



Covalently Attached Hollow Capsules Resistant to Etching of Polar Solution

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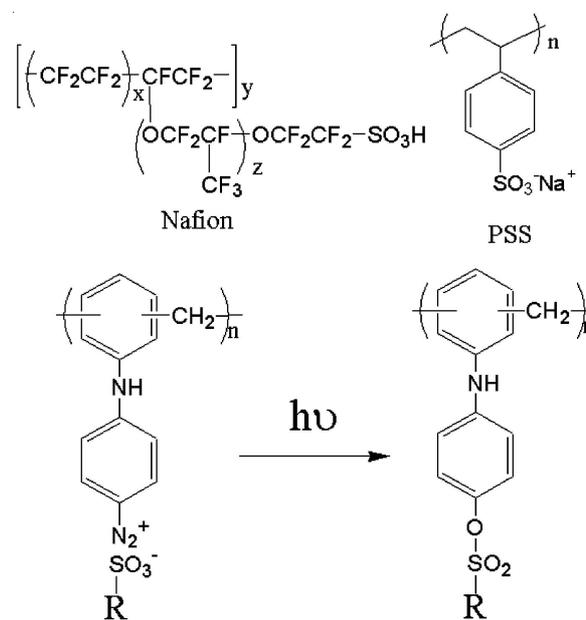
Hollow capsules with nano-scaled walls were prepared by electrostatic layer-by-layer deposition of diazo-resin in alternation with nafion onto microparticles templates, followed by dissolution of the cores with acid solution or organic solvent. The stepwise growth of multilayers was followed by UV/VIS spectra. The formation of hollow capsules was verified by confocal laser scanning microscopy and atomic force microscopy. After application of UV irradiation, the linkage of hollow capsules was converted from an ionic bond to a covalent bond and the conversion was verified by FTIR and UV/VIS spectra. As a result, the stability of hollow capsules to polar solution increased dramatically.

Key Words: Hollow capsules, Diazoresin, Self-assembly.

INTRODUCTION

Many researchers are interested to study the hollow-sphere structures, due to their potential to encapsulate large quantities of guest molecules within the empty core domain for membrane separation, release, transport and storage¹. They are widely exploited as drug carriers, as protective containers for cells and enzymes and as confined reaction vessels, transfection vectors in gene therapy, carrier systems in heterogeneous catalysis, dye dispersants²⁻⁵. However, the stability of such capsules depends on nature of solvent and is not always adequate. Deformation and rupture of multilayer capsules under shear stress or solvent etching may apparently limit the use of these novel structures^{6,7}.

The electrostatic layer-by-layer self-assembly technique offer new ways to generate exciting nano-architectures⁸. It was found that the stability of multilayer films increased by converting its linkage from an ionic bond to a covalent bond upon application of UV light or heat⁹⁻¹¹. Nafion represents a unique family of polyelectrolyte, which consists of a perfluorinated backbone and short pendant chains terminated by sulfonic acid groups¹²⁻¹⁵. Here, we demonstrate the fabrication of covalently attached multilayer capsules by means of photoreacting of diazonium and sulfonate group of Nafion at the interface to form a crosslinking structure (**Scheme-I**). The generality of the technique was further verified with poly(styrene sulfonate sodium salts) (PSS).



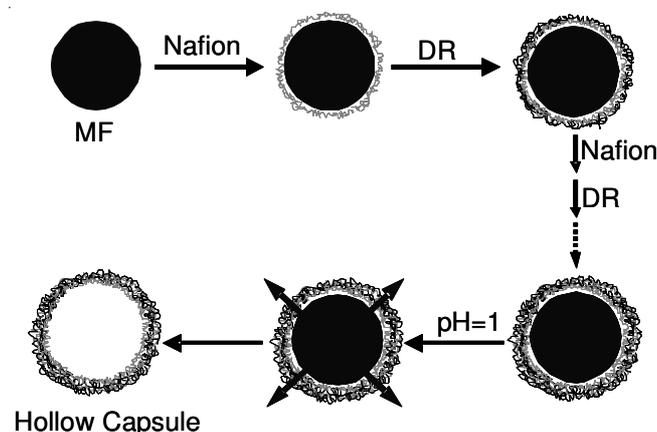
Scheme-I. Structure of chemicals used and their photoreaction with diazoresin

EXPERIMENTAL

Poly(styrene sulfonate sodium salts) (m.w. 70 000) and Nafion (a 5 % w/v mixture in water and lower aliphatic alcohols, 1100

equivalent weight; *i.e.*, 1100 g of polymer per mole of $-\text{SO}_3\text{H}$ groups) were purchased from Aldrich. Diphenylamine-4-diazo-resin (DR) was synthesized according to the reported method⁹. Amine-labeled silica (3 μm), melamine formaldehyde (MF, 4 μm) and polystyrene (PS, 5 μm) particles were purchased from microparticles GmbH, Berlin Germany.

