Organosilane Grafted Silica: Quantitative Correlation of Microscopic Surface Characters and Macroscopic Surface Properties

Tuo Ji,^[a] Chi Ma^[b], Logan Brisbin,^[a] Liwen Mu,^[a] Christopher G. Robertson,^[c] Yalin Dong^[b] and Jiahua Zhu^{[a]*}

[a] Intelligent Composites Laboratory, Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, OH 44325 USA

[b] Department of Mechanical Engineering, The University of Akron, Akron, OH 44325 USA

[c] Eastman Chemical Company, 260 Springside Dr, Akron, OH 44333

*Corresponding author. E-Mail: jzhu1@uakron.edu. Tel: 1-(330)972-6859.

ABSTRACT

In polymer composites, organosilanes are often used to modify the surface property of silica nanoparticles and improve the interfacial properties. Surface properties of the modified silica, such as grafting density and consequent surface energy, largely depend on the molecular structure of the silane. Achieving maximum interfacial bonding between the filler and polymer requires precise control of silica surface property. In this work, four silanes with similar molecular structure but different alkyl chain lengths, trimethoxy(propyl)silane, trimethoxy(octyl)silane, hexadecyltrimethoxysilane and trimethoxy(octadecyl)silane, are selected as model agents to study their roles in influencing silica surface property. The grafting density of silane on the silica is well controlled by regulating the reaction conditions. Three main surface characters, silane grafting density, surface energy and surface potential, are measured. More importantly, a linear relationship has been correlated when plotting grafting density vs. surface energy and grafting density vs. surface potential. Utilizing these relationships, a linear model has been developed to predict grafting density and surface energy by simply measuring surface potential. This model has been validated by both commercial silica and synthesized silica particles of different sizes.

Keywords: Silica, silane grafting density, surface energy, surface potential, linear correlation

1. INTRODUCTION

Surface functionalization of silica nanoparticles has become an essential for its numerous successful applications, such as drug delivery, support of heterogeneous catalyst, reinforcing filler and *etc.*[1-6] Organosilane, abbreviated as silane in this work, is the most widely used chemical agent for silica surface modification. Silane molecules are typically comprised of two functional parts, one part reacts with the silica surface to form covalent bond and the other forms physical/chemical interactions with the surrounding materials. The wide variety of silane structures, including alkyl chain length, terminal functional groups and number of reactive sites,[7] provides a great platform to design silica surface functionalities. Numerous work has been reported on the assembling behavior and patterning of silane molecules on different substrates.[8-11] Silane grafting has resulted in a variety of practical benefits in terms of material performance. For instance, bis(triethoxysilylpropyl) tetrasulfane can enhance the dispersion and compatibility of silica nanoparticles in the dense membrane of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), which affects methanol diffusion selectivity in the liquid.[12] Also, it is possible to design nanoparticles with superhydrophobic properties.[13, 14] Indeed, the silane molecule structure determines the subsequent surface properties to a great extent, but it is not the only factor since silane patterning and surface coverage also govern surface properties in most cases.[7, 15] Therefore, the silane's molecular structure and surface coverage are equally important to achieve the desired surface properties.

The determination of interfacial bonding and quantification of silane grafting density have been studied by using different characterization techniques.[16-18] For example,

nuclear magnetic resonance (NMR) and fourier transform infrared (FT-IR) are very useful qualitative tools to identify covalent bond formation, surface group species and cross-linking.[18, 19] To further quantify the amount of grafted molecules, thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM) were used to provide specific surface information on loading, atomic ratio of different elements, and grafting coverage, respectively.[16, 20-22] A microscopic understanding of silane function requires a precise quantification of silane grafting density (or coverage) on silica surface. Traditionally, only a partial surface property can be accessed by using single characterization technique, which provides only limited information and it is difficult to correlate the macroscopic surface properties. Therefore, tremendous research efforts have been devoted to obtain quantitative information on surface functional groups by combining different techniques.[23] For example, Fischer et al. found the relationship between fluorescence and XPS signals, which allows a direct correlation between an analysis of fluorescence and quantification of XPS.[20] However, it met significant challenges to quantify the grafting density of silane without nitrogen element such as silanes with aliphatic chains.[24] M. Rostami et al. utilized tensile strain experiments and dynamic mechanical thermal analysis to provide information on interfacial adhesion. By controlling the loading of silane-treated silica, it was shown that interfacial interactions were directly proportional to the amino silane content on silica nanoparticles.[25] Those methods mentioned above require lengthy sample preparation and skillful operation of expensive instruments, which greatly restricts their use in practical applications.

