# **Supporting Information**

# 1. Modification of silica nanoparticles Materials

Methyl methacrylate (MMA), divinylbenzene (DVB), potassium persulfate (KPS), surfactant, sodium dodecyl sulphonate (SDS), buffer, sodium bicarbonate (NaHCO<sub>3</sub>), methanol, ethanol, were purchased from Sinopharm Chemical Reahent Co., Ltd China. Methyl methacrylate (MMA) was distilled under reduced pressure before use and other reagents were used without further purification.

## Preparation of MPS grafted silica

0.1g MPS was added to a suspension of silica (10g) and SDS (0.05g) in 60ml water for 24h at room temperature under stirring. The suspension was washed by centrifuged/redispersed 3 cycles in ethanol. The MPS grafted silica particles were dried in a vacuum oven at 60 °C for 24h.

#### Preparation of PMMA grafted silica

PMMA grafted silica microspheres were synthesized by emulsion polymerization. In a typical experiment, the MPS grafted silica (5.0g) dispersed in 15ml of ethanol was added into a solution of SDS (0.15g), NaHCO<sub>3</sub> (0.4g), water (180ml) under ultrasonication for 10min, and then were placed into a four-neck flask with a machine stirring under an argon atmosphere for 20min. For core-shell PMMA grafted silica particles, 15g MMA and 0.15g KPS were added. For cross-linked core-shell PMMA grafted silica particles, 1.2g DVB<sub> $\times$ </sub> 15g MMA and 0.15g KPS were added. The polymerization was carried out for 5h at 70 °C. The suspension was purified by centrifuging/redispersing in water for 3 cycles. The PMMA grafted silica particles were dried in a vacuum oven at 60 °C for 24 h.

#### Characterization

1.0g PMMA grafted silica particles solid were dispersed in 50ml THF under vigorous stirring for 24 h at room temperature. Then the mixture was centrifuged. This process was repeated 3 times to ensure the complete extraction of the ungrafted PMMA from the residue. The ungrafted PMMA was collected by adding methanol to the supernatant solution. The residue was dried in a vacuum oven at 60 °C for 24 h. Then 0.5g PMMA grafted silica was dispersed in 30 ml THF, then, aqueous HF(48wt%, 2ml) was added into the mixture under stirring for 48h at room temperature. The mixture was then precipitated twice in excess of methanol and then the residue containing the grafted PMMA was dried at 60 °C for 24h. The molecular weight of PMMA was measured by Malvern Viscotek 270max triple-detector gel permeation chromatography (GPC) and THF was used as eluent at a flow rate of 1.0 mL/min. The molecular weights of grafted and ungrafted PMMA are shown in Table S1.

Table S1. The molecular weight of grafted and ungrafted PMMA in PMMA@silica nanoparticle.

	M <sub>w</sub> (g/mol)	$M_n(g/mol)$	$M_w/M_n$
Grafted PMMA	493,000	218,000	1.85
Ungrafted PMMA	178.000	105,000	1.7

Dynamic strain sweeps from 0.1 to 5 were performed at 0.628rad/s.

Thermo gravimetric analysis were conducted by TGA instrument (Q5000IR, TA Instruments, USA) with a heating rate of 20 °C /min under nitrogen atmosphere from 40 °C to 700 °C.

Differential scanning calorimetry (DSC) measurements were conducted on Q2000 (TA Instruments). The samples were measured twice using the same thermal cycle: heated to 190 °C at 10 °C/min, isothermal annealing at 190 °C for 5min, and then cooled to 40 °C at 10 °C/min.

Field Emission Scanning Electron Microscopy (FE-SEM) images were checked using SEM (Nova Nanosem 450, USA). Samples were prepared by drying particles solution on silicon wafers. After drying, platinum sputtering was used to apply an ultrathin metal layer ( $\sim 0.5$  nm) to enhance the quality of images acquired in the experiments. SEM and TEM images of different modified silica particles are shown in Fig. S1.



Figure S1. SEM images of the bare silica nanoparticle (a), MPS@silica nanoparticle (b). TEM images of the PMMA@silica nanoparticle (c) and cPMMA@silica nanoparticle (d).

