

In Situ Measurement of Surface Functional Groups on Silica Nanoparticles Using Solvent Relaxation Nuclear Magnetic Resonance

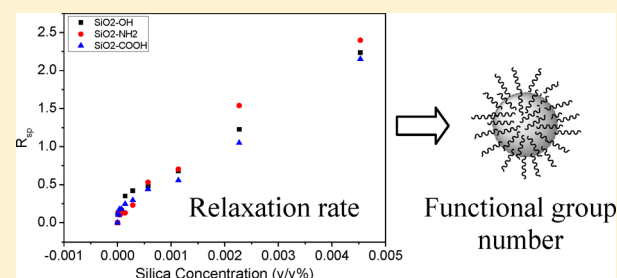
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Supporting Information

ABSTRACT: *In situ* analysis and study on the surface of nanoparticles (NPs) is a key to obtain their important physicochemical properties for the subsequent applications. Of them, most works focus on the qualitative characterization whereas quantitative analysis and measurement on the NPs under their storage and usage conditions is still a challenge. In order to cope with this challenge, solvation relaxation-based nuclear magnetic resonance (NMR) technology has been applied to measure the wet specific surface area and, therefore, determine the number of the bound water molecules on the surface of silica NPs in solution and the hydrophilic groups of various types grafted on the surface of the NPs. By changing the surface functional group on silica particles, the fine distinction for the solvent-particle interaction with different surface group can be quantitatively differentiated by measuring the number of water molecules absorbed on the surface. The results show that the number of the surface hydroxyl, amine, and carboxyl group per nm² is 4.0, 3.7, and 2.3, respectively, for the silica particles with a diameter of 203 nm. The method reported here is the first attempt to determine *in situ* the number of bound solvent molecules and any solvophilic groups grafted on nanoparticles.



INTRODUCTION

In situ sensitive detection on the surface physicochemical properties of engineered nanoparticles (NPs) in aerosol and colloidal solution is an important task and still a major challenge in analytical chemistry. Many technologies can be used to investigate functional groups on surfaces of NPs, each sensitive to a particular facet of the surface functional groups, such as inductively coupled plasma atomic emission spectrometry (ICP-AES),¹ thermogravimetric analysis (TGA),¹ X-ray photoelectron spectroscopy (XPS),² near-infrared (NIR),³ fluorescent labeling,⁴ grazing incidence X-ray fluorescence analysis,⁵ titration,⁶ element analysis,⁷ ¹H nuclear magnetic resonance (NMR)¹ methods, etc. However, *in situ*, non-destructive analysis and measurement of the relative number of the interacting partners, e.g., the solvent molecules and the surface functional groups on the particles, under their storage and usage conditions is a challenging task. As most particles are hydrophilic, the liquid water molecules as the probe to investigate the particle-solvent interaction is distinctly useful and facile compared with the gaseous molecules, e.g., N₂, Ar, and He, or the condensed molecules, e.g., surfactants, polymers, metal ions, and other small organic compounds.

Recently, low field NMR, i.e., solvation relaxation NMR has been proven to be a useful technology to study the interaction on the interface between the suspended matter and the solvent via probing the change of the magnetic relaxation time of the

hydrogen-containing solvent molecules in both free and bound state.⁸ The solvent molecule as a probe for surface interactions has an advantage over other methods because it avoids introducing new species that is selectively adsorbed to the active sites to be measured. The ability for the bulk solvent relaxation technology to distinguish the solvent molecules on particle surface and those in the bulk solution has been used to obtain valuable information on the interfacial interactions and structure,⁸ where a single, averaged relaxation time can be observed but is not generally true in the case of larger molecules like some surface functional groups.⁹ As solvent motion within such a layer is restricted, both the spin–lattice and spin–spin relaxation times, i.e., T_1 and T_2 , respectively, are significantly reduced.¹⁰ Depending on the relaxation time, the number of the adsorbed water molecules and, therefore, the surface functional groups on the particles can be measured *in situ*, respectively.

