Supporting Information

Study of dispersion mechanisms of modified SiC powder: electrostatic repulsion and steric hindrance mechanism

Yanan Wei[1], Youxing Liu[2,3]

[1]*College of Sciences, Hebei University of Science and Technology, Shijiazhuang 050018, P.R. China*

[2]*Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, P.R. China*

[3] *Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China*

*Corresponding Author E-mail: liuyxpost@163.com

The number of Figures: 14.

The number of Tables: 6.

1. Reagents and instruments

Fig.S1 Particle size distribution of SiC powder.

Table S1 Particle characteristics and composition of SiC powder.

2. XPS analysis

Fig.S2 XPS spectra of original SiC powder.

Fig.S3 Si_{2p} XPS spectra of the original SiC powder.

3. FT-IR analysis

Fig.S4 FT-IR spectra of different powder, (a) SiC powder, (b) PVP modified SiC powder and (c) PVP and TMAH co-modified SiC powder.

4. **Orthogonal experiment of PVP and TMAH co-modification**

Table S2 The factors and levels table of orthogonal experiment about the modification of SiC powders.

Table S3 Schemes and results of orthogonal experiment about the modification of SiC powder.

Table S4 Analytical table of range for viscosity.

Table S5 Analytical table of range for solid content.

5. Comparison the performance of different slurry

Fig.S5 Minimum viscosity contrast of slurry prepared with SiC powder modified with different modifier.

Fig.S6 Maximum solid content contrast of slurry prepared with SiC powder modified with different modifier.

Table S6 Summarization of performances of modified SiC powder.

Fig.S7 Fracture surface SEM image of SiC ceramic green body fabricated by different modified SiC powder, (a) PVP modified SiC powder, (b) TMAH modified SiC powder, (a) PVP and TMAH co-modified SiC powder.

Fig.S8 Effect of shear rate on viscosity (45 Vol% of solid content).

6. **XRD analysis**

Fig.S9 XRD patterns of the original SiC powder (a), PVP modified SiC Powder (b), TMAH modified SiC Powder (c) and (d) TMAH and PVP co-modified SiC powder.

7. **Subside model of different SiC particles in water medium**

Fig.S10 Subside model of original SiC powder in water medium.

Fig.S11 Subside model of TMAH modified SiC powder in water medium

Fig.S12 Subside model of PVP modified SiC powder in water medium

Fig.S13 Subside model of PVP and TMAH modified SiC powder in water medium

8. Diagrammatic sketch of entanglement among long chains of PVP

Fig.S14 Diagrammatic sketch of entanglement among long chains of PVP

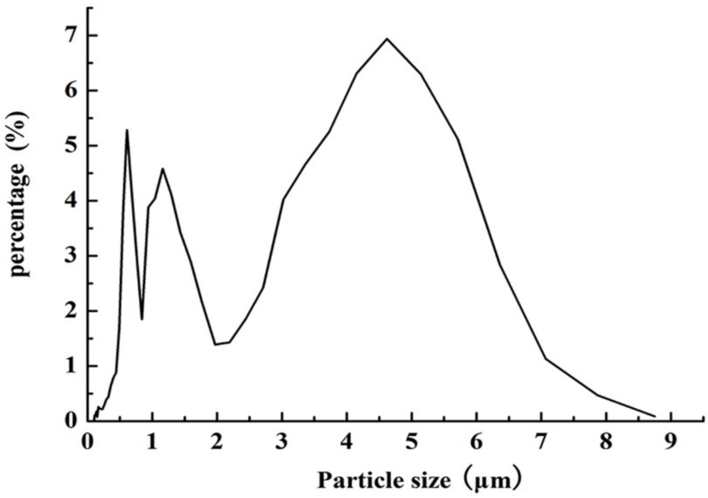

Fig S1. Particle size distribution of SiC powder.

Table S1 Particle characteristics and composition of SiC powder.

