Liquid-crystalline Organic-inorganic Hybrid Dendrimer: Dendron-promoted Self-organization of Gold Nanosphere

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Nanoparticle-based periodic structure formation has attracted considerable attention in material science, because new synergistic functions could be derived from the periodic structure. Among organic soft materials, liquid-crystalline (LC) organic dendron is one of the most representatives to form spherical dendrimer-like structures by the self-assembling property. Such a spherical assembly spontaneously forms a multi-dimensional self-organized periodical structure. Thus, we focused our attention on introduction of such self-organization ability of organic dendrons into inorganic nanospheres. One representative strategy to obtain organic dendrimers is achieved by modification of internal core with hyper branch molecules. Here, if monodispersed gold nanospheres are used as an internal core, well-defined organic-inorganic hybrid dendrimer would be formed as a novel-type functional material. Initially, CO₂H-modified monodispersed gold nanospheres A₁-A₃ as an internal core were prepared by the reduction of chlorauric acid in the presence of dodecane thiol and thiohexadecanoic acid. Modification amount of CO₂H on A₁, A₂, and A₃ were 240, 220, and 100 molecules/sphere, respectively. From TEM images in Fig. 1(a)-(c), the size of A₁, A₂, and A₃ were calculated to be 5.9, 6.8, and 6.8 nm, respectively. On the other hand, 1st, 2nd, and 3rd generation dendrons G₁-G₃ with an amino-group were also prepared. The modification of A₁-A₃ by G₁-G₃ was carried out by amidation reaction to encapsulate gold nanospheres into dendron monolayers. Since in the case of G₂/A₂, the number of modified-dendron molecules/sphere was calculated to be 280, amidation reaction with G₂ proceeded almost stoichiometrically. G₂/A₂ spontaneously formed a highly periodical hexagonal structure with the interparticle distance of 14 nm on a TEM grid (Fig. 1(d)). SAXS and DSC experiments showed that G₂/A₂ exhibited thermotropic LC phases in wide range of temperatures. G₂/A₂ formed a simple cubic (SC) LC phase at 170 °C. The SC structure is displayed in Fig. 1(e), the unit cell parameter a of the SC phase was 12.5 nm. This result shows that the self-organization ability of dendrons was introduced into gold nanospheres by the convergent-like process using gold nanospheres as the internal core and G₂/A₂ spontaneously self-organized in cubic LC phase with SC structure. The effects of dendron generations and modification amounts have also been investigated.

Fig. 1. TEM images of (a) A₁; (b) A₂; (c) A₃; (d) G₂/A₂. The scale bar in (a) is common for all images. (e) The most plausible self-organized LC structure of G₂/A₂.