Fairhurst et al. used solvation relaxation NMR as a tool to study the dispersion and formulation behavior of various nanostructured carbon materials, and the technology is shown to give a good measure of the wet surface area comparable with

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that measured by TEM and BET.¹¹ Wang and Su et al. have studied the characterization of water molecules and their distribution in fiber materials¹² and the pore size distribution (PSD) of soft microspheres¹³ by solvation relaxation low-field nuclear magnetic resonance (LF-NMR) and found that the fastest fraction can be assigned to the water molecules trapped by hydrogen bond owing to the surface chemical group. Kato et al. characterized the nanoparticles in aqueous solution with bound water molecules using pulsed field gradient nuclear magnetic resonance and found that the slow diffusion of water molecules is attributed to the small amount of them bound strongly to PS-latex particles.¹⁴ Despite this, the quantitative determination of the number of hydroxyl group on solid particles is usually carried out by solid state ²⁹Si NMR, which Kickelbick et al. used to investigate the surface hydroxyl content of silica and other oxide particles with and without surface modification and determine the number of OH per nm² to be about 3.0 and 3.6 for aerosil 90 and spherosil, respectively.¹⁵ However, the number of non Si-bound groups can not be determined by ²⁹Si NMR or even ¹³C NMR due to complex structure of the carbon-containing ligands on the surface of a particle. *In situ* measurement on the number of any carbon-containing groups on the surface of a particle in its suspension state is a challenge, particularly the ligands that are not directly grafted to the surface of the particles via the R-[SiO_{1.5}]-bonds and, to the best of our knowledge, no such method that can differentiate the fine distinction among the various hydrophilic groups, such as -OH, -NH₂, and -COOH has been reported until now.

In this work, the solvation behavior of nanoparticles with different surface functional groups, such as hydroxyl (-OH), amine (-NH₂), and carboxyl (-COOH) in solution, has been systematically investigated using solvation relaxation NMR to determine *in situ* the coverage of the water molecules bound on the particles with different functional groups via measuring their wet specific surface area. It is the first attempt to quantitatively study the interaction between the surface groups on the particles and the solvent molecules in the layer restricted at the interface using solvation relaxation NMR technology.

EXPERIMENTAL SECTION

THEORY

The measurement model of relaxation NMR for pure solvent can be expressed as eq 1.⁸ In a simple suspension (solution) system, the solvent relaxation behavior can be understood by means of a rapid exchange between the solvent molecules constrained at an interface (bound) with a short relaxation time T_{2b} , and the free solvent molecules in the bulk with a longer time T_{2f} . Although the solvent molecules have different relaxation behaviors due to different status in a suspension system, a single-exponent magnetization can be obtained, which is related to the number of solvent molecules in each status, and the dynamically averaged relaxation rate between the two different environments can be given by eq 2.

$$M_y(t) = M_y(0)e^{(-t/T_2)} \quad (1)$$

$$\frac{1}{T_2} = \frac{1 - p_b}{T_{2f}} + \frac{p_b}{T_{2b}} \quad (2)$$

(where T_2 is the observed relaxation time and p_b is the fraction of the protons in the bound environment (or the fraction of the

time each proton spends in this environment, T_{2b}).¹⁶ Hence, the shorter the overall relaxation times, the more solvent molecules are bound on the surface. It is more convenient to demonstrate the results in terms of the averaged relaxation rate R_{av} , which is defined as $1/T_2$, or the specific relaxation rate R_{sp} , and describes the relaxation rate with respect to pure solvent, i.e., water.

$$R_{sp} = \frac{R_{av}}{R_f} - 1 \quad (3)$$

where $R_f = 1/T_{2f}$ of a standard, usually ultrapure water.