Preparation of hollow capsules by electrostatic layer-by-layer self-assembly technique: Capsules were fabricated with positively charged diphenylamine-4-diazo-resin (0.2 mg/mL in a 9:1 methanol/water mixture) and the negatively charged species including poly(styrene sulfonate sodium salts) (1 mg/mL in 0.5 M NaCl) and Nafion (1 mg/mL, in a 9:1 methanol/water mixture, pH = 3), diphenylamine-4-diazo-resin and Nafion or poly(styrene sulfonate sodium salts) were assembled onto the surface of templates including silica, MF or PS microparticles by layer-by-layer adsorption according to the method reported previously^{1,8}. The added species with charge opposite to that of the templates surface or the last layer deposited was allowed to adsorb for 15 min. The excess added species were removed by three repeated centrifugation (2000 g, 5 min)/washing/redispersion cycles with diluted aqueous NaCl in each deposition step. The subsequent layers were deposited in the same manner with the oppositely charged species. After completion of the desired number of deposition cycles, hollow capsules were prepared by dissolving the silica core with 0.1 N hydrofluoric acid, melamine formaldehyde cores with 0.1 N HCl or polystyrene core with tetrahydrofuran (THF) (**Scheme-II**). The resulting hollow polymer capsules were then centrifuged at 500 g for 5 min and washed with the corresponding solvent and water three times. All the above procedures were carried out in dark.



Scheme-II: Illustration of the growth of alternating Nafion/DR capsules templated on melamine formaldehyde latex particles

Photoreaction induced by UV light: Irradiation was performed using UV lamps. The hollow capsules in aqueous solution were irradiated for 15 min.

Infrared spectroscopy: Spectra of the hollow capsules samples were acquired using a Varian resolution fourier transform infrared spectrometer (Varian FTS 3100, USA) equipped with a wide-band MCT detector, collected with 512 background scans and 4 cm^{-1} resolution. Variable angle specular reflectance mode (VASRM) spectra were acquired with the 86° incidence angle. The single beam spectrum of the variable

angle specular reflectance mode accessory was used as a background. Scanning was conducted in the mid-IR range from 4000 to 400 cm^{-1} . Spectra manipulations performed on the data, such as baseline correction and CO_2 peak removal (from 2405 to 2250 cm^{-1}) were performed using the Varian resolution pro software package.

RESULTS AND DISCUSSION

Formation of hollow capsules: Confocal micrographs were taken with a confocal laser scanning microscope (CLSM) Aristoplan from Leica, providing strong evidence for the successful formation of hollow capsules of $(\text{PSS}/\text{DR})_4$ and $(\text{Nafion}/\text{DR})_4$. The representative confocal laser scanning microscope images of hollow capsules are shown in Fig. 1a. Circular two-dimensional structures were obtained by removal of the templating cores. Scanning force microscopy (SFM) images obtained by means of a digital instruments nanoscope IIIa in the tapping mode provides further evidence for continuous capsules when adsorbed onto the polar mica substrate after drying (Fig. 1b). One can clearly see that the shells are flattened and exhibit creases and folds arising from evaporation of the aqueous content. The wall thickness was directly related to the number of deposition cycles. Typically, the average thickness of the capsule of $(\text{diphenylamine-4-diazo-resin}/\text{Nafion})_4$ is approximately 15.8 nm per single bilayer of diphenylamine-4-diazo-resin/Nafion according to a minimum height of about two superimposed shell walls.

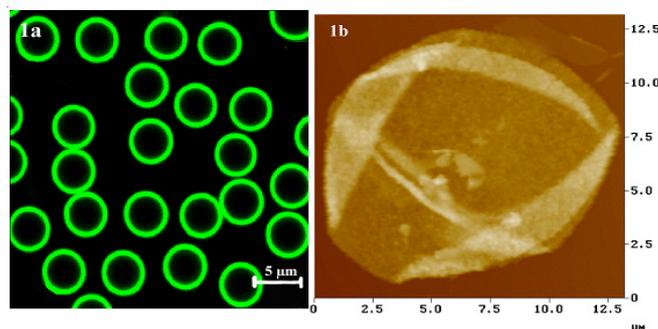


Fig. 1. Confocal laser scanning microscope (a) and scanning force microscopy (b) images of hollow capsule of $(\text{DR}/\text{Nafion})_4$

The deposition process was monitored by UV-VIS absorption spectra performed on a Cary 4E UV/VIS spectrophotometer. Fig. 2 shows the absorption spectra of hollow capsules in THF dependent of the number of diphenylamine-4-diazo-resin/Nafion bilayers. The characteristic peak at 375 nm is assigned to the $\pi-\pi^*$ transition of the diazonium group of diphenylamine-4-diazo-resin. It was found that the absorbances at 375 nm increase almost linearly with the number of deposition cycles, indicating that the layer-by-layer fabrication proceeded reproducibly and controllably and that the homogeneity of the film is excellent.