Powder	SiC wt%	Fe_2O_3 wt%	f-C wt%	f-Si wt%	Others wt%
Silicon carbide	99.27	0.27	0.18	0.09	0.19

2. XPS analysis

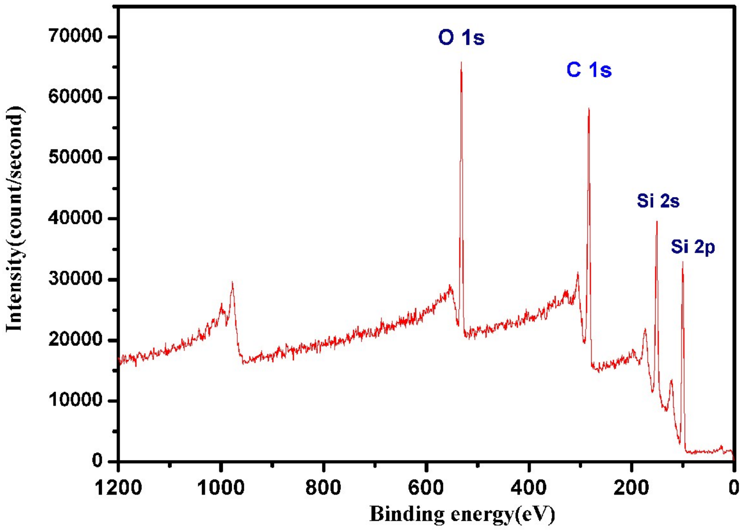

Fig.S2 XPS spectra of original SiC powder.

Figure S2 shows the XPS spectra of original SiC powder. As can be seen from Fig. S2, in addition to silicon and nitrogen, required element of SiC powder, oxygen also appears on the surface of SiC powder.

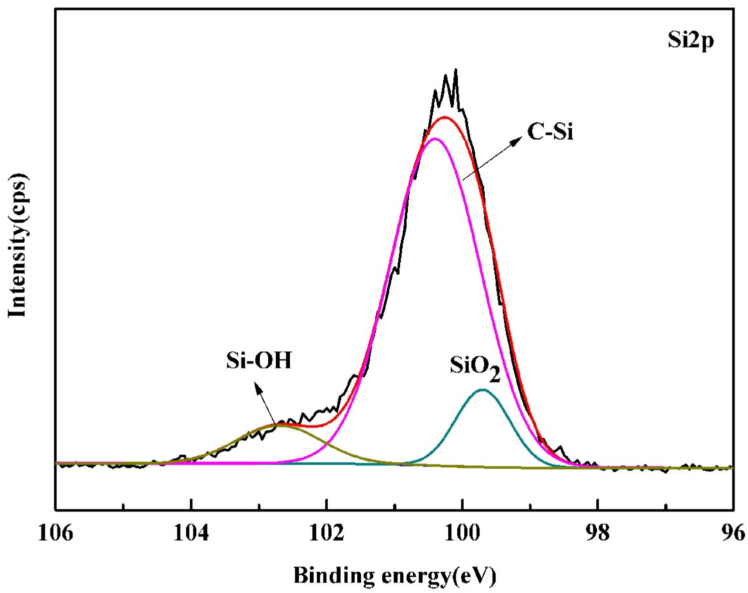

Fig.S3 Si_{2p} XPS spectra of the original SiC powder.

Figure S3 shows the high-resolution Si_{2p} XPS spectra of row SiC powder. Three peaks at 99.8 eV, 100.4 eV and 102.5 eV are associated with the Si-O of SiO_2, Si-C and Si-OH bonds respectively [1]. It indicates that the compounds of SiC, SiO_2 and Si-OH appear on the surface of SiC powder. The composition of SiO_2 at 99.8 eV and Si-OH at 102.5 eV mainly resulted from the oxidation of the silicon element and the adsorption of H_2O in air.