Besides the techniques mentioned above, some other macroscopic surface properties,

such as surface potential, wettability and surface energy[26, 27] can be used to quickly index the surface property as well. However, a quantitative correlation between microscopic information and macroscopic surface properties is not available right now. Once a mathematical model between microscopic surface information and macroscopic surface properties can be built, then, the microscopic information can be directly speculated by macroscopic surface properties without involving lengthy sample preparation and expensive instrumental analysis.

In this work, we selected four different silanes with similar molecular structure but different alkyl chain lengths to modify the silica surface. By controlling the silane grafting density across a wide range, different surface properties including surface energy and surface potential can be obtained. The relationship among silane grafting density, surface energy and surface potential on both commercial silica and synthesized silica are explored. A linear model is built and validated to predict the silane grafting density and silica surface energy from zeta potential. Comparing with conventional quantification methods, like NMR, XPS, this method provides obvious advantages of convenient sample preparation and short testing time.

2. EXPERIMENTAL

2.1 Materials

Triethoxy(ethyl)silane (TEES, 99%), trimethoxy(propyl)silane (TMPS, 97%), trimethoxy(octyl)silane (TMOS, 96%), hexadecyltrimethoxysilane (HDTMS, 85%), trimethoxy(octadecyl)silane (OTMS, 90%), methanol ($\geq 99.8\%$), commercial silica nanoparticles (α -SiO₂, ~16 nm) and tetraethyl orthosilicate (TEOS, 98%) were purchased

from Sigma Aldrich. Formic acid (97%) was purchased from Acros Organics. Ammonium hydroxide (28%) was purchased from BDH chemicals. Ethanol was purchased from Decon Labs. Inc. The structural and compositional information of silane molecules are provided in Table 1. All chemicals were used as received without further purification. Deionized water (Millipore) was used throughout the experiment.

Table 1. Detailed information of silanes used in this work.

Silane	Structure	Molecular formula	Mw (g·mol ⁻¹)	r _{a/s}
TEES		C ₈ H ₂₀ O ₃ Si	192.3	0.15
TMPS		C ₆ H ₁₆ O ₄ Si	164.3	0.26
TMOS		C ₁₁ H ₂₆ O ₃ Si	234.4	0.48
HDTMS		C ₁₉ H ₄₂ O ₃ Si	346.6	0.65
OTMS		C ₂₁ H ₄₈ O ₃ Si	374.7	0.68

r_{a/s}: molecular weight ratio of alkyl chain to whole silane molecule.

2.2 Silica surface modification by silanes

One unit of silane was sonicated in 10.0 g of methanol:water (90:10) for 10 min and 1.0 g of formic acid was added into the mixture solution. After 30 min, 0.5 g of c-SiO₂ powder was added to above mixture solution and then reacted at 65 °C for 24 h. The ratio of silane/silica is 2.0, 2.5, 3.0, 3.5 and 4.0 mol% for TMPS, and the ratio is controlled at 0.5, 1.0, 2.0, 3.0 and 4.0 mol% for TMOS, HDTMS and OTMS. The resulting samples were separated

and rinsed with 200 mL methanol. The samples were then dried at 80 °C for 12 hours. The modified silica particles were named in the format of “silane-#”. “silane” represents the five selected silanes in this work, *i.e.* TEES, TMPS, TMOS, HDTMS and OTMS. “#” means the mole percentage of silane used to modify the silica nanoparticles. For example, TMPS-2, TMPS-2.5, TMPS-3, TMPS-3.5 and TMPS-4 were named for c-SiO₂ grafted by 2, 2.5, 3, 3.5 and 4 mol% of TMPS.

