Journal of Colloid and Interface Science 531 (2018) 160–167

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

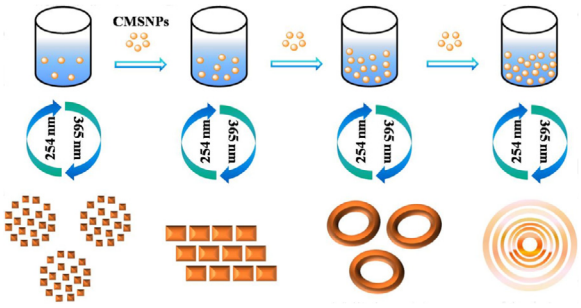
journal homepage: www.elsevier.com/locate/jcis

Photocontrolled self-assembly of silica nanoparticles at two scales

Chang Peng [a], Tianqi Zeng [a], Yong Yu [a], Ling Li [a,b,*], Ruoxi Wu [c,*]

[a] College of Science, Hunan Agricultural University, Changsha 410128, PR China
[b] State Key Laboratory for Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, PR China
[c] Zachry Department of Civil Engineering, Texas A&M University, 3126 TAMU, TX 77840, USA

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 June 2018
Revised 12 July 2018
Accepted 13 July 2018

Keywords:
Self-assembly
Controlled morphologies
Photoresponse
Superhydrophobic

ABSTRACT

The photocontrolled self-assembly of coumarin-functionalized silica nanoparticles is fabricated and investigated. When these nanoparticles are uniformly dispersed in $CHCl_3$ solution under 365 nm light illumination, four novel kinds of patterns are self-assembled on the bottom of glass beakers: circle patterns, square plate patterns, semi-annular and annular patterns, swirling patterns, which can be seen with the naked eye. Furthermore, these four patterns exhibit similar nanoscale morphologies: ring-like necklaces in nanoscale dimensions, and reveal interesting superhydrophobic property. In short, there exist two kinds of self-assembly of functionalized silica nanoparticles in two radically different dimensions, which can be potentially applied in self-cleaning fields and the construction of photocontrolled nanoscale structures and macroscale structures.

1. Introduction

The self-assembly of well-organized structures or patterns has attracted attention for developing functional hybrid materials [1–8]. Over the past decades, the stimuli-responsive self-assembly of inorganic nanoparticles has aroused great attention and interest, because the resultant material can exhibit thermal, magnetic, optical or electronic properties [9–13]. Among them, light represents unique performance that can be delivered instantaneously in precise time and space [11,12].

It is well know that photoresponsive materials usually undergo reversible structural transformations upon irradiation with light at specific wavelengths, such as the photoisomerization of spiropyran, azobenzene and the photodimerization of coumarin [14–16]. According to the research, numerous studies have concentrated specifically on the self-assembly of inorganic nanoparticles for generating nanoscale or microscale morphologies [17–19]. But to date, to the best of our knowledge, little attention has been focused on the self-assembly of functional hybrid materials to form macroscale patterns by light controlled, particularly two kinds of assemblies with different dimensions.

* Corresponding authors at: State Key Laboratory for Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, PR China (L. Li).
E-mail address: xhd3152@126.com (L. Li).

https://doi.org/10.1016/j.jcis.2018.07.054
0021-9797/

2. Experimental

7-hydroxycoumarin (98%), 6-chloro-1-hexanol (95%) and fumed silica (14 nm) are purchased from Sigma Aldrich. Potassium iodide, anhydrous potassium carbonate, 2,4-toluene diisocynate (TDI), and all solvents used are purchased from Sinopharm Chemical Reagent Co Ltd.

2.1. Synthesis of 7-(6-hydroxy hexyloxy) coumarin (Scheme S1)

In a typical experiment, 7-hydroxycoumarin (2.5 g, 15 mmol), 6-chloro-1-hexanol (4.2 g, 41 mmol), potassium iodide (1.2 g, 7 mmol) and anhydrous K_2CO_3 (4.4 g, 32 mmol) are added in N,N-dimethylformamide (DMF) (50 ml). Then the mixture is heated to 60 °C for 24 h. The obtained precipitate is filtered off and washed with DMF. Water is added to the solution, and then stirred for 6 h at room temperature. The residue is extracted with water (3 × 100 ml) and evaporated in vacuum drying oven at room temperature, and then the final product is obtained as a white solid of 3.5 g (yield, 86.6%, mp 52.1–53.1 °C). FT-IR (KBr) of 7-(6-hydroxy hexyloxy) coumarin: 3417 cm^{-1} (O—H), 2935 cm^{-1}, 2858 cm^{-1} (—CH_2—), 1734 cm^{-1} (O—C=O), 1057 cm^{-1} (R—CH_2—OH), 1012 cm^{-1} (R—O—R′). 1H NMR ($CDCl_3$) δ [ppm]: 1.2–1.9 (m, 8H, CH_2), 3.677 (t, 2H, CH_2OR), 4.020 (t, 2H, —OCH_2), 6.23 (d, 1H, aromatic). 6.79–6.84 (m, 2H, aromatic), 7.36 (d, 1H aromatic) 8.02 (d, 1H, aromatic), 7.64 (d, 1H, aromatic) (see Scheme 1).

