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Hybrid cyclotriphosphazene–polysiloxane–nano-SiO_2 composites with improved mechanical properties

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1. General Methods and Materials

Materials. Tetraethoxysilane and 3-mercaptopropyltrimethoxysilane were purchased from ABCR. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) were purchased from Sigma-Aldrich. All chemicals were used without further purification. Ethanol and toluene were distilled before use.

Characterization. The morphology of SH-functionalized silica nanoparticles was characterized by scanning electron microscopy (SEM). The observations were carried out using Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in secondary electron mode at 5 kV accelerating voltage and at working distance 8-10 mm. The target-oriented approach was utilized for the optimization of the analytic measurements.[1]

TEM images were obtained using LEO912 AB OMEGA transmission electron microscope.

Mechanical properties of samples were evaluated on LLOYD Instruments LR5K Plus testing machine with 50 mm/min compression speed. For uniaxial compression tests, samples were compressed to 90% of its original size.

Thermogravimetric analysis (TGA) was performed by Derivatograph Shimadzu DTG-60H (Japan) on samples with the weight of about 5 mg at a heating rate of 10 ^{o}C/min in air and argon. The temperature at which a weight loss of 1% was detected was considered to be the decomposition onset temperature.

2. Synthesis

*Silica nanoparticles (**2**).* To the solution of tetraethoxysilane (3.346 mL) in ethanol (14.5 mL) the mixture of water (0.54 mL), 12% aqueous NH_3 (2.2 mL) and 15 mL ethanol was added. The reaction mixture was stirred at room temperature for 24 h. After the reaction was complete silica nanoparticles were centrifuged and washed with ethanol three times.

*SH-functionalized silica nanoparticles (**3**).* To the dispersion of silica nanoparticles **2** (obtained in the previous experiment) in toluene (30 mL) 3-mercaptopropyltrimethoxysilane (3 mL) was added and the reaction mixture was stirred at room temperature for 24 h. After the reaction was complete SH-functionalized silica nanoparticles **3** were washed with toluene three times and dried in vacuum.

*2,2,4,4,6,6-Hexakis(2-propen-1-yloxy)cyclotriphosphazene (**4**).* It was synthesized from hexachlorocyclotriphosphazene and allyl alcohol by the method described earlier [2].

*Synthesis of thiol-containing oligomer (**5**).* It was synthesized from 3-mercaptopropyltrimethoxysilane and hexamethyldisiloxane by the method described earlier by us [3] with such characteristics: M_n=780, M_w= 840, PDI=1.08.

*Preparation of nanocomposite based on cyclophosphazene, polysiloxane and SH-functionalized silica nanoparticles precursors (**X1-3**).* 2,2,4,4,6,6-Hexakis(2-propen-1-yloxy)cyclotriphosphazene **1** (0.535 g), thiol-containing oligomer **2** (1.465 g), SH-functionalized silica nanoparticles **3** (5 % (***X1***), 10 % (***X2***) or 20 % (***X3***) by mass) and DMPA (0.003 g) are dispersed in toluene and brought the general volume of solution up to 10 mL. Then the solution is placed in a plastic syringe by 10 mL capacity and irradiated by UV lamp (365 nm, 8W) for 30 min. After the gel is formed toluene slowly evaporates during 2 weeks. Nanocomposites are obtaining as opaque samples.