2.3 Synthesis of Silica particles

Silica particles with different sizes were prepared following the well-known Stöber method.[28] Firstly, ethanol and deionized water were mixed and kept in a sonication bath. Then, TEOS was dropwise added into the mixture and kept sonicating for 20 min. At last, ammonium hydroxide was added into the mixture and kept sonication for another hour. A white turbid suspension was formed afterwards. All the experiments were conducted at room temperature. Following the procedure, silica particles with three different sizes were synthesized by adjusting the mass ratio of reactants (TEOS:H₂O:Ethanol:NH₄OH), namely s1-SiO₂ (1:5.8:39.3:104.7), s2-SiO₂ (1: 27:19.7:52.3) and s3-SiO₂ (1:5.8:19.7:74.6). The synthesized silica were then modified with HDTMS and TMPS (silane/silica ratio equals to 3 mol%) via the same experimental procedure as used for the modification of c-SiO₂.

2.4 Characterization

The morphology of c-SiO₂ was characterized by transmission electron microscopy (FEI Scanning TEM). Samples for the TEM characterization were prepared by drying a drop of sample powder ethanol suspension on carbon-coated copper TEM grids. Brunauer–Emmett–Teller (BET) surface area analysis of c-SiO₂ was performed using a

TriStar II 3020 surface analyzer (Micromeritics Instrument Corp., USA) with N₂ adsorption–desorption isotherms at 77 K. Fourier transform infrared (FT-IR) spectra were recorded with a Digilab Excalibur FTS 3000 series FT-IR Spectrometer using KBr pellets. The silane loading was determined by thermogravimetric analysis (TGA, TA instrument Q500) in air from 20 to 700 °C with a heating rate of 10 °C/min. Contact angle images of c-SiO₂ and silane-grafted c-SiO₂ were collected by Rame-hart image system. The silica particles were tightly pressed on a glass slide with double sided tape. The unattached particles were removed by blowing air. Eight liquid drops (2.0 µL for both water and ethylene glycol) on each sample were recorded for the static contact angle (CA) measurement and the average value was reported. Zeta-potential were measured in 0.1 wt% particle suspension with a Malvern Fetasizer Nano ZS apparatus (Malvern, UK) at 25 °C.

3. RESULTS AND DISCUSSION

Fig.1. (a) TEM image of c-SiO₂ and (b) N₂ adsorption–desorption isotherms.

The morphology and surface area of the pure c-SiO₂ nanoparticles were characterized by TEM and N₂ adsorption-desorption isotherms, Fig. 1. The average diameter of c-SiO₂ nanoparticles is 16 nm with narrow size distribution in the range of 8-22 nm, Fig. 1(a). The

statistic particle size distribution is analyzed from 300 samples. Nitrogen adsorption-desorption isotherms were conducted at 77 K to characterize the pore structure and surface area of the silica particle, Fig. 1(b). The major adsorption occurred at high relative pressure ($0.6 < p/p_0 < 1.0$) and a slender hysteresis loop was observed. The shape of the curves belongs to the type IV isotherm with a H_1 hysteresis loop, which indicates the presence of mesopores.[29, 30] Looking at the aggregation structure of the c-SiO₂ particles in Fig. 1(a), it is not difficult to understand the existence of mesopores those are actually packing voids of c-SiO₂ nanoparticles. Analyzed by the multi-point BET method, the surface area of the c-SiO₂ is calculated as 199 m²/g.

Fig. 2. FT-IR spectrum of c-SiO₂ and silane grafted c-silica particles.

In order to confirm the successful grafting of silane on the c-SiO₂ surface, FT-IR spectrum was performed on both c-SiO₂ and silane-modified c-SiO₂, Fig. 2. The band

intensity of the pure c-SiO₂ at 480, 803, 947 and 1100 cm⁻¹ corresponds to the O-Si-O deformation, SiO₄ tetrahedron ring, Si-OH stretching and asymmetrical Si-O-Si stretching, respectively.[31] Besides these characteristic vibration bands from c-SiO₂, two additional CH₂ absorption bands at 2920 (asymmetric stretching) and 2840 cm⁻¹ (symmetric stretching) were observed in modified c-SiO₂. These CH₂ adsorption bands are attributed to the alkyl chain of silane molecules on the c-SiO₂ surface.[1, 32] The CH₂ bands are very much likely from the surface grafted silane. However, since polycondensation may occur during hydrolysis, it is difficult to exclude the possibility that the CH₂ may also come from the condensed aggregates.

