Thermoreversible Organogels Formed in Polyols System for the Preparation of Sn Nanoparticles Encapsulated in Carbon

Experimental section

1) Materials and method

Materials.

Hexadecylamine (purity≧90%, Aldrich), oleic acid, Tin(II) chloride ($SnCl_2 \cdot 2H_2O$), sodium borohydride ($NaBH_4$), sodium hydroxide, ethylene glycol were purchased from Sinopharm Chemical Reagent Co. Ltd (SCRC). All the reagents were of analytical reagent and used without further purification.

Characterization.

Small-angle X-ray diffraction patterns were measured using Cu KS radiation (λ =1.5406 Å) on D8 advance X-ray diffraction (Bruker). Diffraction data for all samples were recorded between 0.8° and 10° (2θ).

High-resolution transmission electron microscopy (HRTEM) was performed with a JEM-2010FEF field emission electron microscope operating at 200 kV, equipped with an EDAX Phoenix EDS analyzer. A drop of sample suspensions in ethanol was deposited on a TEM carbon grid and dried in air.

Optical microscopy images were observed under an Olympus BX51 optical microscope equipped with crossed polarization lenses. A drop of heated solution was placed on a glass plate and allowed to form a gel. The photographs of the gel fibers were acquired digitally.

FT-IR spectra were recorded on a NICOLET model FT/IR-5700 Fourier transform infrared spectrophotometer.

AFM imaging was conducted with a Pico Scan atomic force microscope (Molecular Imaging, USA). Freshly prepared samples were mounted on AFM stage and imaged under MAC Mode in air (relative humidity = 40%—50%, T = ~25^{o}C) using MAC lever type II probes (spring constant = 2.8 N/m, resonant frequency = ~75 kHz, Molecular Imaging, USA). Scan rates were set at about 1.5 line/s. The images were rastered at 256 × 256 pixels, unfiltered and flattened when needed.

2) Synthetic route

Gel synthesis

Gel 1: Sodium hydroxide was dissolved in ethylene glycol (50g) under ultrasonic conditions. Then the solution was transferred into a three-neck round-bottomed flask, and oleic acid (2.0g), hexadecylamine (2.0g) were added sequentially with magnetic stirring. The flask was continuously purged with nitrogen. A condenser was attached to the flask, and the mixture was heated to 100 ^{o}C and remained at this temperature for 30min to produce a light yellow solution. After cooling to room temperature, a white gel was attained.

Gel 2: Similar to gel 1, gel 2 was prepared with extra Tin(II) chloride ($SnCl_2 \cdot 2H_2O$, 0.5g) added into the mixture.

Gel 3: The ethylene glycol solution of sodium hydroxide (50g) was separated into two equal parts: part 1 and part 2. Solution A was acquired with oleic acid, hexadecylamine and Tin(II) chloride appended to part 1 with the similar procedure in gel 1, while sodium borohydride ($NaBH_4$, 0.5g) dissolved in part 2 to produce solution B. Then, solution B was added dropwisely into solution A within 30min, and maintained for 30min at 100 °C. After cooling to room temperature, gel 3 was obtained.

Preparation of Sn@C composites

Sn/C composites were attained by the carbonization of gel 3. The process was performed with heating the gel to 200 ^{o}C for 2h under nitrogen atmosphere in a tube furnace, then 700 °C for 3h at 5 °C/min ramp.

Figure S1. FT-IR spectrum for gels

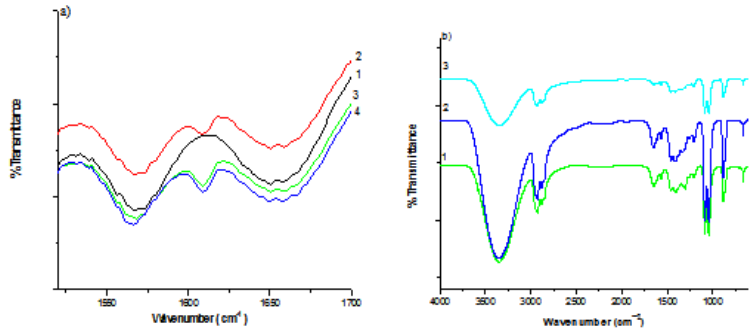


Figure S1. a) FT-IR spectrum of the solution at 70 °C （1） and the sol-gel transition after the heated solution was cooled to room temperature for 0 (2), 10 (3), 30 min (4); b) FT-IR spectrum of the gel without $SnCl_2$ (1), the gel with $SnCl_2$ (2), and after the reduction of $SnCl_2$ (3).