3. Figures

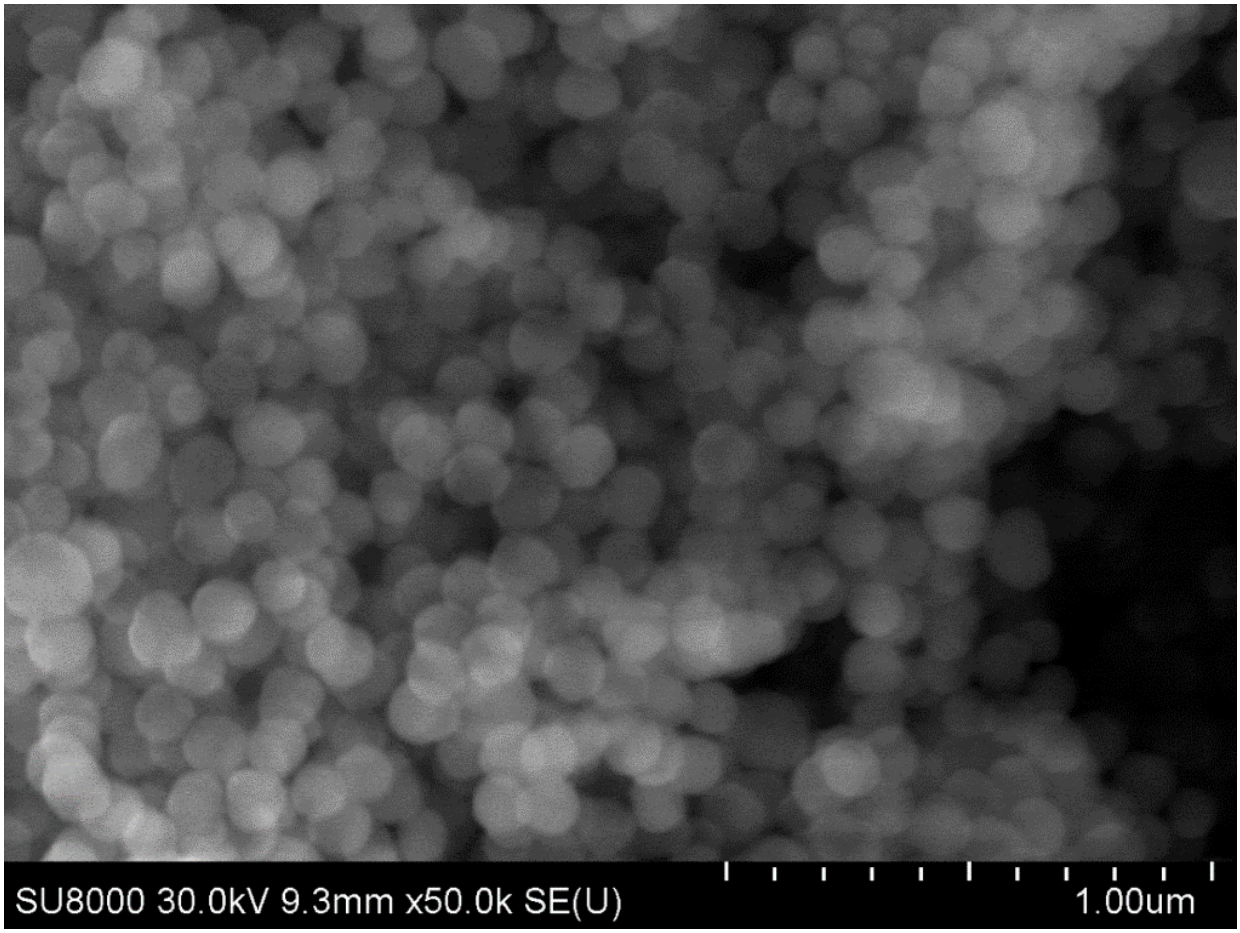

Figure S1 SEM image of SH-functionalized silica nanoparticles **3**.

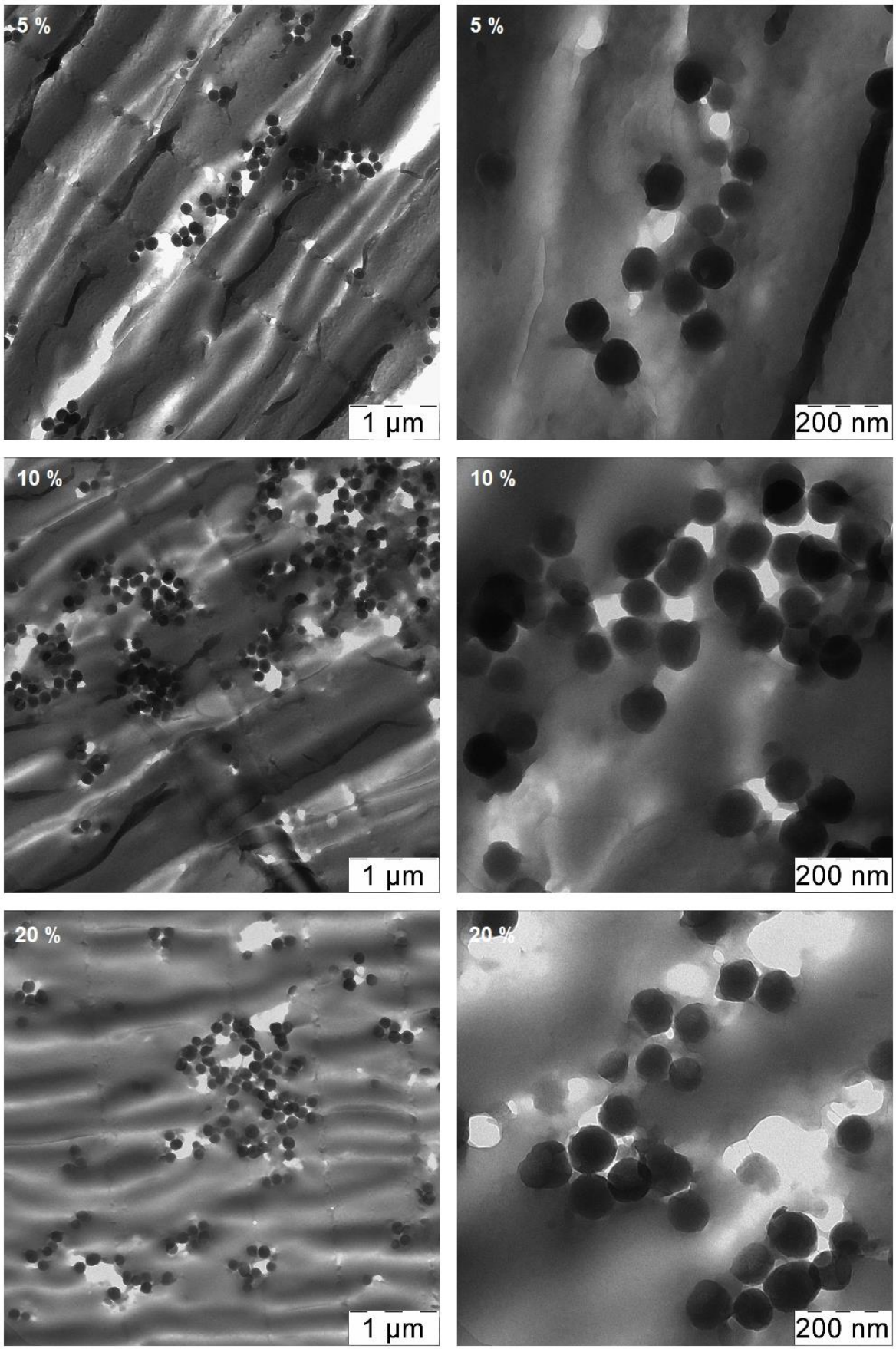

Figure S2 TEM images of samples **X1** (5 %), **X2** (10 %), **X3** (15 %) at different magnifications.

4. References

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