The proton deflection of water molecule and restoration to its original state after the relaxation can be detected and divided into two parts: one is the proton relaxation time for the free water molecules (T_{2f}), and the other one is that of the ones adsorbed on the surface of the particles (T_{2b}). The detailed formula derivation process for the calculation of the wet specific surface area (S_w) is shown in eq 4–10.¹¹ As seen in eq 10, the key to determine S_w is to obtain the relativity coefficient of wet specific surface area, K_A , which can be experimentally fitted according to eq 9.

$$R_{av} = P_f R_f + P_b R_b \quad (4)$$

$$P_b = 1 - P_f = \psi_p S L \rho_p \quad (5)$$

$$R_{av} = (1 - P_b) R_f + P_b R_b \quad (6)$$

$$R_{av} = \psi_p S L \rho_p (R_b - R_f) + R_f \quad (7)$$

$$K_A = L \rho_p (R_b - R_f) \quad (8)$$

$$R_{av} = \psi_p S K_A + R_f \quad (9)$$

$$S_w = (R_f R_{sp}) / (\psi_p K_A) \quad (10)$$

where R_{av} is the averaged relaxation rate, R_b is the relaxation rate of the liquid molecules bound on particle surfaces, R_f is the relaxation rate of the free liquid far from particles, P_f is the fraction of the free solvent molecules, P_b is the fraction of the solvent molecules bound on the particle surfaces, ψ_p is the particle volume to liquid volume ratio, S is the dry specific surface area, which is usually determined by gas sorption, e.g., BET, or by geometry calculation if the particles are monodispersed with known size, and S_w is the wet specific surface area of the particles. L is the thickness of the solvent layer bound on the particle surface, ρ_p is the density of the particles, and K_A is the relativity coefficient of wet specific surface area, which relates to the wettability of the particles and can be obtained by linear fitting as shown in Figure 5.

Materials. The colloidal silica nanoparticles used in this work were provided by the Technical Institute of Physics and Chemistry, CAS, and were synthesized by a modified Stöber process and functionalized by the corresponding silane coupling agent, e.g., (3-Aminopropyl) triethoxysilane (APTES) and then succinic anhydride (SA) to form NH₂- and COOH-COO-NH-grafted SiO₂ NPs, labeled as SiO₂-NH₂ and SiO₂-COOH, respectively. The as-synthesized sample is labeled SiO₂-OH. Prior to NMR tests, the silica nanoparticles were suspended in ethanol and centrifuged at 5000 rpm for 15 min to remove the supernant, and the washing procedure was repeated five times. The wet samples were dried under vacuum overnight. Finally, a given amount of SiO₂ dry

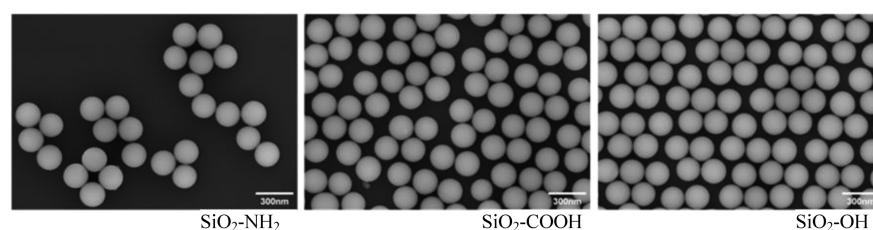


Figure 1. SEM images of the silica particles with different functional groups.

powder was dispersed in ultrapure water by sonication probe to form the particle suspensions with different concentration.

Pulse-NMR Measurement. All single-pulse experiments and ^1H NMR relaxation (T_2) measurements were carried out on a XiGo Nanotools - Acorn area working at a resonant frequency of 13 MHz for protons. For T_2 measurement, the 90° and 180° pulse durations were 7 and 14 μs , respectively, and the number of scans per sample, interpulse spacing (τ), and recycle delay were 4, 0.5, and 11000 ms, respectively. The measurement temperature was maintained at 22°C using an external temperature control unit connected to the sample chamber.

The CPMG pulse sequence was used to generate and collect the magnetization and the corresponding echo and determine the solvent relaxation time for the suspended sample. The method simply involved collecting the magnetization echo intensity after a 90° pulse and stopping the collection after the 180° pulse.