Fig. 3. TGA results of c-SiO₂ grafted by (a) TMPS, (b) TMOS, (c) HDTMS and (d) OTMS of different loadings.

The mass fraction of the organic chains in each silane-modified c-SiO₂ is measured by

TGA in air up to 700 °C. For c-SiO₂, the weight loss was observed between 40 and 200 °C, which is due to the desorption of physisorbed water.[15] For silane modified silica, the weight loss was similar to that of the c-SiO₂ samples before 200 °C. However, a significant weight loss occurred from 200 to 650 °C, which is due to the decomposition of the alkyl chain grafted on the c-SiO₂ surface.[21, 33-35] It is assumed that all alkyl chains of silane were combusted at 650 °C and the rest of the siloxy groups stayed on the surface. Then, the grafted silane molar percentage ($M_s\%$) on silica can be calculated by following equation (1):

$$M_s\% = 1 / (1 + \frac{Mw_{silane}}{Mw_{silica}} \cdot (\frac{r_{a/s}}{\Delta m} - 1)) \quad (1)$$

where Mw_{silane} and Mw_{silica} are the molecular weight of silane and silica, respectively, Δm is the weight loss that occurred between 200 to 650 °C from the TGA results, $r_{a/s}$ is defined as the molecular weight ratio of the alkyl chain versus the whole silane molecule. For example, the Δm of TMPS-2 is 1.1% after subtracting 0.8% of the weight loss occurred to c-SiO₂. The $r_{a/s}$ is 0.26 and Mw_{silane} is 164.3 for TMPS. According to equation (1), the actual TMPS molar percentage is calculated as 1.5% for TMPS-2. Considering the measured surface area of 199 m²/g, the silane grafting density on c-SiO₂ can be further calculated as 0.79/nm². Theoretical calculation by Material Studio gives the cross-section area of 0.32 nm² for TMPS, TMOS, HDTMS and OTMS. Based on the assumption of single layer grafting and vertical alignment of each TMPS molecule on silica surface, the silane surface coverage of TMPS-2 achieves 25.2%. Following this methodology, the actual surface coverage and grafting density of silanes in each sample are calculated and summarized in Table 2.

Table 2. Summary of surface silanes in each c-SiO₂.

$\Delta M(\%)$	$M_s(\%)$	$D_c(\%)$	N_s / nm^2
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TMPS-2	1.09	1.56	25.20	0.79
TMPS-2.5	1.30	1.88	30.22	0.94
TMPS-3	1.57	2.28	36.74	1.15
TMPS-3.5	1.71	2.49	40.16	1.26
TMPS-4	2.04	3.00	48.31	1.51
TMOS-0.5	1.53	0.39	6.32	0.20
TMOS-1	2.10	0.71	11.36	0.36
TMOS-2	2.43	0.89	14.32	0.45
TMOS-3	2.93	1.17	18.87	0.59
TMOS-4	3.60	1.56	25.07	0.78
HDTMS-0.5	1.78	0.26	4.27	0.13
HDTMS-1	2.28	0.40	6.49	0.20
HDTMS-2	2.71	0.52	8.42	0.26
HDTMS-3	3.03	0.61	9.87	0.31
HDTMS-4	3.19	0.66	10.61	0.33
OTMS-0.5	2.21	0.34	5.49	0.17
OTMS-1	2.42	0.39	6.33	0.20
OTMS-2	2.86	0.50	8.09	0.25
OTMS-3	3.28	0.61	9.79	0.31
OTMS-4	3.50	0.66	10.69	0.33

Ms: molar ratio, Dc: degree of coverage, Ns: silane number per nm².

Fig. 4. Contact angle of water and ethylene glycol on c-SiO₂ grafted by (a) TMPS, (b) TMOS, (c) HDTMS and (d) OTMS.

