Spin crossover-graphene nanocomposites: facile syntheses, characterization, and magnetic properties

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Experimental section

Materials and physical measurements

Graphene was prepared by graphite (purchased from XFNANO, China) with the combination of microwave radiation and thermal decomposition1; Fe(BF₄)₂·6H₂O, Htrz, Triton X-100 (CP), n-pentanol (AR), hexamethylene (AR) and ethanol (AR) were all purchased from Sigma-Aldrich. Ultrapure milli-Q water (18.2 MΩ. cm) was used in all experiments.

The Fourier transform infrared (FT-IR) were taken from FA-LA2000 FT-IR spectrometer (ABB Bomen Canada). The Raman spectra were obtained from Invia Raman spectra (Reinshaw England) with the excitation wavelength at 758 nm. XRD patterns were collected on a D8 Advance X-ray diffractometer (Bruker AXS Germany) with Cu Kα radiation in a 2θ range from 5° to 60°, and the scan speed was 2° min⁻¹. The size and morphology of the samples were observed by S4800 scanning electron microscope (SEM) (Rili Japan) and JEM-2100 (HR) transmission electron microscopy (TEM) (JEOL Japan). The samples of SEM analysis were collected by solid powder. And TEM analysis were obtained by dipping a holy grid to nanoparticles ethanol solution and evaporated in air at room temperature. The TG curves were carried out by using TGA/1100SF thermo grabinetric analyzer (Mettler Toledo Switzerland) with a temperature range of 25-800 °C. The DSC curves were...
obtained by (PE) DSC-8000 (PE US) from 300 K to 400 K with rate of 10 K min\(^{-1}\). The magnetic properties of nanocomposites were analyzed using a MPMS-XL-7 super strong quantum interference magnetometer (Quantum Design US). The samples were testing at two temperature stages, which were from 300 K to 400 K, and then back to 300 K and the sweep rate was 3 K min\(^{-1}\). Data was corrected for the diamagnetic contribution calculated from Pascal constants.

**Synthesis of \([\text{Fe(Htrz)}_2(trz)](\text{BF}_4)\) nanoparticles**

0.15 mL aqueous solution of \(\text{Fe(BF}_4)_2\cdot6\text{H}_2\text{O}\) (67.5 mg, 0.2 mmol) was added dropwise into a solution of Triton X-100 (1 mL), n-amyl alcohol (1 mL), and cyclohexane (4 mL). The mixed solution was kept stirring and the whole progress of reaction was maintained in nitrogen atmosphere. Next, 0.15 mL aqueous solution of Htrz (41.5 mg, 0.6 mmol) was added dropwise into the mixed solution until it had become a clear water-in-oil microemulsion. The mixture was stirred at room temperature for 24 h in dark. Then acetone (5 mL) was used to break the structure of the microemulsion and the nanoparticles were recovered from centrifugation. The nanoparticles were washed with ethanol (8 mL) by three times. The resulting nanoparticles were dried at 60 °C under vacuum overnight. IR (KBr cm\(^{-1}\)): \(\nu = 3177, 2924, 2826, 1640, 1496, 1451, 1221, 634\).

**Synthesis of SCO-G nanocomposites**

SCO-G1: Graphene (5 mg) was dispersed in ethanol (15 mL) by supersonic for 10 min. The similar procedure was applied to the above SCO nanoparticles (10 mg). The two solutions were combined and stirred for 6 h at room temperature, then filtered off with microporous membrane (F.φ50*0.22) by vacuum. Finally, the nanocomposite was washed with ethanol, and dried at 60 °C under vacuum overnight. The whole progress of reaction was kept in nitrogen atmosphere. IR (KBr cm\(^{-1}\)): \(\nu = 3177, 2924, 2826, 1640, 1496, 1451, 1221, 634\).

SCO-G2: Graphene (5 mg) was dispersed in ethanol (15 mL) by supersonic for 10 min. The similar procedure was applied to the above SCO nanoparticles (3 mg). The
two solutions were combined and stirred for 6 h at room temperature, then filtered off with microporous membrane (F.φ50*0.22) by vacuum. Finally, the nanocomposite was washed with ethanol, and dried at 60 °C under vacuum overnight. The whole progress of reaction was kept in nitrogen atmosphere. IR (KBr cm⁻¹): ν = 3177, 2924, 2826, 1640, 1496, 1451, 1221, 634.

Fig. S1 FT-IR spectra of [Fe(Htrz)₂(trz)](BF₄) (a), [Fe(Htrz)₂(trz)](BF₄)-G1 (b), [Fe(Htrz)₂(trz)](BF₄)-G2 (c).

Fig. S1 shows the FT-IR spectra of [Fe(Htrz)₂(trz)](BF₄), SCO-G1, SCO-G2, respectively. Obviously, compared with [Fe(Htrz)₂(trz)](BF₄), the spectra of the two SCO-G nanocomposites exhibited similar features corresponding to the peaks of the spin crossover complex. Though the FT-IR spectra of the two SCO-G samples showed weakly in some characteristic peaks, all of them revealed the out-of plane vibration modes of the triazole ligand at 634 cm⁻¹, and a stretching of 1,2-coordinated triazole ligand was also proved at 1221 cm⁻¹ and 1496 cm⁻¹. The band attributed to a stretching of the triazole ring was observed at 1451 cm⁻¹ consisting with the low-spin state of iron(II) center at 298 K.²
The TG curves of [Fe(Htrz)$_2$(trz)](BF$_4$)$_2$ NPs and SCO-G nanocomposites exhibited two obvious weight losses in the range of 85 °C to 800 °C, which might be attributed to the loss of physically adsorbed solvents and the decomposition of organic ligands. Compared with [Fe(Htrz)$_2$(trz)](BF$_4$)$_2$ NPs, the decomposition temperature of SCO-G nanocomposites obviously enhanced 8 °C, suggesting that the thermostability of [Fe(Htrz)$_2$(trz)](BF$_4$)$_2$ NPs increased because of the addition of graphene. The strengthened thermostability could be attributed to the interactions between [Fe(Htrz)$_2$(trz)](BF$_4$)$_2$ NPs and graphene. As shown in Fig. S2(b) and Fig. S2(c), the weight loss of organic in the second stage were 32% and 11% indicating that the [Fe(Htrz)$_2$(trz)](BF$_4$)$_2$ NPs occupied 54.3% and 18.6% in the SCO-G1 and SCO-G2, respectively.