RESULT AND DISCUSSION

Characteristics of Colloidal SiO_2 . Figure 1 shows that the size of the silica particles with different functional groups is almost identical and smooth on the surfaces. The size of silica microspheres measured by SEM is 198, 199, and 198 nm for $\text{SiO}_2\text{-OH}$, $\text{SiO}_2\text{-NH}_2$ and $\text{SiO}_2\text{-COOH}$ sample, respectively, as shown in Table 1. These results are quite close to the

Table 1. Characteristics of Silica Particles

sample	mean diameter (SEM/nm)	sedimentary diameter (DCS/nm)	hydraulic diameter (DLS/nm)	zeta potential (mV)
$\text{SiO}_2\text{-OH}$	198	203	225	-31.2
$\text{SiO}_2\text{-NH}_2$	199	203	241	-6.63
$\text{SiO}_2\text{-COOH}$	198	203	221	-41.4

diameter (203 nm, see Supporting Information Figure S1) measured by differential centrifugal sedimentation (DCS) in gradient sucrose solution, where the bulk density of the silica particles is $2.2\text{ g}\cdot\text{cm}^{-3}$. The hydraulic diameter measured by DLS is 225 nm for $\text{SiO}_2\text{-OH}$, 241 nm for $\text{SiO}_2\text{-NH}_2$, and 221 nm for $\text{SiO}_2\text{-COOH}$, respectively, which is significantly larger than that measured by SEM. Zeta-potential of the bare silica particle, i.e., $\text{SiO}_2\text{-OH}$ is -31.2 mV , while the $\text{SiO}_2\text{-NH}_2$ sample is only -6.63 mV , indicating that the amine group is not fully grafted on the surface of $\text{SiO}_2\text{-OH}$, and the sample is unstable in solution, as visible precipitate can be seen in few minutes after sonication. The zeta potential for $\text{SiO}_2\text{-COOH}$ is -41.4 mV representing the formation of stable colloidal solution.

Surface Vibrational Structures of Colloidal SiO_2 . Figure 2 shows the ATR-IR spectra of the $\text{SiO}_2\text{-OH}$, $\text{SiO}_2\text{-NH}_2$, and

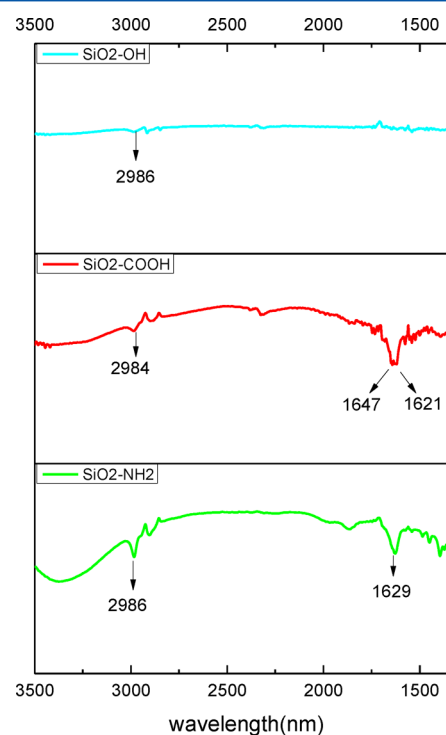


Figure 2. FTIR spectra of the silica particles with different functional groups.

$\text{SiO}_2\text{-COOH}$ nanoparticles used in this study. The typical peak at 2986 cm^{-1} corresponds to the $-\text{CH}_2-$ group from the ligand or the remaining solvent molecules, e.g., EtOH adsorbed on the particle surface. In addition, the peaks at 1647 and 1621 cm^{-1} correspond to COOH group, while the one at 1629 cm^{-1} can be attributed to amine groups, indicating that the different targeting functional groups are introduced to the surface of the silica nanoparticles. Figure S2 shows the FT-IR spectra of the as-synthesized SiO_2 NPs after washing five times and that calcined at 550°C for 6 h labeled as $\text{SiO}_2\text{-OH}$ and $\text{SiO}_2\text{-OH-calcined}$, respectively (see the Supporting Information). The peaks at 2986 , 2361 , 1402 cm^{-1} correspond to the CH_2/CH_3 group that is considered to come from ethanol molecules and can be completely removed by calcination.

