

Oil loaded multifunctional composite nanocontainers

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Introduction

Suslick, Gedanken and coworkers have demonstrated a method to prepare aqueous suspensions of proteinaceous microcapsules filled with water-insoluble liquids using high-intensity ultrasound. Herein we developed a new method to make polyglutamate/polyelectrolyte nanocontainers. First, aqueous polyglutamate nanocontainers filled with water-insoluble liquid were made by applying high intensity ultrasound to a two-phase system of aqueous polyglutamate solution and nonaqueous liquid. Then, the obtained polyglutamate nanocontainers were coated with polyelectrolytes using layer-by-layer (LBL) deposition. The major advantage of this technique is that LBL assembled polyelectrolyte shells not only make the polyglutamate containers more stable but also can be easily modified to target specific organs or tumor types by incorporating biochemical functions.

Experimental

Poly-L-glutamic acid sodium salt (polyglutamate, Mw~50,000-100,000), polyethyleneimine (PEI, Mw~25,000), polyacrylic acid (PAA, Mw~50,000), were purchased from Sigma-Aldrich. Iron pentacarbonyl ($\text{Fe}(\text{CO})_5$, tech 99.9%, $\rho=1.45\text{g/ml}$) was kindly provided by Tianyi Co. (China),

Apparatus and procedures

5% (w/v) TPP toluene solution or Iron

pentacarbonyl and toluene (2.5% v/v, $\text{Fe}(\text{CO})_5$: toluene) were layered over 5% (mg/ml) polyglutamate aqueous solution with sodium dodecyl sulfate (SDS) as surfactant. The mixture was sonicated for 3 min at ambient conditions. For fabrication of the layer-by-layer assembled polyelectrolyte shell, 0.05 mL PEI or PAA solution (2mg/mL in 0.5M NaCl) was mixed with 1 mL suspension of polyglutamate containers at pH=6.5.

Results and Discussion

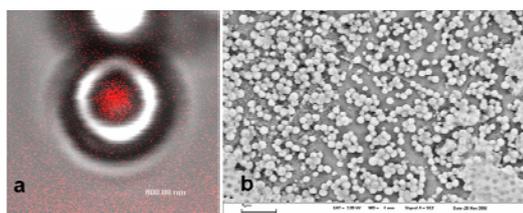


Fig.1 Confocal microscope image of polyglutamate containers made in fluorescence TPP (a) and SEM image of polyglutamate/polyelectrolyte nanocontainers (b).

Fig.1(a) shows that a core-shell structure was formed with a fluorescent interior and non-fluorescent shell. The central fluorescent core can be assigned to the TPP dissolved in toluene while the more hydrophilic polyglutamate shell does not adsorb non-polar TPP. The hydrophobic core and protein shell of the nanocontainers are very important for biomedical applications since the core may contain a variety of water-insoluble materials. A lot of monodisperse 600 nm toluene-loaded nanocontainers with LBL

modified shell were obtained in SEM image (Figure 1b).

Since lipophilic dyes can be incorporated into composite nanocontainers by applying ultrasonic irradiation and LBL deposition. Herein, our interest extends to fabricate magnetic proteinaceous nanocontainers by using this combined technology. Gedanken et al. reported fabrication of magnetic microspheres from BSA and iron pentacarbonyl as well as from BSA and iron acetate. It demonstrated that the produced microspheres were composed of iron oxide-filled and coated BSA and the total percentage of iron oxide in the microspheres was about 40%. Their study inspired us to combine the ultrasonic technology of decomposition of volatile metal compounds with LBL assembly to fabricate magnetic composite nanocontainers. First, iron pentacarbonyl toluene solution were layered over polyglutamate aqueous solution for ultrasonic treatment, then the produced precipitates were isolated from the toluene/polyglutamate dispersion and deposited with alternating polyelectrolytes.

Core-shell structured 50-300nm polyglutamate nanocontainers with 6 layers polyelectrolytes deposition were observed clearly.(Fig.2a) The largest nanocontainer in Fig.2a is 300nm and its shell thickness is 35nm revealing the shell made up of assembled polyelectrolyte layers. The dark center may be assigned to Fe₂O₃ nanoparticles produced upon decomposition of Fe(CO)₅ in toluene and the grey shell may be attributed to the polyglutamate/polyelectrolyte shell with several nanometers thickness while the more hydrophilic polyglutamate shell

does not adsorb non-polar toluene. Moreover, the weak crystalline electron microdiffraction patterns of the core-shell structured nanocontainers could also be observed (Fig.2b.2c), which may be explained by the small amount crystalline Fe₂O₃ entrapped into the nanocontainers.

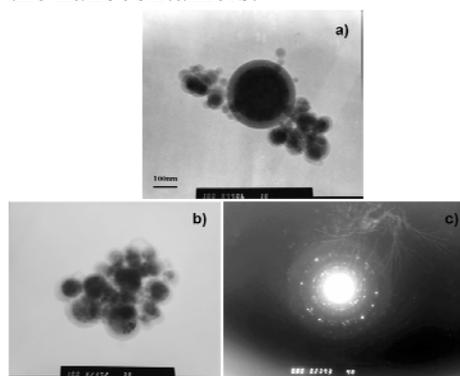


Fig.2 Fe₂O₃ loaded polyglutamate/polyelectrolyte nanocontainers. (a) (b) TEM image of nanocontainers; (c) electron microdiffraction pattern of (b) measured by TEM.

Conclusion

A novel simple technology was used to fabricate oil-loaded polyglutamate/polyelectrolyte containers. Encapsulation of amorphous Fe₂O₃ into polyglutamate/polyelectrolyte nanocontainers by sonochemical decomposition of Fe(CO)₅ and layer by layer assembly of polyelectrolytes has been carried out successfully. The smart core-shell structure nanocontainer is full of prospect in biomedical and industrial applications.

Reference

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