterisation of nanosilica

3.2.1 TEM observation of nano- SiO_2 : Usually, TEM analysis of particulates can provide the morphological information on a nanometre scale. Fig. 2 shows the TEM photographs of the surface-modified nano- SiO_2 (M- SiO_2) and unmodified nano- SiO_2 (UM- SiO_2) dispersed in absolute ethanol. UM- SiO_2 particles show signs of severe aggregation, possibly because of relatively strong interactions among the particles (Fig. 2a). After surface modification by HMDS (Fig. 2b), resultant nanosilica with a uniform particle size distribution (mean diameter 35–40 nm) appear as less severely aggregated spherical particles. This may

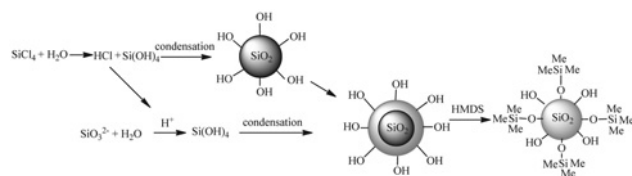


Figure 1 Formation mechanism of surface-modified nanosilica

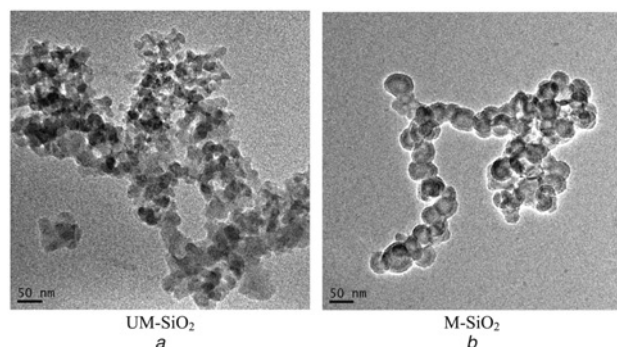


Figure 2 TEM photographs
a UM- SiO_2
b M- SiO_2 nanoparticles

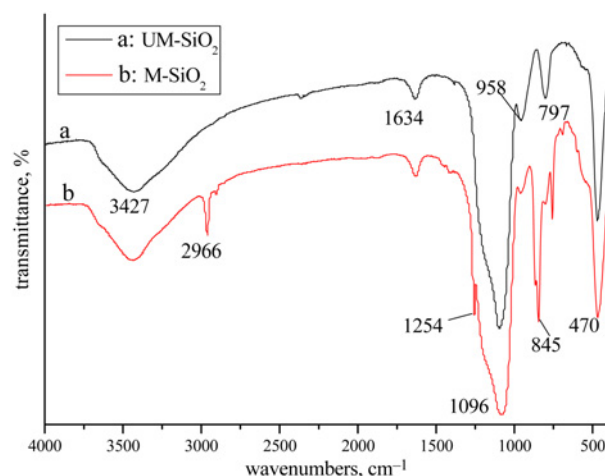


Figure 3 FTIR spectra of UM- SiO_2 and M- SiO_2

be closely related to the substitution of $-\text{OH}$ groups on the surface of nanosilica by $-(\text{CH}_3)_3$ groups of HMDS resulting in increased organophilic characteristics and inter-particle repulsion.

3.2.2 FTIR analysis: Fig. 3 shows the FTIR spectra of the surface-modified and unmodified nanosilica. The absorption bands around 3427 and 1634 cm^{-1} are attributed to the silanol group and adsorbed water. The absorption band near 2966 cm^{-1} corresponds to the stretching vibration of $-\text{CH}_3$. The absorption peaks at 1254 and 845 cm^{-1} are assigned to the stretching vibration of $\text{Si}-\text{CH}_3$. The above-mentioned FTIR analytical results confirm that the functional groups of HMDS have been successfully introduced onto the surface of nanosilica [12].

3.3. Dispersibility and hydrophobicity of nano- SiO_2 : As-prepared surface-capped nanosilica can be well dispersed in various organic solvents such as diesel oil, liquid paraffin, propanediol and CCl_4 affording transparent solutions (see Fig. 4a: the optical micrographs of diesel oil and CCl_4 containing surface-modified nanosilica). Besides, these organic solvents can rapidly spread over the film made of surface-capped nanosilica, which implies that the surface-capped nanosilica shows superior lipophilicity. In one word, surface-capped nanosilica can be well dispersed in apolar solvents, which is attributed to polar to weak polar or apolar conversion of its surface after being capped by HMDS. In the meantime, surface-capped nanosilica is superhydrophobic and tends to float atop water (Fig. 4a).]

