Convenient and Template Free Route to One Pot Green Synthesis of Polyrhodanine Core-Shell Nanoparticles

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EXPERIMENTAL SECTION

Materials: All solvents and chemicals including Rhodanine, and Cu(OAc)2 were purchased from Sigma Aldrich and used without further purification. Deionized water was used for the experiments.

Characterization: Transmission electron microscopy (TEM) photographs were obtained using a Hitachi HT7700 microscope operated at 100 kV accelerating voltage. The TEM samples were prepared by dropping the pRh colloidal solution in ethanol/water onto carbon-coated copper grids. SEM images were taken at 15 kV accelerating voltage on a Hitachi SU1510. The UV-vis spectra was measured at 25 °C with a Cary 50-scan spectrophotometer using 10 mm optical path length quartz cuvettes. Fourier Transform infrared spectra (FT-IR) was recorded on Thermo Scientific Nicolet 6700. The microwave synthesis was carried out in Biotage Initiator 2.5 microwave reactor. All microwave reactions were carried out at 80 °C in a microwave tube.

[1] Microwave Synthesis of pRh core shell nanoparticles with Copper acetate: In a typical procedure, Rhodanine monomer (0.2 mM) was dissolved in ethanol (15 mL) under stirring in a 20 mL Biotage microwave vial, then Copper (II) acetate (0.2 mM) was introduced into the Rhodanine solution at room temperature. As soon as Cu(OAc)2 was added to the stirred solution a green precipitate of the Cu(II)-Rh complex was formed which was then heated in the microwave at 80 °C for 10 hours. During this period, the reaction was monitored intermittently by UV-vis and FT-IR spectroscopy. After 9-10 hours of the reaction, a black precipitate was obtained. This black precipitate was centrifuged and the supernatant was a greenish yellow solution, which was carefully separated and discarded. The black solid was washed 4 times with 3 mL of ethanol and air dried for 24 hours. The same procedure was repeated using deionized water as the solvent.

[2] Thermal Synthesis of pRh core shell nanoparticles with Copper acetate: In a typical procedure, the Rhodanine monomer (0.2 mM) was dissolved in a 150 mL two neck round bottom flask followed by 15 mL of ethanol. Then Copper (II) acetate (0.2 mM) was introduced into the Rhodanine solution at room temperature. As soon as Cu(OAc)2 was added to the stirred solution an olive green precipitate of the Cu(II)-Rh complex was formed which was then heated in an oil bath at 75 °C. After 96 hours of the reaction at 75 °C, a black precipitate was
obtained. The black precipitate was centrifuged and the supernatant solution was carefully separated and discarded. The solid black product was washed 4 times with 3 mL of ethanol, air dried for 24 hours and analyzed. The same procedure was repeated using deionized water as the solvent.

[3] Microwave Synthesis of pRh with composite catalysts: Rhodanine monomer (0.2 mM) was dissolved in Ethanol (15 mL) under stirring in a 20 mL Biotage microwave vial, Copper (II) acetate (0.2 mM) was introduced into the Rhodanine solution at room temperature. To the green suspension of Cu(II) Rh complex formed by the above reaction, potassium permanganate (0.2 mM) was added. This reaction was heated in the microwave at 80 °C and intermittently analyzed by UV-vis and FT-IR spectra. The supernatant solution was colorless and a black precipitate was obtained after 4 hours of the reaction. The reaction was deemed complete now and mixture was centrifuged. After centrifugation, a black solid was obtained, which was washed four times with 3 mL of ethanol and then air dried for 24 hours and analyzed. The FT-IR and UV-vis analysis of the supernatant liquid show no traces of unreacted Cu(II)Rh complex or polyRhodanine.

[4] Synthesis of pRh with KMnO₄ as oxidant: Rhodanine monomer (0.2 mM) was dissolved in ethanol (15 mL) under stirring in a 20 mL Biotage microwave vial and potassium permanganate (0.2 mM) was added to this solution. No precipitation/suspension formation occurs at room temperature and after heating the reaction at 80 °C in the microwave for 4 hours, a black precipitate was obtained. The solid was centrifuged, washed four times with 3 mL of ethanol and air dried for 24 hours. The FT-IR and UV-vis analysis of the supernatant liquid show no traces of unreacted mono or polyRhodanine.

[5] Adsorption of Methyl Orange (MO) by pRh: In a 50ml round bottom flask, 20 mL of 0.00303M methyl orange solution prepared by dissolving 0.001 moles of MO in 0.330 L of deionized water was stirred at room temperature and 0.0140 g of pRh was added to this solution. The suspension was stirred at room temperature and monitored by UV-vis spectra. For UV-vis measurement, a 3 mL aliquot of the reaction mixture was taken out every hour and centrifuged. The supernatant liquid was collected and 0.2 mL of this solution was diluted with 3.4 mL of deionized water for every UV-vis measurement.
Figure S1: IR of the Rhodanine and Olive green Rhodanine-Cu Complex

Figure S2: IR of the Rhodanine and PolyRhodanine Nanospheres obtained under Microwave conditions
Figure S3: UV-Vis monitoring of the PolyRhodanine Nanospheres formation under Microwave conditions

Figure S4: TEM of PolyRhodanine Nanospheres obtained under Microwave conditions
Figure S5: SEM of PolyRhodanine Nanospheres obtained under Microwave conditions

Figure S6: Overlay of Raman Spectra of Rhodanine (Red) and PolyRhodanine Nanospheres (Blue) obtained under Microwave conditions
Figure S6: TEM monitoring of the PolyRhodanine nanospheres P2 formation under microwave conditions at different time intervals

S6-A: TEM image taken after 3h of the reaction

S6-B: TEM image taken after 6h of the reaction
TEM images taken after 9h of the reaction