To quantify the surface energy of c-SiO₂ after grafting different loadings of silanes,

both water and ethylene glycol were used as probing liquids to measure the CA of each sample. As shown in Fig. 4, the c-SiO₂ shows an apparent hydrophilic surface with CA_(water)=30° and CA_(ethylene glycol)=54°, respectively. After grafting silane molecules, the water contact angle increased significantly, indicating the transition of surface property from hydrophilic to hydrophobic. By applying the Owens–Wendt model,[36] both dispersive and polar contributions to the surface energy can be calculated using equation (2):

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_S^D \gamma_L^D} + 2\sqrt{\gamma_S^P \gamma_L^P} \quad (2)$$

where γ_L^D and γ_L^P are the dispersive component and polar component of the surface energy of the liquid probe (mN /m²). Likewise, γ_S^D and γ_S^P are the dispersive component and polar component of surface energy of the solid (J/m²). Knowing the contact angles of both water and ethylene glycol, the γ_S^D and γ_S^P can be calculated and the surface energy is 96.1 mN·m⁻¹. The contact angle and surface energy of all the samples are summarized in Table 3. It's obvious that the surface energy decreases with increasing silane grafting density, Fig. 5, which is the case for all the four selected silanes due to their low surface energy alkyl terminal groups. Moreover, a highly linear relationship has been found correlating the grafting density of four silanes and surface energy of modified c-SiO₂ with a correlation factor $R^2 \geq 0.96$, from linear fitting on the solid triangle data points in Fig. 5. In other words, the surface energy of the modified-silica is directly related to the silane surface coverage. From the linear regression equations of the four silanes, it is not difficult to find a larger slope from the fitting line of silanes with longer alkyl chains. With a similar silane grafting density on silica, a longer alkyl chain in silane leads to a lower surface energy. This phenomenon is consistent with previous literature which reports that longer alkyl chains facilitate more

ordered structure and thus lower surface energy.[21, 37]

Fig. 5. Relationship of grafting density vs. zeta potential and grafting density vs. surface energy for silica grafted by (a) TMPS, (b) TMOS, (c) HDTMS and (d) OTMS.

The grafted silane on silica surface also changes its surface charge, which reflects in the change of zeta potential. According to the double-layer theory, silica nanoparticles in suspension tend to attract ions to their surface.[27] The electric potential that exists at the diffusion boundary will be affected by any property change on the silica particles including but not limit to grafted organic groups.[38, 39] The measured zeta potential of silane-modified c-SiO₂ is summarized in Table 3. As expected, the c-SiO₂ acquires the lowest potential of -32.2 mV. The zeta potential increased but remained a negative value after grafting the silanes. The silica becomes less hydrophilic after grafting silanes since partial hydrophilic sites have been replaced by hydrophobic organic groups. These grafted organic groups are not able to attract ions from solution and therefore decrease the potential across

the double layer. In Fig. 5 (square symbol), the surface potential has a strong linear relationship with silane grafting density having a correlation factor of $R^2 \geq 0.90$. All these results reveal a good linear relationship between silane grafting density, surface energy and surface zeta potential. By acquiring one of these properties, the other two can be conveniently accessed from the linear relationship.

Table 3. Surface property of silane-modified silica particles.

	<i>Dc</i> / %	<i>Ns</i> / nm ²	θ_{water} / °	θ_{EG} / °	<i>G</i> / mN·m ⁻¹	<i>Zeta potential</i> / mV
c-SiO ₂	0	0	30	54	96.1	-32.2
TMPS-2	25.2	0.79	76	36	41.4	-22.8
TMPS-2.5	30.2	0.94	87	49	38.6	-20.7
TMPS-3	36.7	1.15	102	58	30.1	-18.5
TMPS-3.5	40.2	1.26	112	83	23.3	-16.9
TMPS-4	48.3	1.51	125	68	13.8	-13.5
TMOS-0.5	6.3	0.20	50	70	79.6	-25.8
TMOS-1	11.4	0.36	90	40	54.4	-24.7
TMOS-2	14.3	0.45	72	35	40.3	-22.0
TMOS-3	18.9	0.59	125	60	24.4	-23.2
TMOS-4	25.1	0.78	128	78	8.9	-17.3
HDTMS-0.5	4.3	0.13	62	65	47.3	-28.4
HDTMS-1	6.5	0.20	86	56	31.4	-24.5
HDTMS-2	8.4	0.26	90	64	26.1	-22.1
HDTMS-3	9.9	0.31	105	43	10.5	-20.6
HDTMS-4	10.6	0.33	121	67	8.2	-18.5
OTMS-0.5	5.5	0.17	98	55	43.4	-28.2
OTMS-1	6.3	0.20	99	60	40.7	-25.8
OTMS-2	8.1	0.25	103	56	23.0	-23.9
OTMS-3	9.8	0.31	113	34	16.0	-23.4
OTMS-4	10.7	0.33	114	53	7.9	-20.7