3. FT-IR analysis

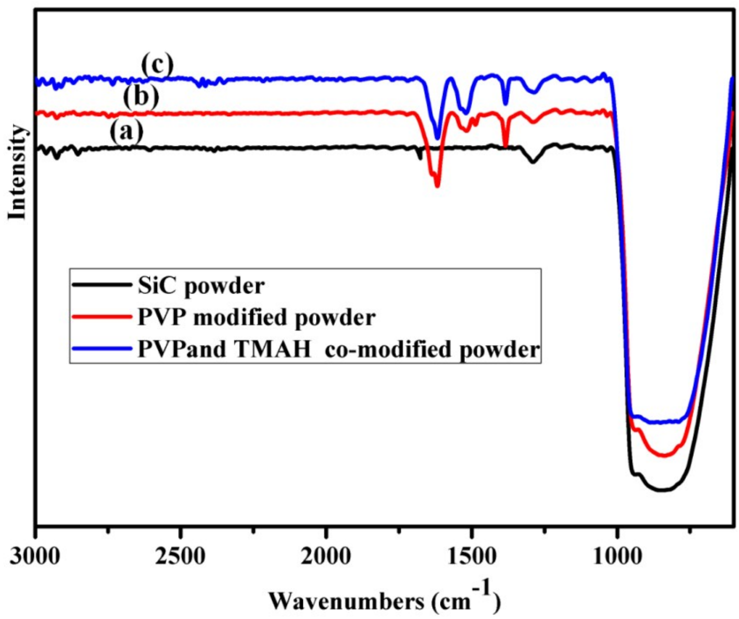

Fig.S4 FT-IR spectra of different powder, (a) SiC powder, (b) PVP modified SiC powder and (c) PVP and TMAH co-modified SiC powder.

Fig.S4 shows the FT-IR spectra of different powder. For PVP modified SiC powder, the wavenumber of 1635 cm^{-1} belongs to stretching vibration of C=O, and the wavenumber of 1340 cm^{-1} is associated with the stretching vibrations of C-N. The presence of this two absorption peak indicates that PVP has been adsorbed on the surface of modified SiC powder. In addition, the absorption peak at 1490 cm^{-1} belongs to bend vibration of C-H. TMAH adsorbed on SiC surface can increase the peak intensity (Fig.S4 (c)). In a word, FT-IR test also proves that the modifiers have been adsorbed on the surface of SiC powder.

Modified time in the first step is 1 h fixedly in this paper. The orthogonal experiments are designed, and the experimental factors and levels of orthogonal experiments are shown in Table S1. Table S2 shows the schemes and results of orthogonal experiment.

4. Orthogonal experiment of PVP and TMAH co-modification

Table S2 The factors and levels table of orthogonal experiment about the modification of SiC powders.

Level	A	B	C	D
1	0.8	0.6	1.0	250
2	1.0	0.8	1.5	300
3	1.2	1.0	2.0	350

(A) The addition amount of PVP (wt%), (B) The addition amount of TMAH (wt%), (C) Modified time in second step (h), (D) Rotating speed of mill (rpm).

Table S3 Schemes and results of orthogonal experiment about the modification of

SiC powder.

Number	A	B	C	D	Viscosity	solid content
	wt%	wt%	h	rpm	Pa · s	Vol%
1	0.8	0.6	1.0	250	0.732	55.0
2	0.8	0.8	1.5	300	0.519	57.6
3	0.8	1.0	2.0	350	0.244	64.0
4	1.0	0.6	1.5	350	0.663	57.2
5	1.0	0.8	2.0	250	0.372	56.5
6	1.0	1.0	1.0	300	0.232	58.9
7	1.2	0.6	2.0	300	0.612	54.4
8	1.2	0.8	1.0	350	0.564	50.0
9	1.2	1.0	1.5	250	0.765	57.0

Table S4 Analytical table of range for viscosity.

	A (wt%)	B (wt%)	C (h)	D (rpm)
F_1	1.495	2.007	1.528	1.869
F_2	1.267	1.455	1.947	1.363
F_3	1.941	1.241	1.228	1.471
f_1	0.498	0.669	0.509	0.623
f_2	0.422	0.485	0.649	0.454
f_3	0.647	0.414	0.409	0.490
Range	0.225	0.255	0.100	0.169
Optimum scheme	A2	B3	C3	D2

The viscosity range of orthogonal experiments is analyzed and the results are shown in Table S3. F_1, F_2 and F_3 are the sum of viscosity value of each factor corresponding to the different levels respectively. In addition, f_1, f_2 and f_3 are the viscosity average of each factor corresponding to the different levels respectively. Table S3 shows that the ranges of the four factors are 0.225, 0.255, 0.1 and 0.169 respectively. The orthogonal test shows that the influences of TMAH addition, PVP addition, ball mill speed and modified time on the viscosity decrease successively. The optimal solution is 1.0 wt% of PVP, 1.0 wt% of TMAH, 2h of modified time and 300 rpm of ball mill speed.

Table S5 Analytical table of range for solid content.

