**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)⁸ 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.⁹ 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, 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., T₁ and T₂, 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...
that measured by TEM and BET.\textsuperscript{11} Wang and Su et al. have studied the characterization of water molecules and their distribution in fiber materials\textsuperscript{12} and the pore size distribution (PSD) of soft microspheres\textsuperscript{13} 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.\textsuperscript{14} Despite this, the quantitative determination of the number of hydroxyl group on solid particles is usually carried out by solid state \textsuperscript{29}Si 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 nm\textsuperscript{2} to be about 3.0 and 3.6 for aerosil 90 and spherosil, respectively.\textsuperscript{15} However, the number of non Si-bound groups can not be determined by \textsuperscript{29}Si NMR or even \textsuperscript{13}C 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\textsubscript{1.5}]\textemdash -bonds and, to the best of our knowledge, no such method can differentiate the fine distinction among the various hydrophilic groups, such as –OH, –NH\textsubscript{2}, 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 (–NH\textsubscript{2}), 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.

\section*{EXPERIMENTAL SECTION}

\section*{THEORY}

The measurement model of relaxation NMR for pure solvent can be expressed as eq 1.\textsuperscript{6} 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 $T_2$. 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.

\begin{equation}
M_p(t) = M_p(0)e^{-t/T_2}
\end{equation}

\begin{equation}
\frac{1}{T_2} = \frac{1 - P_b}{T_{2f}} + \frac{P_b}{T_{2b}}
\end{equation}

(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, $T_{2b}$).\textsuperscript{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 $R_w$, which is defined as $1/T_2$, or the specific relaxation rate $R_p$, and describes the relaxation rate with respect to pure solvent, i.e., water.

$$R_p = \frac{R_w}{R_1} - 1$$

where $R_1 = 1/T_{2f}$ 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.\textsuperscript{14} As seen in eq 10, the key to determine $S_w$ is to obtain the relatitivity coefficient of wet specific surface area, $K_w$, which can be experimentally fitted according to eq 9.

\begin{equation}
R_w = P_b R_f + P_b R_w
\end{equation}

\begin{equation}
P_b = 1 - P_r = \psi_p S L \rho_p
\end{equation}

\begin{equation}
R_w = (1 - P_b) R_f + P_b R_w
\end{equation}

\begin{equation}
R_w = \psi_p S L \rho_p (R_b - R_f) + R_f
\end{equation}

\begin{equation}
K_w = L \rho_p (R_b - R_f)
\end{equation}

\begin{equation}
R_w = \psi_p S K_w + R_f
\end{equation}

\begin{equation}
S_w = \frac{(R_w R_p)}{\left(\psi_p K_w\right)}
\end{equation}

where $R_w$ is the averaged relaxation rate, $R_w$ 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, $P_b$ is the fraction of the solvent molecules bound on the particle surfaces, $\psi_p$ 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, $\rho_p$ is the density of the particles, and $K_w$ is the relatitivity 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.

\textbf{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 NH\textsubscript{2} and COOH\textemdash NH\textsubscript{2} and COOH-grafted SiO\textsubscript{2} NPs, labeled as SiO\textsubscript{2}\textemdash NH\textsubscript{2} and SiO\textsubscript{2}\textemdash COOH, respectively. The as-synthesized sample is labeled SiO\textsubscript{2}\textemdash OH. Prior to NMR tests, the silica nanoparticles were suspended in ethanol and centrifuged at 5000 rpm for 15 min to remove the supernatant, and the washing procedure was repeated five times. The wet samples were dried under vacuum overnight. Finally, a given amount of SiO\textsubscript{2} dry
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 $^1$H 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 us, respectively, and the number of scans per sample, interpulse spacing ($\tau$), 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 SiO$_2$−OH, SiO$_2$−NH$_2$ and SiO$_2$−COOH sample, respectively, as shown in Table 1. These results are quite close to the 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 g·cm$^{-3}$. The hydraulic diameter measured by DLS is 225 nm for SiO$_2$−OH, 241 nm for SiO$_2$−NH$_2$, and 221 nm for SiO$_2$−COOH, respectively, which is significantly larger than that measured by SEM. Zeta-potential of the bare silica particle, i.e., SiO$_2$−OH is −31.2 mV, while the SiO$_2$−NH$_2$ sample is only −6.63 mV, indicating that the amine group is not fully grafted on the surface of SiO$_2$−OH, and the sample is unstable in solution, as visible precipitate can be seen in few minutes after sonication. The zeta potential for SiO$_2$−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 SiO$_2$−OH, SiO$_2$−NH$_2$, and SiO$_2$−COOH nanoparticles used in this study. The typical peak at 2986 cm$^{-1}$ corresponds to the −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 SiO$_2$−OH and SiO$_2$−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$_2$O 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 SiO₂−NH₂ and SiO₂−COOH, which come from the ligand on the surface of the particles. The N and C element found in the as-synthesized SiO₂−OH sample are thought to come from the adsorption of ammonia (NH₃·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 SiO₂ 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 SiO₂−OH, SiO₂−NH₂ and SiO₂−COOH is 13.77%, 13.87%, and 11.75%, respectively, compared with that (6.25%) of the calcined sample, SiO₂-calced as shown in Table S2 (see Supporting Information). Of them, the volatile organic compounds (VOCs) are 4.54%, 7.72%, and 3.92% for SiO₂−OH, SiO₂−NH₂, and SiO₂−COOH, respectively. In combination of differential weight loss (DTG) and heat change (DTA), the first DTG peak accompanying the endothermal 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 395−527 °C can be attributed to the decomposition of the R−NH₂ group grafted on SiO₂−NH₂ particles, while 405−670 °C and 440−510 °C can be attributed to that of the NH₄OH and R−NH−R’ group adsorbed/grafted on SiO₂−OH and SiO₂−COOH samples, respectively. The decomposition of the propyl group occurs in a quite broad temperature range, e.g., 150−790 °C for SiO₂−NH₂ particles, 228−775 °C for SiO₂−COOH particles, and 203−484 °C for that of the ethyl group on SiO₂−OH particles. The additional DTG peak between 220 and 365 °C for the SiO₂−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 SiO₂−OH sample in low concentration and SiO₂−NH₂ sample in higher concentration, while the one for SiO₂−COOH decreases smoothly. The relative relaxation rate is calculated by eq 2−3 according to the data shown in Figure 3, and the obtained results are shown in Figure 4. The slope of Rsp for the three samples changes gradually due to different solvation degrees on the surface of the particles, where a linear relationship can be found between Rsp and its concentration.

![Figure 3](image3.png)

**Figure 3.** Spin−spin relaxation time (T₂) of the protons in the silica particle dispersions versus particle fraction (v/v).

![Figure 4](image4.png)

**Figure 4.** Relative relaxation rate (Rsp) of the protons in the silica particle dispersions to that of the DI water versus particle fraction (v/v).
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 physicochemical properties of the surfaces of silica particles can be differentiated.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 function-alized 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

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## REFERENCES