Fig. 6. Correlation between the slope of fitting lines (Fig. 5) and carbon number in the alkyl chain of different silanes.

Besides the linear relationship among the surface properties of each silane in Fig. 5, it is also found that the slope of the fitting lines changes monotonously with increasing the carbon number of the alkyl chain. The correlation between the slope of the fitting lines (both surface energy and zeta potential) and alkyl chain carbon number of different silanes is plotted in Fig. 6. A highly linear relationship with correlation factor of $R^2 \geq 0.97$ was found among different silanes. This linear relationship is useful to predict the slope of fitting lines for other silane molecules with C3-C18 alkyl tail chains. It is also worth noting that the intercept of the fitting lines (both grafting density vs. surface energy; grafting density vs. surface potential) in Fig. 5 are very close to each other. Therefore, a linear prediction model was constructed by taking the calculated slope and average intercept. According to two linear regression formulas in Fig. 6, the following two equations (3) and (4) can be derived to

predict silane grafting density (N'_s) and surface energy (G'):

$$N'_s = \frac{Z+32.1}{1.4x+7} \quad (3)$$

$$G' = -(14.7x + 7.6)N'_s + 93.5 \quad (4)$$

where x is the alkyl chain carbon number of silane and Z is the measured zeta potential. By inputting the alkyl chain carbon number and measured zeta potential, silane grafting density can be calculated by equation (3). Based on the calculated silane grafting density, surface energy can be further calculated by equation (4).

To test the validity of these two derived equations, another set of silica samples modified with different ratios of silane were prepared and named TMPS-1.5, TMOS-3.5, HDTMS-2.5, OTMS-3.5 and TEES-2.5. By measuring the zeta potential (Z) of these silica particles and inputting the carbon number (x), N'_s and G' could be calculated from equations (3) and (4), respectively. The detailed calculations on grafting density and surface energy of these four samples are summarized in Table 4. Meanwhile, TGA and contact angle measurements were conducted to quantify the silane grafting density and surface energy, respectively. The error percentage between the calculated results and the experimental results is mostly around 7-17%. To further verify the applicability of the regressed equations in predicting the properties of silica modified with other silanes, TEES was used to modify c-SiO₂. Similar prediction accuracy could be obtained, Table 4. To conclude, this method could serve as a useful tool to quickly predict silane grafting density and surface energy from simple and fast zeta potential measurement.

Table 4. Comparison of calculated and measured results with c-silica.

Calculated value	Measured value	Error
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Sample	Z /mV	Ns' /nm ²	G' /mN·m ⁻¹	Δm /%	θ_{water}	θ_{EG}	Ns /nm ²	G /mN·m ⁻¹	E_{Ns} /%	E_G /%
TMPS-3.25	-20.5	1.04	40.0	2.1	84.0	49.4	0.94	35.8	10	12
TMOS-3.5	-23.2	0.49	32.3	2.4	101.4	56.4	0.45	30.2	9	7
HDTMS-2.5	-25.9	0.21	42.3	2.1	83.3	46.3	0.18	38.2	17	11
OTMS-3.5	-22.8	0.29	14.9	3.3	114.2	38.8	0.31	16.2	8	8
TEES-2.5	-21.4	1.27	65.2	1.8	41.8	12.3	1.39	55.6	9	15

Table 5. Summary of physical properties of synthesized silica particles.