	A (wt%)	B (wt%)	C (h)	D (rpm)
F_1	176.6	166.6	163.9	168.5
F_2	172.6	164.1	171.8	170.9
F_3	161.4	179.9	174.9	171.2
f_1	58.8	55.5	54.6	56.2
f_2	57.5	54.7	57.3	56.9
f_3	53.8	59.9	58.3	57.1
Range	5.1	4.4	1.1	0.9
Optimum scheme	A1	B3	C3	D3

The solid content range of orthogonal experiments is analyzed and the results are shown in Table S4. F_1, F_2 and F_3 are the sum of solid content of each factor corresponding to the different levels respectively. In addition, f_1, f_2 and f_3 are the solid content average of each factor corresponding to the different levels respectively. Table S4 shows that the ranges of the four factors are 5.1, 4.4, 1.1 and 0.9 respectively. The orthogonal test shows that the influences of PVP addition, TMAH addition, modified time and ball mill speed on the solid content decrease successively. The optimal solution is 0.8 wt% of PVP, 1.5 wt% of TMAH, 2h of modified time and 350 rpm of ball mill speed.

5. Comparison the performance of different slurry

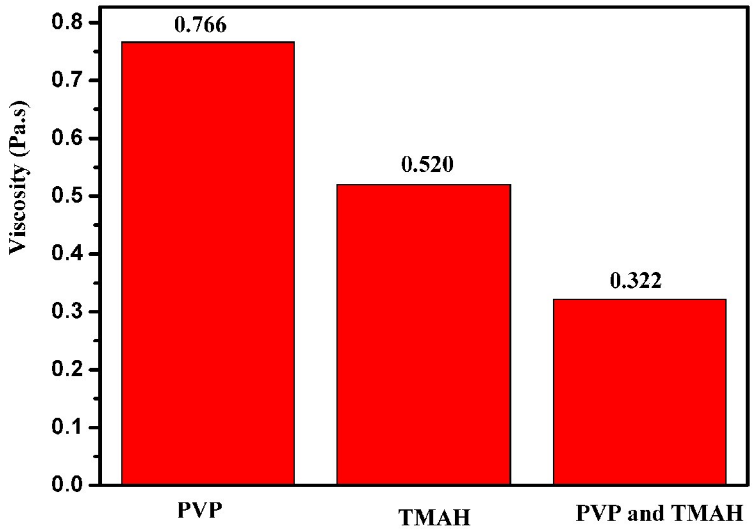

Fig.S5 Minimum viscosity contrast of slurry prepared with SiC powder modified with different modifier.

The minimum viscosity of slurry fabricated with SiC powder modified with PVP, TMAH and double modifiers are measured respectively, as shown in Fig.S4. It is obvious that the slurry prepared with SiC powder co-modified with PVP and TMAH owns the lowest minimum viscosity among the modified SiC powder.

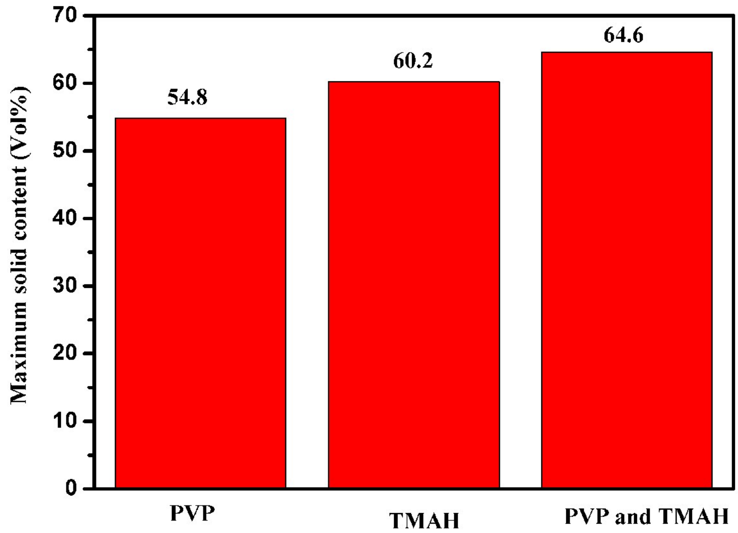

Fig.S6 Maximum solid content contrast of slurry prepared with SiC powder modified with different modifier.

The maximum solid content of slurry prepared with different modified powder, including PVP modified SiC powder, TMAH modified SiC powder and double modifiers co-modified SiC powder, is compared, as shown in Fig.S5. Apparently, the slurry fabricated with double modifiers co-modified SiC powder possess the largest maximum solid content among the modified SiC powder.

