

Supporting Information

Self-assembled nanofibers from Leucine Derived Amphiphiles as Nanoreactors for Growth of ZnO Nanoparticles

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1. Experimental

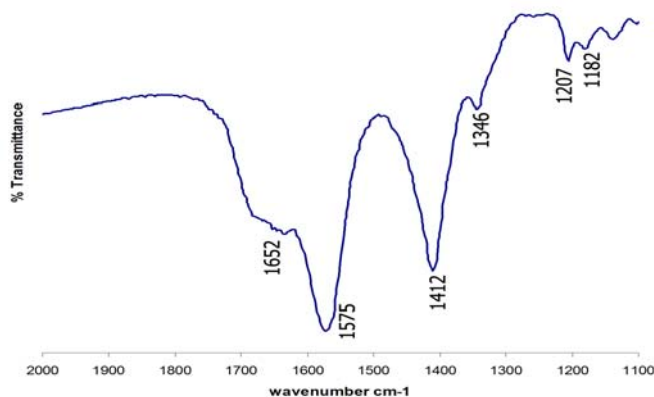
1.1 Materials

N-(3-dimethylaminopropyl)-N-ethylcarbodiimide (EDAC), *N*-Boc-1,6-hexanediamine hydrochloride, *N*-hydroxysuccinimide, (NHS), triethylamine, DMF, methanol, acetone, DMSO-*d*₆ with 0.1% v/v TMS, diethyl ether and TFA were purchased from Sigma-Aldrich and used as received. BOC protected Leucine was a gift from K. Fath at Queens College. Buffer solutions of various pH values and hydrochloric acid were purchased from Fisher Scientific.

1.2 Synthesis of Diamino-Leucine derived Amphiphile

BOC-protected leucine and *N*-Boc-1,6-hexanediamine hydrochloride (with one free amine and the other amine protected with BOC group) were coupled, followed by deprotection of the BOC groups, to yield the diamino-amphiphile. Briefly, to 50 mL of DMF solution, BOC-protected leucine, (0.5 g, 2.1mmol), 0.15 g of NHS and 0.25 g of EDAC were added. The solution was stirred for an hour at 2°C. Then, 0.41 g (1.7 mmol) of *N*-Boc-1,6-hexanediamine hydrochloride was added slowly, under vigorous stirring. The reaction was left stirring at room temperature for 24 hours, after which the solvent was evaporated by rotary evaporation. In order to deprotect the BOC groups, the product was treated with TFA (10 mL) in methylene chloride solvent (40 mL) for one hour under constant stirring at room temperature. After completion of the reaction, the reaction mixture was treated with sodium bicarbonate and then extracted with methylene chloride. The solvent was removed by rotary evaporation and the obtained product was

placed in diethyl ether and left to sit at room temperature for 3 hours followed by filtration to isolate the product. The pale yellow product obtained was recrystallized from methanol/acetone. The product was obtained in 65% yield. (^1H DMSO- d_6) δ 8.1 (s, 1H), δ 5.09 (s, 4 H), δ 3.41 (t, 1H), δ 3.19 (t, 2H), δ 2.72 (t, 2H), δ 1.73 (m, 1H), δ 1.25-1.36 (m, 6 H), δ 1.56 (m, 4H), δ 0.96 (d, 6H). The elemental analysis of the $\text{C}_{12}\text{H}_{27}\text{N}_3\text{O}$ compound revealed the following mass %: C 62.79; H 11.52, N 18.29, O 7.4. The calculated values for the compound were: C 62.82; H 11.81; N 18.32; O 7.05. FTIR spectroscopy was also conducted in order to confirm the formation of the product. ESI figure 1, shows the IR spectrum between 1100 cm^{-1} and 2000 cm^{-1} . Peaks at 1652 cm^{-1} (amide I), 1575 cm^{-1} (amide II), 1412 cm^{-1} ($-\text{CH}_2$ bending), 1346 cm^{-1} (C-H bending), 1207 cm^{-1} (C-O bending) and 1182 cm^{-1} (C-C bending) vibrations were observed.



ESI. Figure 1. FTIR spectrum of synthesized Leu-derived amphiphile

1.3 Self-Assembly

Individual stock solutions (10mM) of the Leu-hexyl-amine monomers were prepared in buffer solutions ranging from pH4 to pH10. In general, the materials were allowed to self-assemble for a period of 12-15 days. The assemblies formed were then washed with double distilled water. The sizes and morphologies of the structures formed were examined by TEM, and atomic force microscopy (AFM).

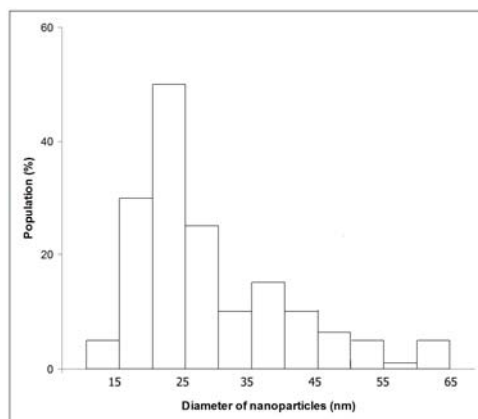
1.4 Transformation of nanospheres to nanofibers.