#### 2. Grafting density

The grafting density of grafted MPS was determined by TGA and was calculated by<sup>1</sup>

Grafting density (µmol/m<sup>2</sup>) = 
$$\frac{\left(\frac{W_{200-700}}{100-W_{200-700}}\right) \times 100 - W_{silica}}{M \times S_{spec} \times 100} \times 10^{6}$$
(1)

where  $W_{200-700}$  is the weight loss from 200 to 700 °C corresponding to the decomposition of the MPS, M is the molar mass of the degradable part of the grafted molecule (248 g/mol). S<sub>spec</sub> (=3000/(R<sub>p</sub> $\rho_{silica})$ =36 m<sup>2</sup>/g ) and W<sub>silica</sub> are the specific surface area and the weight loss of silica determined before grafting, respectively.  $\rho_{silica}$ =2.2 g/cm<sup>3</sup>, R<sub>p</sub> (38nm) is silica particle radius.The grafting density of grafted MPS is 1.5 µmol/m<sup>2</sup> (0.9/nm<sup>2</sup>) as calculated from Eq. (1).



Figure S2. TGA data of the bare silica particle and MPS@silica particle.

The grafting density  $\sigma$  of grafted PMMA on the silica surface was calculated by<sup>2</sup>

$$\sigma = \frac{\rho_{silica} \cdot R_p \cdot N_A}{3M_n \left(\frac{1}{w} - 1\right)} \tag{3}$$

where  $\rho_{\text{silica}} = 2.2 \text{ g/cm}^3$ ,  $R_p$  is the radius of silica nanoparticle,  $N_A$  is Avogadro's number,  $M_n$  is the molecular weight of grafted polymer, W is weight loss of grafted polymer (50% in Figure S3). The grafting density of PMMA is about 0.077 (nm<sup>-2</sup>). The grafting efficiency of PMMA is about 8.9%.

#### 3. Size of nanoparticles

#### 3.1 Bare silica particle and MPS@silica particle

The thickness of the immobilized layer a around individual particles was estimated by<sup>3, 4</sup>

$$a = R_p \left( \sqrt[3]{\left(\frac{\phi_{imm}}{\phi} + 1\right) - 1} \right)$$
(4)

where the immobilized volume fraction  $\phi_{imm}$  was calculated by<sup>3, 4</sup>

$$\phi_{imm} = 1 - C_{P,polymer} / C_{P,polymer} \tag{5}$$

where  $C_{P,polymer}^{0}$  and  $C_{P,polymer}$  are the specific heat capacity of pure polymer and polymer in nanocomposites, respectively. The overall specific heat capacity of nanocomposites included the contributions of the polymer and of the silica. The contribution of the polymer phase ( $C_{P,polymer}$ ) was obtained from a mass balance.<sup>3, 4</sup>

$$C_{P,polymer} = \frac{C_{P,PNC} - C_{P,silica}\omega_{silica}}{\omega_{polymer}}$$
(6)

where  $C_{P,PNC}$  and  $C_{P,silica}$  are the heat capacity of the nanocomposite and silica, respectively.  $\omega_{polymer}$  and  $\omega_{silica}$  are the weights fraction of polymer and of silica, respectively.



Figure S3. (a) TGA data of the bare silica particle, MPS grafted silica particle, the PMMA@silica particle and after extracting of the PMMA@silica particle. (b) TGA data of the bare silica particle, MPS grafted silica particle, the cPMMA@silica particle and after extracting of the cPMMA@silica



Figure S4. Immobolized volume fraction  $\phi_{imm}$  as a function of the silica particle volume fraction  $\phi$ . The solid lines are linear fits to the experimental data.

#### 3.2 PMMA@silica and cPMMA@silica

According to weight loss fraction between silica and grafted polymer, the effective shell thickness a is calculated by

$$\frac{m_{polymer}}{m_{silica}} = \frac{\frac{4}{3}\pi \left( \left(R_p + a\right)^3 - R_p^3\right)\rho_{PMMA}}{\frac{4}{3}\pi R_p^3 \rho_{silica}}$$
(7)

where  $m_{polymer}$  is the weight loss fraction of grafted polymer in grafted silica particle,  $m_{silica}$  was the weight fraction of silica in polymer grafted silica particle.

Particles	Bare silica	MPS@silica	Bare silica	PMMA@silica	cPMMA@silica
In PNC	PSNC	PMNC	PBNC	PCNC	PCCNC
$R_{eff}(nm)$	38	40.3	45	55	72.5

Table S2. The particle size in different PNC systems.

### 4. The effective volume fraction

The volume fraction of silica is evaluated from the weight fraction by

$$m_{silica} = \rho_{silica} \frac{4}{3} \pi R_p^3 \tag{8}$$

Where  $m_{silica}$  is the weight fraction of silica,  $R_p$  is the radius of silica particles. The weight fraction of silica in PNC is determined from the weight loss in TGA (Figure S5).