Table S6 Summarization of performances of modified SiC powder.

	Modifiers	Viscosity (Pa. s)	Solid content (Vol%)	Zete potential (mV)
Ref.2	Tetrapropyl ammonium hydroxides	0.11	42	-40
Ref.3	Polyethylene imine	0.43	40	-35
Ref.4	Polyethylene imine	0.21	35	-30
Ref.5	Silane coupling	11.01	34.13	-30

	agent KH550			
Modified SiC powder	PVP and TMAH	0.32	45	-58.5

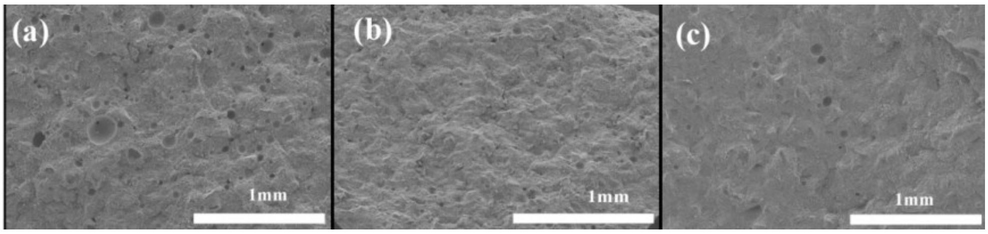

Fig.S7 Fracture surface SEM image of SiC ceramic green body fabricated by different modified SiC powder, (a) PVP modified SiC powder, (b) TMAH modified SiC powder, (a) PVP and TMAH co-modified SiC powder.

As shown in Fig.S6 (a), abundant pore can be seen from fracture SEM image of SiC ceramic green body fabricated by PVP modified powder, indicating the low fluidity when the modified SiC powder is dispersed in water medium. A few pores can be seen from Fig.S6 (b), indicating that TMAH plays an important role in increasing the fluidity of slurry prepared by SiC powder modified with TMAH. Moreover, homogeneous SiC green body can be obtained using PVP and TMAH co-modified SiC powed, as shown in Fig.S6 (c). As we all known, the more pores, the lower ceramic green body density. Therefore, the density of green body fabricated by PVP and TMAH co-modified SiC powder is better than that of green body prepared by SiC powder modified with single modifier.

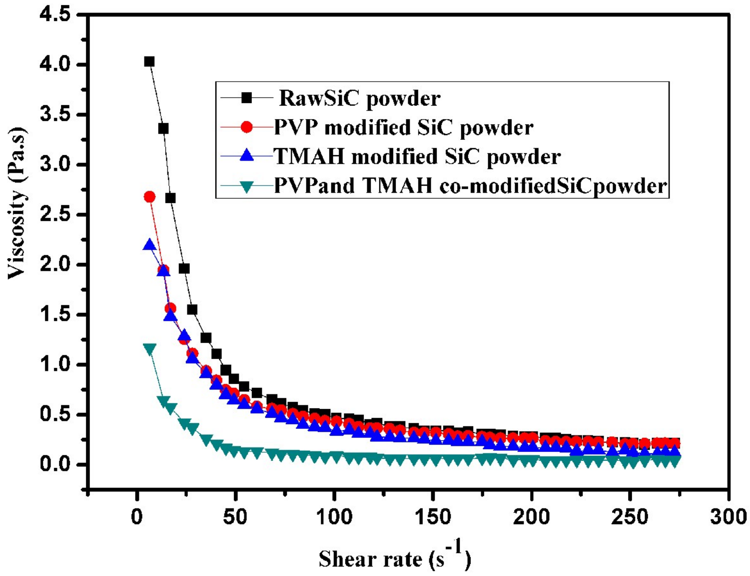

Fig.S8 Effect of shear rate on viscosity (45 Vol% of solid content).

As can be seen from Fig.S6, with the increase of shear rate, the viscosity of slurry prepared with all powder, including unmodified SiC powder and modified powder, decreased significantly, shows shear thinning characteristic. It indicates that the slurry prepared with SiC powder has low thixotropy, facilitating preparing slurry with good flowability under high solid content.