Covalent attachment of hollow capsules via photoreaction: The photodecomposition of the capsules composed of $(\text{DR}/\text{Nafion})_4$ and $(\text{PSS}/\text{DR})_4$ was investigated in aqueous solution by monitoring the absorption spectra of the diphenylamine-4-diazo-resin capsules at different irradiation times (Fig. 3). From both DR/Nafion and DR/PSS systems, we can observe

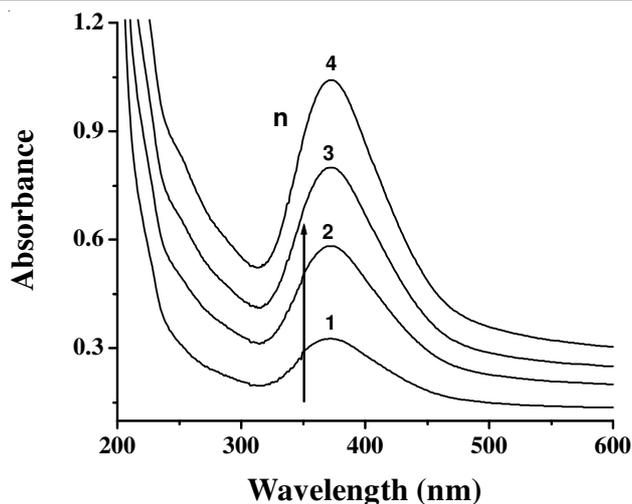


Fig. 2. Absorption spectra of hollow capsules composed of (DR/Nafion)_n with different number of deposition cycles, $n = 1, 2, 3, 4$.

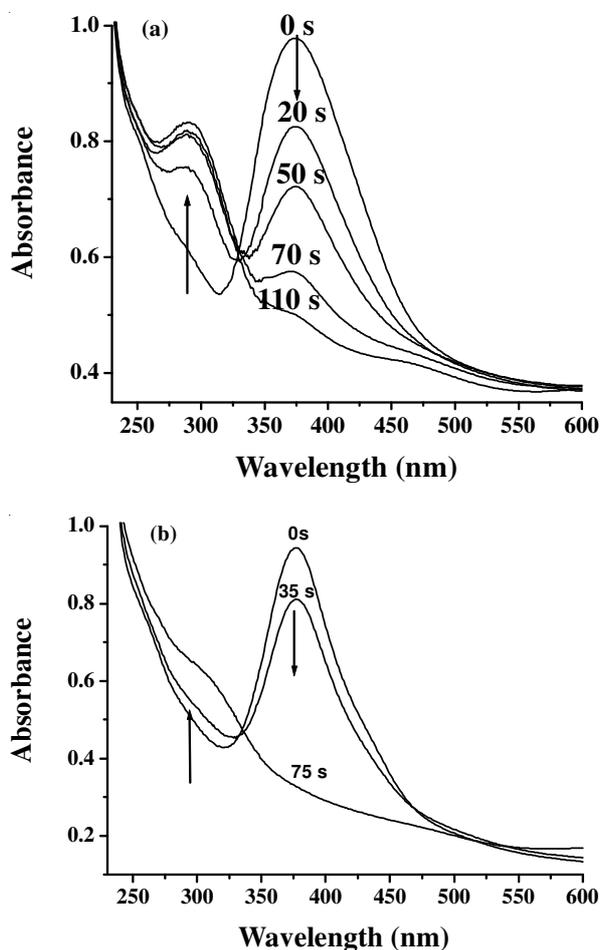


Fig. 3. UV-VIS spectra of hollow capsules composed of (DR/Nafion)₄ (a) and (DR/PSS)₄ (b) with different UV irradiation time

that the absorption band centered around 375 nm, characteristic of the diazonium group, decreases rapidly under UV irradiation due to the decomposition of the diazonium group, concomitantly, the new peak centered around 290 nm appears in the former system, indicating the formation of the new covalent bond. But no apparent peak was seen for the latter, although this characteristic peak was obtained with the dry DR/PSS multilayers on the flat surface¹⁰. The other authors didn't