XPS Spectra Analysis. On a surface that is fully hydroxylated, the H_2O molecules were adsorbed and covered all SiOH groups because of multiple hydrogen bonding. As the temperature increases, the physically adsorbed water begins to be evaporated first, then silanol groups on the surface are dehydrated.¹⁷ As seen from the XPS spectra in Figure S3 (see Supporting Information), all three samples contain N and C

element. It is not strange to observe N and C in $\text{SiO}_2\text{-NH}_2$ and $\text{SiO}_2\text{-COOH}$, which come from the ligand on the surface of the particles. The N and C element found in the as-synthesized $\text{SiO}_2\text{-OH}$ sample are thought to come from the adsorption of ammonia (NH_4^+OH) and solvent (EtOH) in the synthesis due to its negatively charged surfaces, that is, -31.2 mV of the zeta potential. The other elements for these sample are also analyzed by XPS as seen in Table S1 (see Supporting Information), where the Si:O ratio is higher than 1:2, indicating that the formation of nonstoichiometric SiO_x besides the lower element sensitivity of the photogenerated electrons for silicon compared with oxygen.

Thermogravimetric Analysis. Thermogravimetric analysis results show that the total weight loss for $\text{SiO}_2\text{-OH}$, $\text{SiO}_2\text{-NH}_2$ and $\text{SiO}_2\text{-COOH}$ is 13.77%, 13.87%, and 11.75%, respectively, compared with that (6.25%) of the calcined sample, SiO_2 -calcined as shown in Table S2 (see Supporting Information). Of them, the volatile organic compounds (VOCs) are 4.54%, 7.72%, and 3.92% for $\text{SiO}_2\text{-OH}$, $\text{SiO}_2\text{-NH}_2$, and $\text{SiO}_2\text{-COOH}$, respectively. In combination of differential weight loss (DTG) and heat change (DTA), the first DTG peak accompanying the endothermic peak starting from room temperature to 221 °C indicates the desorption/dehydration of the water molecules adsorbed on the surface of the sample, as shown in Figure S4–S7 (see Supporting Information). The mass loss at temperature of $395\text{--}527$ °C can be attributed to the decomposition of the R-NH₂ group grafted on $\text{SiO}_2\text{-NH}_2$ particles, while $405\text{--}670$ °C and $440\text{--}510$ °C can be attributed to that of the NH_4OH and R-NH-R' group adsorbed/grafted on $\text{SiO}_2\text{-OH}$ and $\text{SiO}_2\text{-COOH}$ samples, respectively. The decomposition of the propyl group occurs in a quite broad temperature range, e.g., $150\text{--}790$ °C for $\text{SiO}_2\text{-NH}_2$ particles, $228\text{--}775$ °C for $\text{SiO}_2\text{-COOH}$ particles, and $203\text{--}484$ °C for that of the ethyl group on $\text{SiO}_2\text{-OH}$ particles. The additional DTG peak between 220 and 365 °C for the $\text{SiO}_2\text{-COOH}$ sample is considered the evaporation/decomposition of SA molecules.

Pulse NMR Analysis. It can be seen in Figure 3 that the proton relaxation time decreases with the increase of the solid fraction in the suspension. The decay rate is faster for the $\text{SiO}_2\text{-OH}$ sample in low concentration and $\text{SiO}_2\text{-NH}_2$ sample in higher concentration, while the one for $\text{SiO}_2\text{-COOH}$ decreases smoothly. The relative relaxation rate is calculated by

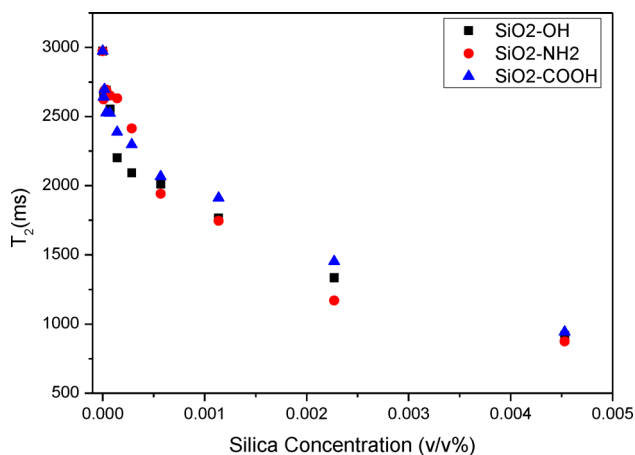


Figure 3. Spin–spin relaxation time (T_2) of the protons in the silica particle dispersions versus particle fraction (v/v).