6. **XRD analysis**

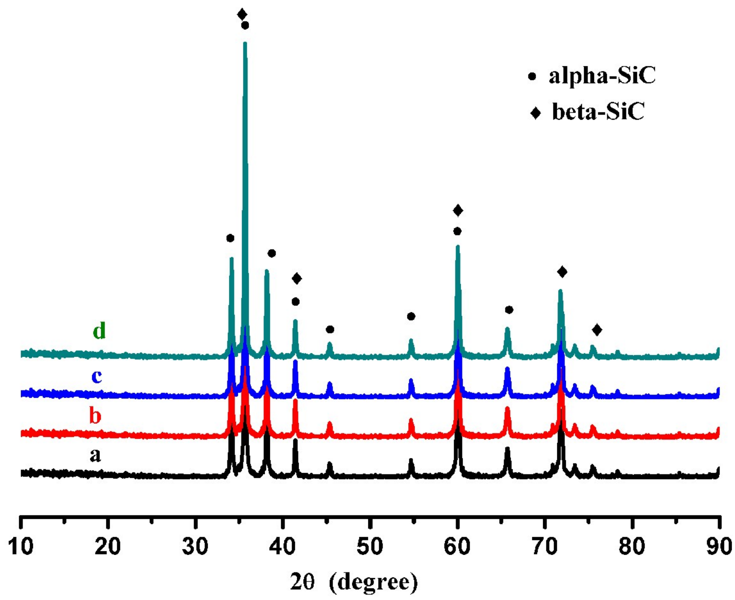

Fig.S9 XRD patterns of the original SiC powder (a), PVP modified SiC Powder (b), TMAH modified SiC Powder (c) and (d) TMAH and PVP co-modified SiC powder.

Figure S7 shows the XRD patterns of original SiC powder and modified SiC powder. As can be seen from Fig.S7, both double modifier modified SiC powder and single modifier modified SiC powder show the same crystal structure with raw SiC powder, indicating our modification method cannot alter the crystal structure of SiC powder.

7. **Subside model of different SiC particles in water medium**

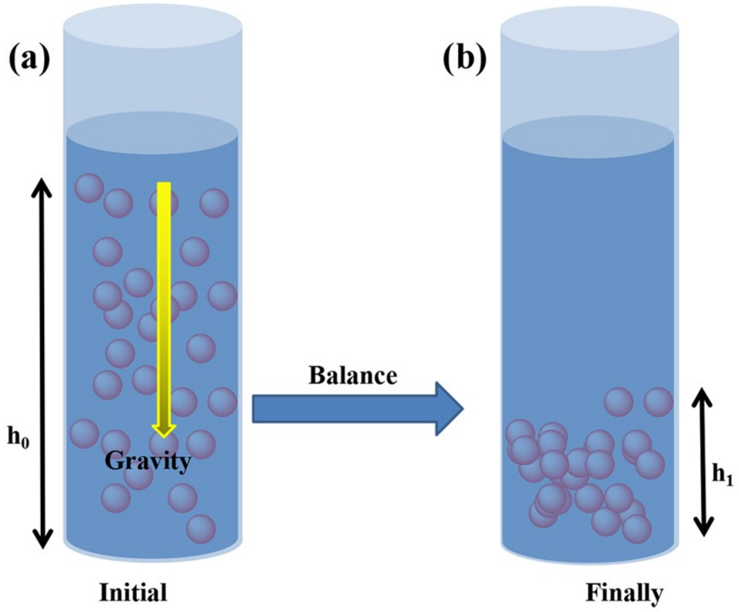

Fig.S10 Subside model of original SiC powder in water medium.

Original SiC powder in aqueous solution is subjected to two forces—one is self gravity and another is buoyancy from water solution. However, the buoyancy of SiC powder is negligible relative to self gravity. Therefore, driven by self gravity, SiC particles in water solution will quickly drop, as shown in Fig.S8 (a). With the increase of time, the particles gradually accumulate at the bottom, resulting balance between support force and gravity, as shown in Fig.S8 (b). The height of solid content at balanced state is $h_{1.}$