	SA /m ² g ⁻¹	D _{particle} /nm	Z ₀ /mV	G ₀ /mN m ⁻¹
s1-SiO ₂	389	264.9±67.7	-53.5	106
s2-SiO ₂	113	61.3±19.1	-55.7	113
s3-SiO ₂	196	14.9±5.5	-53.2	104

Fig. 7. TEM image and statistical particle size distribution of (a) s1-SiO₂, (b) s2-SiO₂ and (c) s3-SiO₂.

To further confirm the applicability of the proposed model for other silica particles, three different sized silica particles (s1-SiO₂, s2-SiO₂ and s3-SiO₂) were synthesized by using the Stöber method. The detailed properties of these synthesized particles refer to Table 5. TEM image and statistical particle size analysis of each silica particle are presented in Figure 7(a-c). All these synthesized silica samples show more negative surface potential and larger surface energy than that of c-SiO₂. The c-SiO₂ is fabricated by a high temperature process where silicon tetrachloride is processed at around 1800 °C. The s(1-3)-SiO₂ is hydrolyzed in liquid, which exposes more hydroxyl groups on the particle surface and behaves more

hydrophilic. The difference in surface wettability causes the large deviation of surface potential and surface energy between c-SiO₂ and s(1-3)-SiO₂. It is worth mentioning that Z_0 and G_0 are about the same for s(1-3)-SiO₂. Therefore, equations (3) and (4) are modified into following equations (5) and (6) considering the difference of surface property between c-SiO₂ and s(1-3)-SiO₂:

$$N_s' = \frac{Z-Z_0}{1.4x+7} \quad (5)$$

$$G' = -(14.7x + 7.6)N_s' + G_0 \quad (6)$$

where the Z_0 and G_0 is the zeta potential and surface energy of synthesized SiO₂. Z_0 and G_0 for each silica is listed in Table 5. These synthesized silica particles were then modified by two different silanes, HDTMS and TMPS, to test the effectiveness of equations (5) and (6) in predicting the properties of modified s(1-3)-SiO₂. The calculation results are summarized in Table 6. The error percentage is relatively larger (max 29%, Table 6) compared to c-SiO₂ (max 17%, Table 4), which might be caused by two factors. Firstly, the change in particle size affects the surface energy measurement since it is very dependent on surface roughness. Secondly, particle size and surface wettability change affect the zeta potential measurement. Both of these factors lead to a shift of calculated properties from experimental results. Considering the difficulties in correlating microscale surface information to macroscale surface properties, the proposed model shows certain benefits in quickly predicting surface properties.

Table 6. Comparison of calculated and measured results with synthesized silica.

Silane	Silica	Z	Calculated value		Measured value		Error	
			N_s'	G'	N_s	G	E_{Ns}	E_G

		/mV	/nm ²	/mN·m ⁻¹	/nm ²	/mN·m ⁻¹	/%	/%
HDTMS	s1-SiO ₂	-46.2	0.25	47.6	0.22	66.4	13	28
HDTMS	s2-SiO ₂	-49.0	0.23	59.4	0.18	78.6	27	24
HDTMS	s3-SiO ₂	-44.2	0.31	32.0	0.26	45.3	18	29
TMPS	s1-SiO ₂	-42.2	1.01	61.5	1.18	83.2	14	26
TMPS	s3-SiO ₂	-42.7	1.27	62.7	1.08	79.1	13	21

4. CONCLUSION

Microscopic silane grafting density and macroscopic surface properties has been linked from silica nanoparticles grafted with five different alkyl chain terminated silanes (TMPS, TMOS, HDTMS, OTMS and TEES). By successful control of silane grafting density, linear relationships of grafting density vs. surface energy and grafting density vs. surface potential have been explored in silane-grafted silica. Moreover, based on the slope of the fitting lines from four selected silanes, a linear prediction model can be built to correlate fitting line slope and alkyl chain length and then to be used to predict surface property of silica grafted by other silanes with similar alkyl terminal groups. Using all the collected surface information, a model has been built to predict silane grafting density on silica surface and surface energy of the modified silica by taking surface potential and alkyl chain carbon number as inputs. This model has been verified by both commercial SiO₂ and wet-chemical synthesized SiO₂ with different particle sizes. This method provides quick access to the silica surface properties by a simple, fast and convenient surface potential measurement.

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