Fig. 4b shows a water droplet on surface-modified and unmodified nanosilica films. Surface-modified nanosilica film has a water contact angle of about 165°, which indicates that surface-modified nanosilica possesses excellent hydrophobicity. This drastically differs from unmodified nanosilica prepared with the same

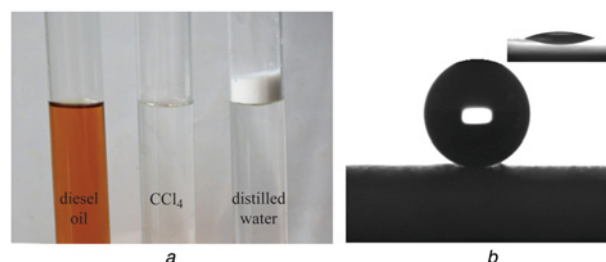


Figure 4 Dispersibility of surface-modified nanosilica in diesel oil, CCl_4 and distilled water (Fig. 4a), and shape of water droplet on nanosilica film (Fig. 4b)

method, since unmodified nanosilica has a water contact angle of about 21° (see the inset at the upper right corner of Fig. 4b).

The hydrophobicity of the surface-modified nanosilica mainly depends on its surface properties. On the one hand, the bulky $-\text{CH}_3$ groups in the surface-modifying layer of surface-capped nanosilica are repulsive against each other and are hydrophobic as well. On the other hand, the rough surface of microvoids (see Fig. 5) can store more air and entrap air therein, leading to hydrophobicity of surface-modified nanosilica with the assistance of the air bubbles [13–15]. As a result, the trimethylsilyl groups of the surface modifier and the air bubbles stored in the rough film surface jointly result in superior hydrophobicity of surface-modified nanosilica.

3.4. Application of surface-modified nanosilica in oil–water separation: The exploitation of oil reservoirs depends greatly on water flooding that is limited by lipophilic to hydrophilic transformation of porous core walls thereon after a long period of operation, leading to greatly increased water discharge and reduced oil recovery [16, 17]. The exploitation efficiency of the crude oil is highly dependent on the selective penetration of oil in the pores of oil reservoirs. Here, as-prepared nanosilica was used to modify quartz sand (referring to the micropores within the oil reservoir rocks), so as to improve the selective penetration of crude oil through the pores of the oil reservoirs.

The experiment of selective penetration of oil was carried out with the setup illustrated in Fig. 6. A total of 30 g of quartz sand modified by superhydrophobic and oleophilic nanosilica was placed into the right funnel, whereas the left funnel was charged with unmodified quartz sand with the same weight. When 50 ml of the total amount of mixture of diesel oil and water with the volume ratio of 1 : 1 was dropped onto the unmodified quartz sand, 19.5 ml of water and 0.8 ml of diesel oil penetrated through the unmodified quartz sand, and about 23.5 ml of diesel oil remained on the surface of the unmodified quartz sand (Fig. 6a). In contrast to the above, 17.5 ml of diesel oil penetrated through the modified quartz sand and fell into the measuring cylinder beneath it, whereas round about 24.0 ml of water (volume fraction of 96% of the total water) remained on the surface of the modified quartz sand (Fig. 6b).

When the mixture of diesel oil and water was poured onto the unmodified quartz sand, both diesel oil and water could penetrate through the sand. However, the sink rate of water with a larger density is greater than that of the oil, and hence a hydration film is easily formed at the surface of the quartz sand. Such a hydration layer prevents successive sinking of the oil and allows penetration of only a small amount of oil, leaving a large amount of oil stuck on the sand surface. This problem is often encountered in crude

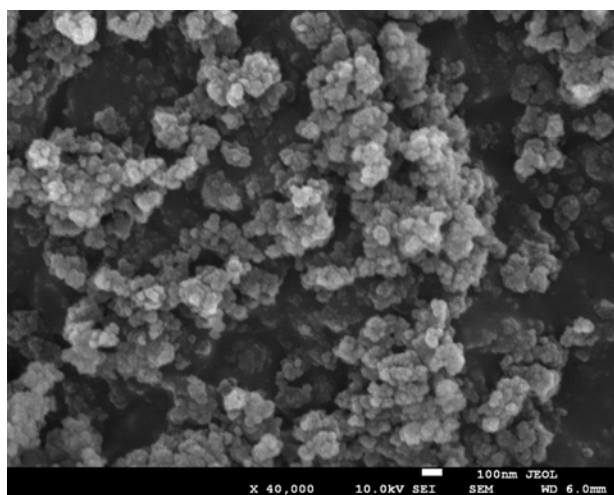


Figure 5 SEM photograph of surface-capped nanosilica



Figure 6 Separation of a mixture of diesel oil and water by unmodified quartz sand (Fig. 6a), and modified quartz sand (Fig. 6b)

oil extraction associated with a large volume of water flooding and significantly reduces oil recovery. Fortunately, after the quartz sand is modified with as-prepared nanosilica of superhydrophobicity and oleophilicity, water cannot pass through the pores but oil can easily pass through the pores. The modified quartz sand has excellent oil selective capability, which makes it feasible to greatly improve crude oil recovery efficiency.