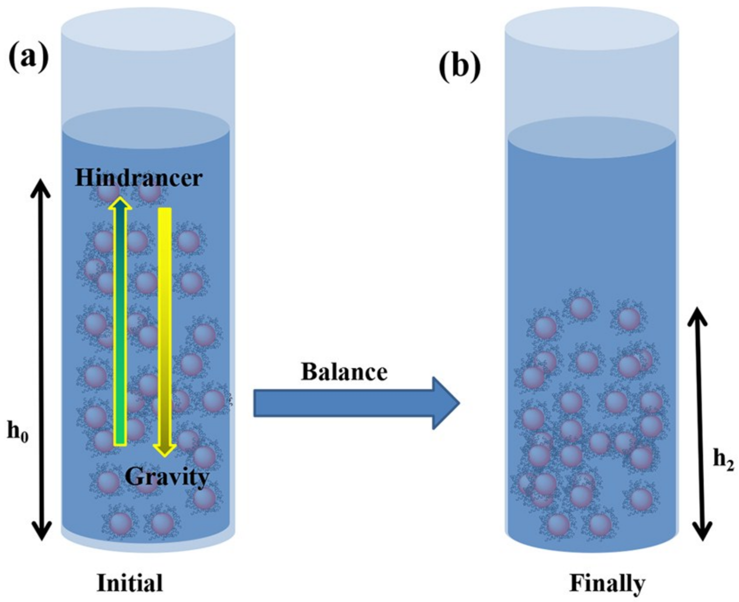

Fig.S11 Subside model of PVP modified SiC powder in water medium.

Figure S9 shows the subside model of PVP modified SiC powder in water medium. In addition to self gravity, PVP modified SiC powder is also subjected to hindrance force from long-chain of polymer, preventing the drop of particles, as shown in Fig.S9 (a). The hindrance among particles is less than gravity, resulting gradual drop of modified SiC powder. When the sum of support force and hindrance force is balanced with gravity, PVP modified SiC particles will not sink, as shown in Fig.S9 (b). At this time, the height of solid content at balanced state is $h_{2.}$

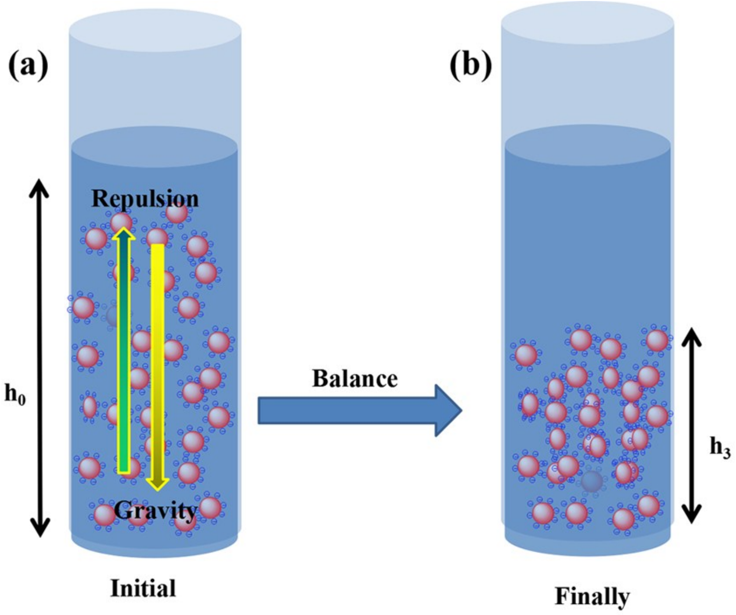

Fig.S12 Subside model of TMAH modified SiC powder in water medium.

As mentioned above, TMAH modified SiC powder is also subjected to two forces predominantly—one is self gravity and another is electrostatic repulsive force. Initially, TMAH modified SiC powder will gradually drop owing to the electrostatic repulsive force is lower than self gravity. With the increase of time, the sum of support force and electrostatic repulsive force is balanced with gravity, resulting that TMAH modified SiC particles will not sink, as shown in Fig.S10 (b). At this time, the height of solid content at balanced state is h_3.

