Abstract

Poly(organosilsesquioxanes) in designing electro, photo, and magnetic functional materials

In this thesis, we demonstrated the novel syntheses and functionalization of octameric and double-decker silsesquioxanes and investigated their utility as nanoconstruction sites for a variety of applications. In **Chapter 2**, novel precursor mono- and dichloro-functionalized POSS (**1** and **5**) were firstly prepared. Subsequently, **1** and **5** were treated with sodium azide led to a formation of new mono- and diazido-functionalized POSS (**3** and **6**), respectively. The relatively different polarity of a solvent successfully separated and recrystallized *cis*- and *trans*-**6**. Structures of all materials were confirmed by ^{1}H, ^{13}C, and ^{29}Si-NMR, X-rays single crystal analysis, and Maldi-TOF MS.

In **Chapter 3**, the work included introduction of versatilely functionalized macromolecules for higher-order molecular construction of organic–inorganic hybrids to novel precursor 2-arm POSS (**8**) *via* "click" chemistry. The introduction of palladium-catalyzed Sonogashira cross-coupling reaction between **8** and a set of ethynyl polycyclic aromatics to offer two new classes of mono- and oligo(*p*-phenylene ethynylene)s POSS. These materials derived from cubic silsesquioxanes are very robust, exhibiting excellently thermal stabilities to air ($T_{5\%loss} > 333^{o}C$) with highly $T_g > 80^{o}C$. Thus, their optical properties all showed the highly photoluminescence with a range of blue emission and quantum yield > 80% in the solution. In OLED application, we preliminary report some of materials used as active dopant in PVK and PBD matrix in multilayer OLEDs.

We also studied the effect of some organosilsesquioxane on magnetic nanoparticles. Our approach was to synthesize the core–shell type Fe_3O_4 nanoparticles in poly(organosilsesquioxane) (Fe_3O_4@OcTS) in **Chapter 4**, prepared by one-pot synthesis using reverse micelle method. The as-prepared ferrofluid droplets with average size 4–15 nm were in situ encapsulated via polycondensation of molecularly self-assembled octenyltrimethoxysilane (OcTS). The dynamic light scattering and transmission electron microscopy investigations on coated magnetite nanoparticles revealed uniform size of spherical shape and having thin and transparent shells. These nanoparticles showed redispersibility in non-polar solvents without agglomerations due to coated by a layer of hydrophobic shells. The thermogravimetric analysis and infrared spectroscopy suggested the existence of core–shell type. X-ray diffraction confirmed magnetite cores. The superconducting quantum interference device (SQUID) showed that they exhibited superparamagnetic behavior at 300 K and ferromagnetic at 3 K.