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Hybrid materials based on core-shell polyorganosilsesquioxanes modified with iron nanoparticles

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Experimental

For the synthesis of hyperbranched polymethylethoxysiloxane, an AB_2-type sodium oxydiethoxymethylsilane monomer prepared according to a previously described procedure[6(c)] was used.

Anhydrous acetic acid (120 g, 2.0 mol) was added to a toluene solution of sodium oxydiethoxymethylsilane (2.0 mol). After 24 h, the solution was filtered and dried. Volatiles were removed *in vacuo* (1 mbar). Hyperbranched polymethylethoxysiloxane was formed in a yield of 87% (calculated for the theoretical structure $[CH_3SiO(OC_2H_5)]_n$). GPC: *M*w = 800 g mol^{-1}, *M*w/*M*n =1.5. ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 0.02–0.22 (m, 3H, Si−CH_3), 1.16–1.29 (m, 3H, Si−O−CH_2−CH_3), 3.74–3.94 (m, 2H, Si−O−CH_2−CH_3). IR (CCl_4): in the region 3100–3600 cm^{-1}, the characteristic absorption band corresponding to Si−OH is absent.

Synthesis of PMSSO nanogel capped with tetramethyldivinyldisiloxane (TMDVDS).

Presynthesised hyperbranched polymethylethoxysiloxane (5.0 g, 0.041 mol of EtO groups) was boiled for 2 h in acetic acid (16.7 g, 0.278 mol) (30% solution). TMDVDS (11.44 g, 0.0615 mol) and acetyl chloride (0.15 ml, 0.0021 mol) were added to the reaction mixture. The mixture was refluxed for 14 h. Then, the product was extracted with toluene and the organic extract was left overnight over anhydrous Na_2SO_4. Volatiles were removed *in vacuo* (1 mbar). As a result, 5.24 g of the product were obtained. GPC: Mw =4520 g mol^{-1}, Mw/Mn = 2.1, Tg = -58 °C. ^{1}H NMR (250 MHz, $CDCl_3$, δ): 0.11 (s, 3H, Si-CH_3), 0.18 (s, 3H, Si-CH_3); 5.71-6.20 (m, 3H, Si-CH=CH_2). Found (%): Si, 37.8; C, 28.7; H, 6.3. Calc. for $[CH_3SiO_{1,5}][C_2H_3(CH_3)_2SiO_{0,5}]_{0,32}$ (%): Si, 38.3; C, 28.2; H, 6.1. IR (CCl_4) in the region 3100–3600 cm^{-1} absorption corresponding to Si−OH is absent.

The ultra-high molecular weight polyethylene (UHMWPE) powder with a molecular weight of 4.5 MDa was obtained from Hoechst.

Microscopic studies of nanocomposites were performed with a LEO 912AB OMEGA transmission electron microscope (Zeiss).

Varied-temperature ^{57}Fe Mössbauer spectra over 16–300 K were measured with a Wissel electrodynamic spectrometer using a Janis helium cryostat (CCS-850) equipped with a Lake Shore Cryotronics (332) temperature controller. The accuracy of temperature control was better than 0.1 K. ^{57}Co (Rh) was used as a radiation source with an activity of 1.1 GBq. Isomer shifts were taken from the center of hyperfine structure lines (HFS) of α-iron. Mössbauer spectra were fitted by the standard least-square minimization programs (Loren, Win-Normos) assuming Lorentzian line shapes. For higher sensitivity, the bis(toluene)iron samples were deliberately enriched in the ^{57}Fe isotope.

The XPS measurements were performed with a Quantera SXM spectrometer (Physical Electronics) using an Al Kα X-ray source (1486.6 eV). The spectra were measured at room temperature at a pressure of ~$5 \cdot 10^{-8}$ Pa in the analytical chamber. The spectrometer was calibrated against the following peaks: Au $4f_{7/2}$ (84.0 eV), Ag $3d_{5/2}$ (368.3 eV) and Cu $2p_{3/2}$ (932.7 eV).

The apparent iron concentration in the as synthesized nanocomposites was measured with a VRA 30 X-ray fluorescence analyzer (XFA). For the excitation, Mo Kα X-ray tube operated at 50 kV×20 μA was used.

X-ray absorption spectroscopy was performed at the at the Structural Materials Science beamline of the Kurchatov Synchrotron Radiation Source.

The Fe K-edge XANES/EXAFS spectra for the hybrid materials were measured in the fluorescence yield mode using a Si avalanche diode. Analogous spectra of reference compounds, *i.e.*, iron foil and polycrystalline maghemite γ-Fe_2O_3, were measured in the transmission mode using ionization chambers.