eq 2–3 according to the data shown in Figure 3, and the obtained results are shown in Figure 4. The slope of R_{sp} for the

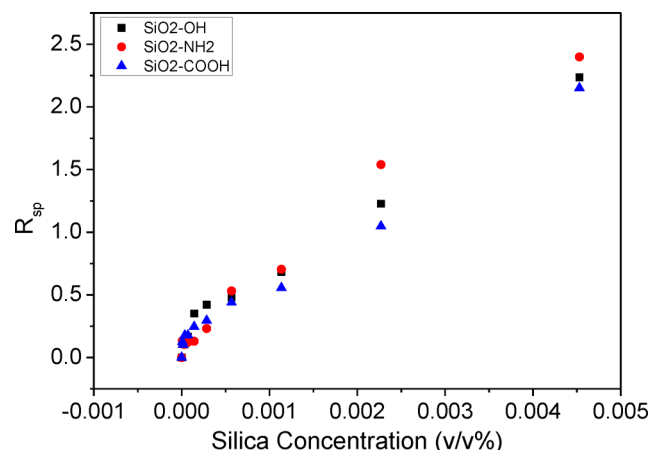


Figure 4. Relative relaxation rate (R_{sp}) of the protons in the silica particle dispersions to that of the DI water versus particle fraction (v/v).

three samples changes gradually due to different solvation degrees on the surface of the particles, where a linear relationship can be found between R_{sp} and its concentration.¹⁰ The relaxation time is proportional to the reciprocal number of the water molecules bound on the particle surfaces with different “wettability” that is influenced by the type and quantity of the functional groups grafted on them. The K_A value can be obtained from the slope of the linearly fitted plot between R_{av} and $S \cdot \Psi_p$ according to eq 9 as shown in Figure 5, where the specific surface area S is measured by gas isothermal sorption, e.g., BET. Thus, the wet specific surface area S_w can be obtained using the above-mentioned K_A and the measured R_{sp} value for a given Ψ_p according to eq 10, and the number of the water molecules (protons) bound on the surfaces is, therefore, determined.

The number of the water molecules bound on the surfaces and that of the surface functional group grafted on the silica particles is determined and listed in Table 2. Lee et al. studied the atomic structure and dehydration mechanism of amorphous silica by ^{29}Si solid-state MAS and ^1H NMR for SiO_2 nanoparticles. Assuming that the broad peak at $3\text{--}8$ ppm mostly consists of hydrogen-bonded silanol, the hydrogen densities of hydroxyl groups in a unit surface area would be 2.4 ± 0.8 OH/nm² for 7 nm amorphous silica nanoparticles and 3.5 ± 1.0 OH/nm² for 14 nm amorphous silica NPs.¹⁸ In our experiments, the number of surface silanol group per nm² is 4.0 obtained by the number of the water molecules constrained on the surface of a particle divided by the coordination number for the water molecules adsorbed around a functional group via H-bonding, i.e., two for the OH group, and larger than that reported by Lee’s results. However, this may be attributed to two reasons. One is that the particles used in this study are significantly larger than that used by Lee et al., and the larger particles have denser surface and more OH per unit surface area as seen in Lee’s work.¹⁸ Another reason is that a quite few micropores, i.e., a total pore volume of 0.11 cm³·g⁻¹, exists on the particles, which favors the formation of capillary condensation of the water molecules inside these pores and causes faster solvent relaxation and lower K_A . The number of the surface amine and carboxyl group per nm² is 3.7 and 2.3,