2.2. Synthesis of SiO_2-TDI (Scheme S2)

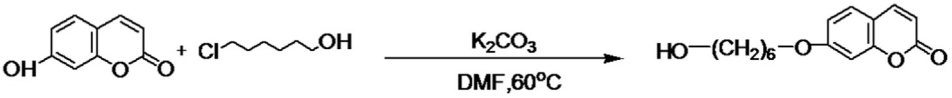
A mixture of fumed silica particles (0.5 g) and 0.52 g TDI are dispersed in 120 ml ethyl acetate by ultrasonication for 10 min, and the reaction mixtures are stirred at 60 °C for 4 h under nitrogen atmosphere. The product is separated by centrifugation and carefully washed with DMF to remove the un-reacted and physical-absorbed TDI. The product, TDI modified silica (SiO_2-TDI), is dried in vacuum at 80 °C for 12 h. FT-IR (KBr): 2297 cm^{-1} (—NCO), 1655 cm^{-1}, 1545 cm^{-1} (—NHCO—), 1616 cm^{-1} (C=O) (see Scheme 2).

2.3. Synthesis of CMSNPs (Scheme S2)

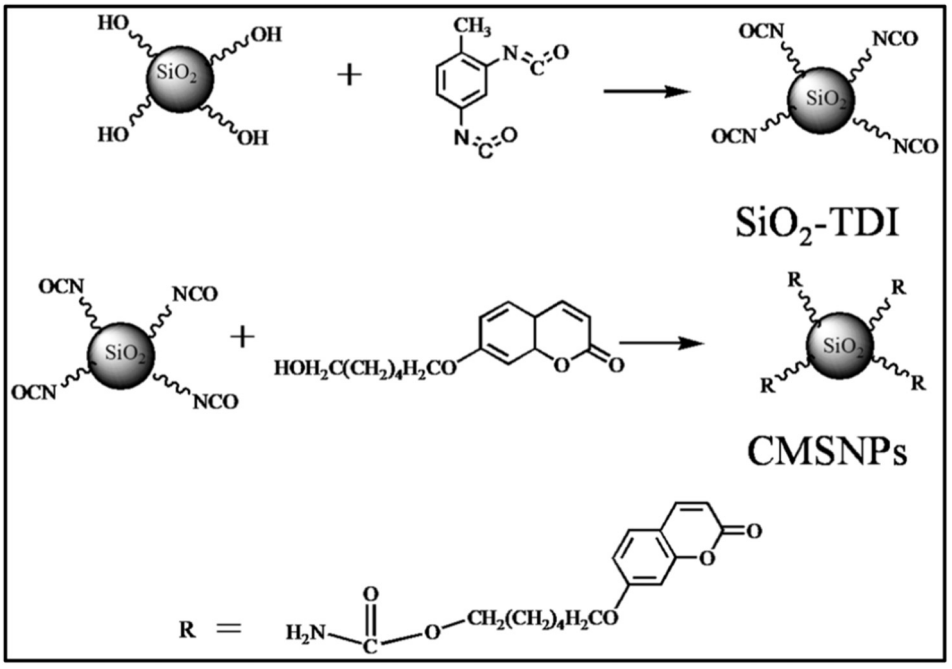
A suspension of 0.25 g SiO_2-TDI particles dispersed in 50 ml DMF is placed in an ultrasonic bath for 10 min, and 0.2 g 7-(6-hydroxy hexyloxy) coumarin is added, then the suspension is placed in an oil bath at 80 °C for 4 h with stirring. The product is isolated by centrifugation, re-dispersed in DMF and centrifuged again, finally dried in vacuum drying oven. FT-IR (KBr): 2925 cm^{-1}, 2856 cm^{-1} (—CH_2—), 1695 cm^{-1} (lactonic —C=O carbonyl), 1545 cm^{-1} (—NHCO—).

2.4. Characterization

Fourier transform infrared spectra (FTIR) are measured with a Nexus 670 FT-IR spectrometer. ^{1}H NMR spectra are recorded on a Mercury Plus 400 Hz spectrometer with trichloromethane solvent. The morphologies are investigated by scanning electron microscopy (SEM, JSM-6700F) and atomic force microscope (AFM, diNaNoMan Vs). Apparent water contact angles [20] and sliding angles are measured at room temperature (21 °C) with deionized water separately on a contact angle goniometer (JC2001) instrument. All the contact angles (CAs) measured at five different points on each sample surface are determined, and report their average values.



Scheme 1. The synthetic process of 7-(6-hydroxy hexyloxy) coumarin.



Scheme 2. The synthetic process of SiO_2-TDI and CMSNPs.