Figure S5. TGA data of different PNC systems. The effective volume fraction was calculated by

$$\phi_{eff} = \left(\frac{R_{eff}}{R_p}\right)^3 \phi_{silica} \tag{9}$$

 Table S3. Weight fraction, volume fraction and effective volume fraction of nanoparticles in different nanocomposites.

					F -					
PCNC				PBNC						
m <sub>silica</sub> (wt%)	1.2	3.8	7.9	12.1	3.6		8.1	14.6	17.6	21.5
¢ <sub>silica</sub> (vol%)	0.6	1.9	4.2	6.4	1.8		4.2	7.9	9.7	12.0
<b>¢</b> <sub>eff</sub> (vol%)	1.8	5.7	12.6	19.2	3.0		7.0	13.0	16.1	19.9
	PMNC				PCCNC			PSNC		
m <sub>silica</sub> (wt%)	7.7	13.8	23.7	3.6	6.8	10.0	13.8	13.9	17.6	28.3
φ <sub>silica</sub> (vol%)	4.0	7.4	13.4	1.8	3.5	5.3	7.4	7.5	9.6	16.3
φ <sub>eff</sub> (vol%)	4.8	8.8	15.9	12.4	24.2	36.6	51.0	7.5	9.6	16.3

5. Strain sweeps



Figure S6. The strain amplitude sweeps of PCNC.

#### 6. Percolation concentration

Percolation concentration of different nanocomposites is determined by the frequency independency of loss tangent.<sup>5</sup>



Figure S7. Loss tangent versus nanoparticle content at extrapolated frequencies.

Table S4. The $\phi_c$ value of each PNC system.							
	PCNC	PMNC	PBNC	PCCNC	PSNC		
$\phi_{c}$ (%)	28±3	64±3	30±3	58±3	10		

7. The loss tangent of PNC



Figure S8. The loss tangent of PMNC (a) and PCCNC (b) and PSNC (c) on that of polymer matrix by a horizontal shift  $a_r$ .

#### 8. Simulation results with different chosen dispersion exponent

In 3D (or 2D) simulations, cluster containing  $N_{Agg}$  particles is generated using the following steps. It always starts with a particle located in the center of coordinates. Then particles are added to the clusters one by one. To add a particle, two (one for 2D case) random numbers are generated in the range [0,  $2\pi$ ] and [0,  $\pi$ ] ([0,  $2\pi$ ] for 2D case), respectively. They represent the azimuthal angle and the polar angle, respectively. Then let the particle approach the cluster along the direction determined by two angles (or one angle in 2D case) until the nearest surface distance between particle and cluster becomes d<sub>min</sub>. Such steps repeat until all N<sub>Agg</sub> particles are added in the clusters. An example in 3D case is shown in Fig. S9a. The particle number is 10000 and 2000 in 3D simulation and 2D simulation, respectively. d<sub>min</sub> is set as one tenth of particle radius, and d<sub>c</sub> is chosen as the particle radius.

To generate a spatial distribution of clusters, the above generated clusters are put into a box (3D) or a square (2D) beginning from the largest clusters. The position of the clusters is specified by their center particles, which is randomly chosen in the space. The only requirement is the nearest surface distance between any two clusters should be larger than d<sub>c</sub>. d<sub>c</sub> controls the intercluster distance, but does not affect the analysis below. An example in 3D case with  $\tau_{3D} = 3.0$  is

shown in Fig. S8b. Several examples in 2D case with different dispersion exponent are shown in Fig. S10a-d.

To correlate the 2D cluster analysis results with the true 3D dispersion exponent, the 3D spatial dispersion (Fig. S9b) was cut into different thin sections. Fig. S9c shows one example in 3D, and its 2D projection is shown in Fig. S9d. Then the cluster number distribution was counted from the 2D projection images, and the distribution are shown in Fig. 4.



Figure S9. (a) A 3D cluster with  $N_{Agg}$ =126. (b) Spatial distribution of clusters with  $\tau_{3D} = 3.0$ . Only clusters with  $N_{Agg}$  larger than 2 are shown. (c) A thin slice with thickness of two times of particle radius. (d) 2D projection of particle positions of (c).



Figure S10. Typical images from 2D simulation with the chosen dispersion exponent (a)  $\tau$ =1.0, (b)  $\tau$ =2.0, (c)  $\tau$ =3.0, (d)  $\tau$ =4.0. (e) The free path distributions from the 2D simulating results for typical dispersion exponents.

#### References

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