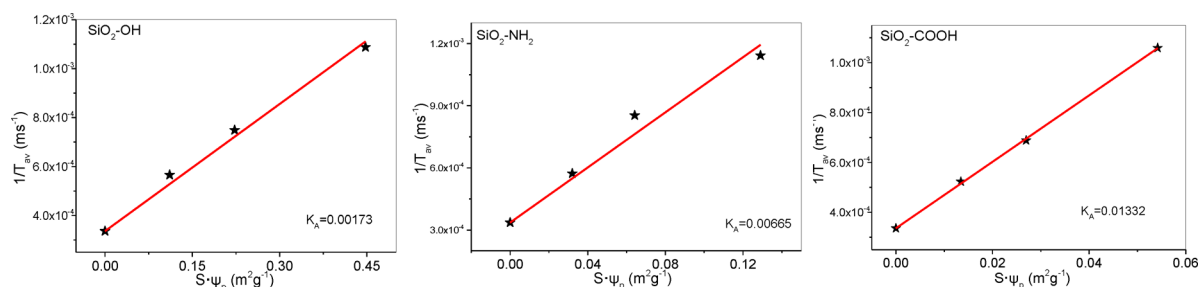


Figure 5. Determination of K_A according to eq 9.

Table 2. Surface Physicochemical Properties of Silica Particles

sample	dry specific surface area ^a (S , m^2/g)	theoretical specific surface area ^b (m^2/g)	wet specific surface area ^c (S_w , m^2/g)	number of water molecules adsorbed per $nm^{2,d}$	number of surface functional groups per $nm^{2,e}$
SiO ₂ -NH ₂	28.1	13.43	31.26	7.5	3.7
SiO ₂ -COOH	11.8	13.43	12.33	7.0	2.3
SiO ₂ -OH	97.5	13.43	116.54	8.0	4.0

^aMeasured by N₂ isothermal sorption (BET). ^bCalculated based on the sedimentary size of the particle. ^cMeasured by pulse-NMR T₂ relaxation according to eq 10. ^dCalculated according to 2.686 Å of the thickness of a layer of H₂O molecules¹⁹ and S . ^eCalculated by the water number divided by the coordinative number of each group.

respectively, according to their water molecule coordination number of 2 and 3 determined by Gaussian calculation. The decrease of the water absorbance indicates the blockage of the micropores due to the grafting of the functional groups. The coordination number of the adsorbed water molecules varies for different surface functional group.^{20–22} One NH₂ group can coordinate with two H₂O molecules, while one COOH and OH molecule can coordinate with three and two H₂O molecules, respectively, as shown in Figure S8.

For monodisperse particles, their surface wettability functionalized with various hydrophilic ligands, and the interaction behavior between them and the surrounding solvent molecules are both quite similar and hardly to be discriminated in a quantitative manner by one single technology such as surface titration, XPS, TGA, ICP-AES, etc. However, solvent relaxation NMR provides a method to analyze and measure the difference in a more efficient and facile way.

CONCLUSION

The interaction between the solvent molecules and the nanoparticles has been investigated and measured using solvation relaxation NMR. The study illustrates that water molecules can be used as a probe to analyze the structural and physicochemical properties of the surfaces of silica particles. By changing the surface functional group on a particle surface, the fine distinction of the solvent–particle interaction with different surface groups can be quantitatively analyzed and differentiated by measuring the number of monolayer water molecules constrained on the surface regardless of whether it is rough or smooth. The results show that the number of surface hydroxyl, amine, and carboxyl groups per nm^2 is 4.0, 3.7, and 2.3, respectively for the silica particles with a diameter of 203 nm. The technology provides a powerful quantitative analysis

approach to determine *in situ* the number and density of any grafted hydrophilic groups on nanoparticles.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b00923.

Particle size distribution by DCS, FTIR for SiO₂-OH samples, XPS results, DTG/DTA data for SiO₂-OH, SiO₂-NH₂, SiO₂-COOH, and SiO₂-cal, and the determination of the coordination number as shown in Figures S1–S8 and Table S1–S2 (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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