4. Conclusions: Functionalised nanosilica has been prepared from sodium metasilicate and SiCl_4 via in-situ surface modification by HMDS, where sodium metasilicate acts as a pH conditioning agent and one of the two Si sources. As-prepared surface-capped nanosilica has been characterised by TEM and FTIR, and its wetting behaviour in water and dispersion behaviour in various organic solvents have been examined. It has been found that as-prepared nanosilica has uniform particle size distribution (mean diameter 35–40 nm). HMDS is combined to the surface of nanosilica and changes the polar surface to an apolar one. As a result, as-prepared surface-capped nanosilica possesses superhydrophobicity and excellent dispersibility in apolar organic solvents such as diesel oil and CCl_4 . The present approach provides a convenient and cost-effective method for dealing with SiCl_4 , the major by-product in the polycrystalline silicon industry. As-prepared superhydrophobic and oleophilic surface-capped nanosilica may find promising application in improving oil recovery efficiency of the petroleum extraction industry.

5. Acknowledgment: This research is financially supported by the National Key Basic Research Programme (project of ‘973’ Plan, grant no. 2013CB632303).

6 References

- [1] Wang Y.F., Nie L.J., Xiang Z.K., Song X.F.: ‘Preparation of high purity low hydroxyl synthetic fused silica glass’, *Adv. Mater. Res.*, 2011, **287–290**, pp. 276–280

- [2] Zhao Y., Pan G.: 'Manufacture of high purity low hydroxyl synthetic vitreous silica from industrial by-product silicon tetrachloride', *J. Non-Cryst. Solids*, 1982, **52**, pp. 521–529
- [3] Ivanov V.M., Trubitsin Y.V.: 'Approaches to hydrogenation of silicon tetrachloride in polysilicon manufacture', *Russ. Microelectron.*, 2011, **40**, pp. 559–561
- [4] Uchino T., Aboshi A., Kohara S., Ohishi Y., Sakashita M., Aoki K.: 'Microscopic structure of nanometer-sized silica particles', *Phys. Rev. B*, 2004, **69**, pp. 155409-1–155409-8
- [5] Liu C.C., Maciel G.E.: 'The fumed silica surface: a study by NMR', *J. Am. Chem. Soc.*, 1996, **118**, pp. 5103–5119
- [6] Heley J., Jackson D., James P.: 'Fine low density silica powders prepared by supercritical drying of gels derived from silicon tetrachloride', *J. Non-Cryst. Solids*, 1995, **186**, pp. 30–36
- [7] Heley J.R., Jackson D., James P.F.: 'The production of ultrafine silica powders from silicon tetrachloride: control of the primary particle size', *J. Sol-Gel. Sci. Technol.*, 1997, **8**, pp. 177–181
- [8] Wang Y.Q., Li Y.P., Zhang R.Y., Huang L., He W.W.: 'Synthesis and characterization of nanosilica/polyacrylate composite latex', *Polym. Compos.*, 2006, **27**, pp. 282–288
- [9] Zou H., Wu S., Shen J.: 'Polymer/silica nanocomposites: preparation, characterization, properties, and applications', *Chem. Rev.*, 2008, **108**, pp. 3893–3957
- [10] Ignatov S.K., Sennikov P.G., Razuvaev A.G., Chuprov L.A., Schrems O., Ault B.S.: 'Theoretical study of the reaction mechanism and role of water clusters in the gas-phase hydrolysis of SiCl_4 ', *J. Phys. Chem. A*, 2003, **107**, pp. 8705–8713
- [11] Zhang Z.J., Zhang J., Xue Q.J.: 'Synthesis and characterization of a molybdenum disulfide nanocluster', *J. Phys. Chem.*, 1994, **98**, pp. 12973–12977
- [12] Zhang Y., Zhang X., Ye H., Xiao B., Yan L., Jiang B.: 'A simple route to prepare crack-free thick antireflective silica coatings with improved antireflective stability', *Mater. Lett.*, 2012, **69**, pp. 86–88
- [13] Feng X., Feng L., Jin M., Zhai J., Jiang L., Zhu D.: 'Reversible super-hydrophobicity to super-hydrophilicity transition of aligned ZnO nanorod films', *J. Am. Chem. Soc.*, 2004, **126**, pp. 62–63
- [14] Li X.H., Cao Z., Liu F., Zhang Z.J., Dang H.: 'A novel method of preparation of superhydrophobic nanosilica in aqueous solution', *Chem. Lett.*, 2006, **35**, pp. 94–95
- [15] Li S., Li H., Wang X., Song Y., Liu Y., Jiang L., *ET AL.*: 'Super-hydrophobicity of large-area honeycomb-like aligned carbon nanotubes', *J. Phys. Chem. B*, 2002, **106**, pp. 9274–9276
- [16] Zheng N., Liu K., Li X.H., Zhang Z.J.: 'Preparation of super-hydrophobic nano-silica aqueous dispersion and study of its application for water resistance reduction at low permeability reservoir', *Micro Nano Lett.*, 2012, **7**, pp. 526–528
- [17] Wang K.L., Liang S.C., Wang C.C.: 'Research of improving water injection effect by using active SiO_2 nano-powder in the low-permeability oilfield', *Adv. Mater. Res.*, 2010, **92**, pp. 202–207