observe the peak at this wavelength with hollow capsules from DR/PSS in solution¹⁶. The photodecomposition is almost complete within 2 min under the experimental conditions. It is proposed that the photoreaction takes place between the diazonium and the sulfonate group linked via electrostatic attraction. Under irradiation of UV light, diphenylamine-4-diazo-resin is converted into its phenyl cationic form releasing N₂, then an S_N1 type of nuclear displacement by sulfonate group occurs as shown in **Scheme-I**. The difference between the DR/Nafion and the DR/PSS systems arises from their different activity. Nafion's acidity ($-H_a \sim 12$ on Hammett's scale) is comparable with that of 100% sulfuric acid¹⁷ implying a nearly complete degree of ionization for pH 3, while poly(styrene sulfonate sodium salts) can not ionize completely in acid solution. Thus, Nafion is more active than poly(styrene sulfonate sodium salts).

FT-IR was employed to further confirm the change taking place in the hollow capsules of (DR/Nafion)₄ before and after irradiation (Fig. 4). For the specimen before irradiation, two quite strong vibration bands appeared at 2227 and 2173 cm⁻¹ could be assigned to the asymmetric and symmetric stretching modes of diazonium, respectively. The appearance of the two distinct absorption bands at 1586 cm⁻¹ and 1119 cm⁻¹, which were attributed to the stretching mode of phenyl group containing substituted diazonium group in diphenylamine-4-diazo-resin and N-O stretching mode between diazonium and sulfonate groups due to strong ionpair effect ($-N-N^+-SO_3^-$), respectively. However, after UV irradiation, the former was separated into two bands at 1606 and 1645 cm⁻¹ and the latter disappeared completely, indicating the decomposition of the diazonium groups in the hollow capsules. The symmetric stretching vibration of the highly polar $-SO_3^-$ group is observed at 1033 cm⁻¹ before and after UV irradiation. Thus, it is concluded that Nafion was photo-polymerized to diphenylamine-4-diazo-resin in hollow capsules, leading to a three-dimension crosslinking network.

Stability of hollow capsules: The effect of UV irradiation on the stability of the hollow capsules in polar solvent was

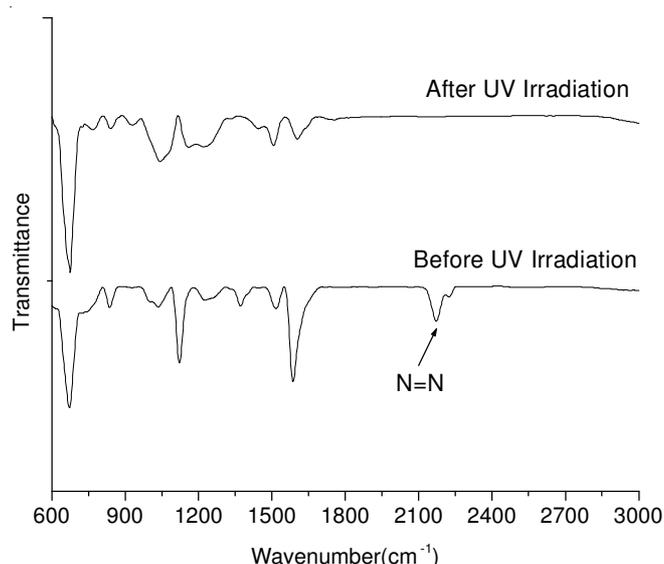


Fig. 4. FTIR spectra of hollow capsules of (DR/Nafion)₄ before and after UV irradiation

investigated. After irradiated and unirradiated capsules of (PSS/DR)₄ and (DR/Nafion)₄ were etched with dimethyl formamide for 0.5 h, solvent was removed after centrifugation and capsules were redispersed in water. The absorbance of the unirradiated capsule solutions detected at 375 nm decreases dramatically, while no apparent damage of the irradiated capsules was observed, according to the absorbance at 290 nm. Confocal laser scanning microscope provides a more direct observation. Before irradiation and after etching with a H₂O-DMF-LiCl (2:4:1 wt %) ternary solvent, no capsule composed of (PSS/DR)₄, (Nafion/DR)₄ was observed by means of confocal laser scanning microscope. In contrast, after irradiation, capsules were shape-persistent, indicating a much greater stability caused by UV irradiation. It can be ascribed to changes of the structure of the multilayer containing diazoresin and Nafion from ionic to covalent and leads to a three-dimension crosslinking network as a result of the photoreaction.

Conclusion

The layer-by-layer technique in combination with photoreaction *in situ* provides a simple and efficient way to obtain covalently crosslinked hollow capsules, which have highly stability resistant to etching of polar solution or against dissolution. In aqueous solution, the photoreaction of the diazonium group and the sulfonate group doesn't always proceed well, it depends on the reaction environment and chemical structure of the substances with the sulfonate group.

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