Figure S2. XRD patterns for gels

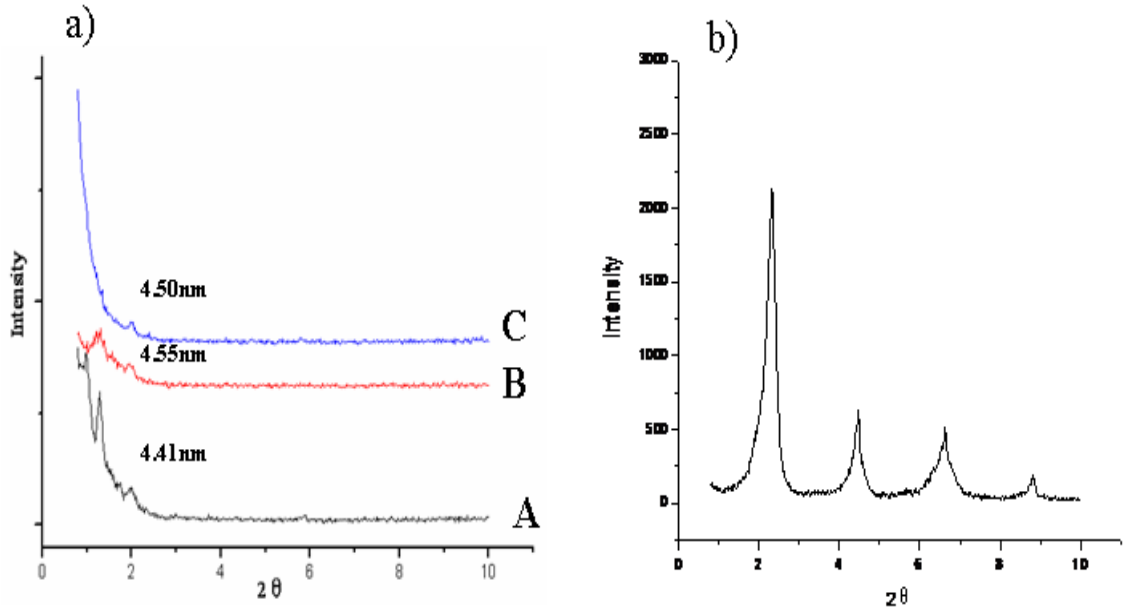


Figure S2. a) Small-angle XRD patterns of the gel without $SnCl_2$ A), the gel with $SnCl_2$ B) and after the reduction of $SnCl_2$ C); b) XRD pattern of the xerogel obtained from the gel without $SnCl_2$ in EG.

Figure S3. XRD patterns for Sn@C composite

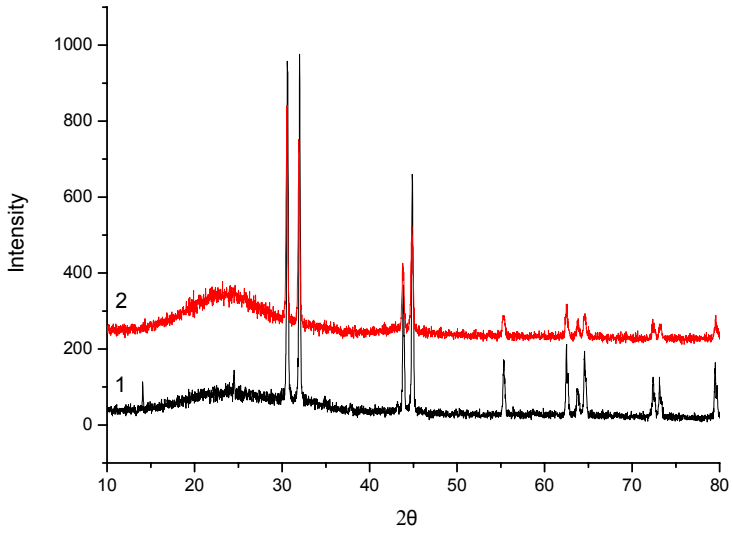
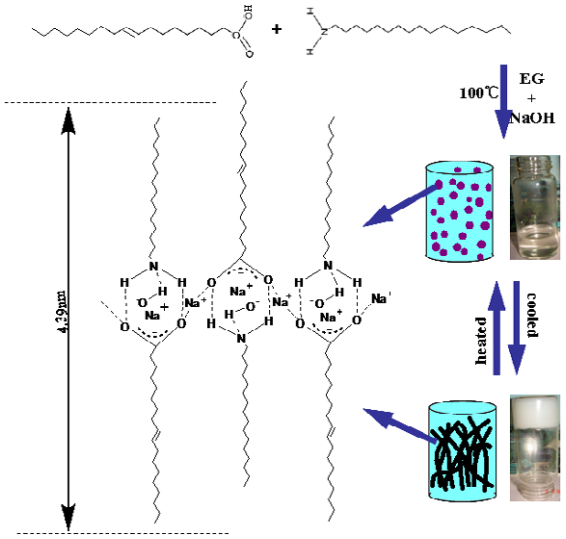


Figure S3. XRD patterns of Sn nanoparticles obtained from the calcination of the gel after the reduction of $SnCl_2$ at 700 °C (1), treated after concentrated hydrogen chloride at 100 °C (2).

Scheme S1. The formation mechanism of organogels



Scheme S1. A schematic to illustrate the formation of nano-asssembly aggregated structure of Na^+-induced organogel based on OA-HDA in EG solution.