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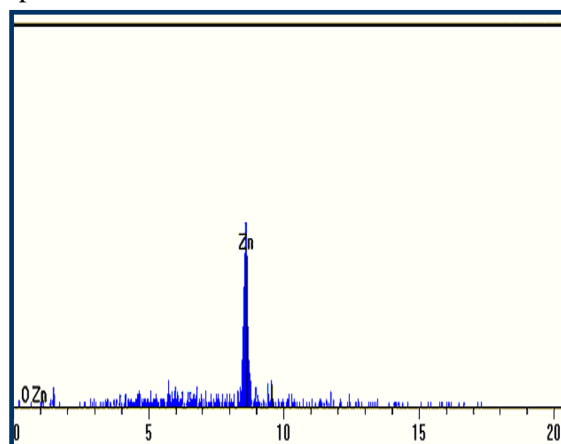
Self-assembled nanospheres (1mL) were placed in separate microcentrifuge tubes, after which 300 μL of $\text{Zn}(\text{CH}_3\text{COO})_2$ (0.1 M) was added to each sample containing 300 μL of buffer solutions at a pH range of 4-9. The samples were incubated for a period of 24 hours, washed and centrifuged. The materials were then analyzed by transmission electron microscopy.

1.5 Preparation of ZnO nanoparticles on nanofibers

Self-assembled nanofibers formed at pH 9 (500 μL) were placed in each microcentrifuge tube, and centrifuged and washed thrice. To the washed samples, additional 200 μL of $\text{Zn}(\text{CH}_3\text{COO})_2$ (0.2 M) was added, followed by the addition of buffer solutions (200 μL) at a pH range of 4-9. The samples were heated for an hour at 60°C, and allowed to sit at room temperature for a period of 1 hour, washed, centrifuged and dried before further analysis. The size distribution of the nanoparticles on the nanofibers is shown in ESI figure 2a, while figure 2b shows the EDX spectrum.



ESI Figure 2a. histogram showing the distribution of ZnO nanoparticle sizes



ESI figure 2b. EDX spectra of ZnO nanoparticles formed sizes on nanofibers

1.6 Degradation of Rose Bengal in the presence of ZnO nanoparticles grown on the nanofibers

The dye rose bengal was used as a model contaminant. For the photo-bleaching studies, 800 μL of ZnO nanoparticles grown on the nanofibers (at pH 9) were washed, centrifuged and then placed in quartz cuvettes, followed by the addition of 200 μL of 0.1 mM rose bengal solution prepared in 50-50 THF/water. The sample was then vortexed for 10 minutes so that the ZnO nanofibers would be dispersed in the solution to allow absorption/desorption equilibrium to establish itself. The solution was then

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bubbled with nitrogen for 10 minutes, prior to irradiation. The samples were then irradiated for a period of 3 hours at 354 nm under UV light. The UV light was delivered using 2 UV lamps (Cole-Parmer) (6W, 254/365 nm) placed at a distance of 3 cm from the sealed samples on each side. The reaction was conducted in triplicate for 3 hours. Absorption spectra of the samples were measured at intervals of five minutes to monitor the reaction and assess the photocatalytic efficiency of the ZnO nanostructures. Absorption measurements were taken at 550 nm, as initial scans showed this wavelength to be the maximum absorbance wavelength for relevant concentrations of the dye. The k values derived from the pseudo-first order plots for each sample (linear fitting coefficient of over 0.99 was obtained) were averaged.

1.7 Instruments

Transmission electron microscopy (TEM) (JEOL 120 EX) operated at 100 kV was used to characterize the self-assembled nanomaterials. Samples were washed twice with distilled water and air-dried onto carbon-coated copper grids.

Atomic Force microscopy (AFM) was carried out using a Quesant Universal SPM Instrument in the tapping mode in air using as silicon nitride cantilever.

FTIR Spectroscopy: FTIR analyses were performed using a Matteson Infinity IR equipped with DIGILAB, ExcaliBuv HE Series FTS 3100 software. The samples were dried under vacuum at 30°C and mixed with KBr to make pellets and then analyzed. All spectra were taken at 4 cm⁻¹ resolution with 100 scans taken for averaging. Sample measurements were carried between 400 to 4000 cm⁻¹.

Absorbance spectroscopy measurements were carried out using Varian Cary3 UV/Visible spectrophotometer with Varian data analysis tools.

Fluorescence Spectroscopy measurements were carried out using a Jobin Yvon Fluoromax 3 fluorescence spectrometer.

Energy Dispersive X-Ray Analysis (EDX)

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EDX analyses were carried out using a Hitachi S-2600N field emission SEM equipped with a Princeton Gamma Tech Model P014B Energy-dispersive X-ray. The SEM was set at 20 keV, and the samples were analyzed at 30° tilt for EDX.