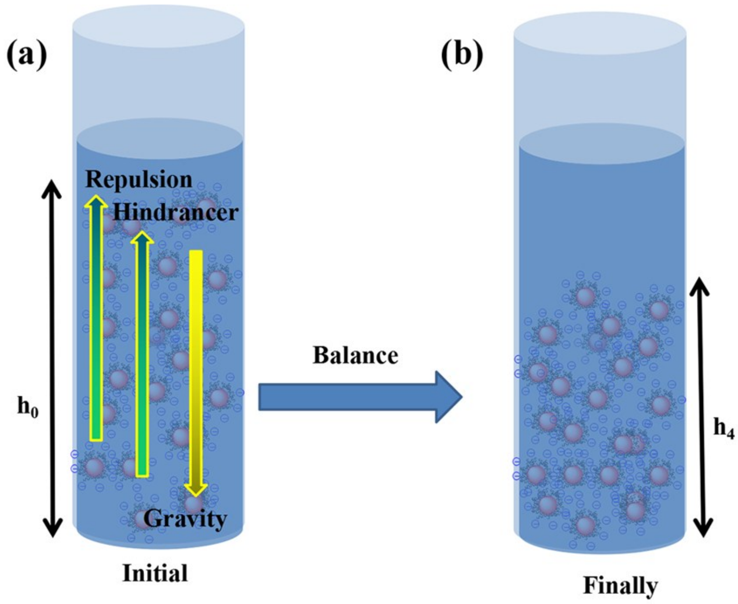

Fig.S13 Subside model of PVP and TMAH modified SiC powder in water medium.

For SiC powder co-modified with PVP and TMAH, modified SiC powder is subjected by three forces, including self gravity, hindrance force and electrostatic repulsive force, as shown in Fig.S11 (a). However, the sum of hindrance force and electrostatic repulsive force is still less than gravity in initial state, leading to drop of modified SiC powder slowly, as shown in Fig.S11 (a). With the increase of time, double modifier co-modified SiC particles will not sink when the sum of support force, hindrance force and electrostatic repulsive force is balanced with gravity, as shown in Fig.S11 (b). The height of solid content at balanced state is h_4.

According the above experimental data and analysis, we can know that the solid phase content height of four cases at balance point is h_4>h_2>h_3 >h_1. It is obvious that the stability of modified SiC powder is higher than that of unmodified SiC powder. In addition, the stability of PVP modified SiC powder is higher than that of TMAH modified SiC powder.

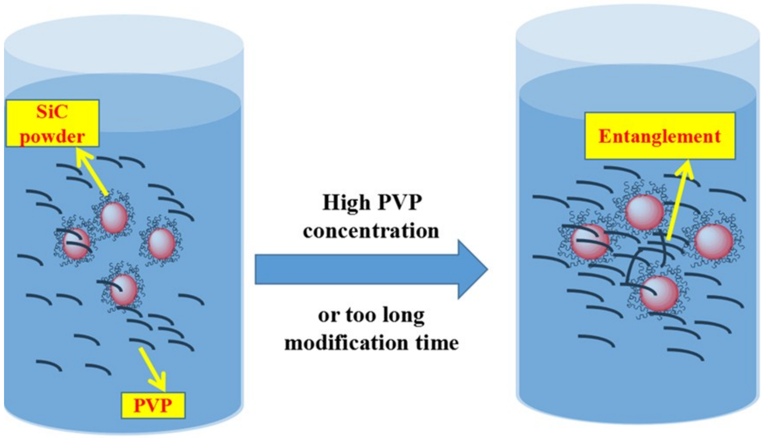

Fig.S14 diagrammatic sketch of entanglement among long chains of PVP

Reference:

[1] Shang, X.; Zhu, Y.; Li, Z. Surface modification of silicon carbide with silane coupling agent and hexadecyl iodiele. Appl. Surf. Sci. **2017**, 394, 169-177.

[2] Huang, Q.; Chen, P.; Gu, M.; Jin, Y.; Sun, K. Effect of surface modification on the rheological behavior of concentrated, aqueous SiC suspensions. Mater. Lett. **2002**, *56*, 546-553.

[3] Sun, J.; Gao, L. Dispersing SiC powder and improving its rheological behaviour. J. Eur. Ceram. Soc. **2001**, *21*, 2447-2451.

[4] Zhang, J.; Xu, Q.; Ye, F.; Lin, Q.; Jiang, D.; Iwasa, M. Effect of citric acid on the adsorption behavior of polyethylene imine (PEI) and the relevant stability of SiC slurries. Colloids Surfaces A **2006**, *276*, 168-175.

[5] Tie, S.; Li, X. Surface Modification of SiC Powder with Silane Coupling Agent. Journal of the Chinese Ceramic Society **2011**, *39*, 409-413.