**Modification of the polyelectrolyte capsule shell by nanodiamonds for remote microwave opening**

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**Abstract**

Nanodiamonds (ND) are one of the most attractive carbon materials for nanotechnology. The impregnation of NDs into the polymer capsule shell in the form of the single nanoparticles insures the control over the thermal conductivity of the capsule shell and increases their sensitivity to the external microwave irradiation. The polymer shell of the polyelectrolyte capsules was modified with NDs by electrostatic adsorption technique. The sensitivity of the capsules with embedded NDs to the external microwave irradiation was demonstrated by scanning electron microscopy leading to the shell rupture and release of the encapsulated agents.

Keywords: nanodiamonds, polyelectrolyte capsules, Layer-by-Layer, modification, microwave absorption.

**1. Introduction**

The Layer-by-Layer (LbL) technique was firstly proposed by Iler in 1966 for the formation of the film by alternating adsorption of inorganic nanoparticles [1] and extended to the formation of polymer film by interaction of oppositely charged polyelectrolytes by Decher and Hong [2]. Lately in 1998 LbL approach was transferred to the hollow polymer capsules fabrication [3] and since then many groups over the world conduct the research in this area.

LbL is versatile procedure allows formation of the polyelectrolyte capsules using wide range of the polymers (synthetic and naturals) as materials of the capsule wall. The advantages of this technique are not only limited to specified shape and size of the capsules, but also to broad variety of the materials to be encapsulated and easy approach of the capsule shell modification.

The polymer shell could be easily modified by various materials including inorganic and organic nanoparticles, dyes, specified ligands etc. The most general approach for the capsule modification is based on alternating adsorption of the preformed nanomaterials from the solution. Adsorption occurs by LbL concept due to electrostatic interaction or other forces (e.g. hydrophobic, hydrogen interactions) that lead to the bonds formation between the capsule wall and the next nanoparticle layer. Moreover, impregnation of the polymer capsule shell with nanoparticles provides additional properties to the final capsule system and functional sensitivity to the external triggering leading to the distant, non-contact release of encapsulated cargo. So, the silver and gold nanoparticles were embedded into the polyelectrolyte capsule shell followed by their opening by the laser irradiation [4]. Shchukin et al. demonstrated modification of the capsule with magnetite nanoparticles that attains the remote ultrasound destruction of the polyelectrolyte shell [5]. Similar effect was achieved by incorporation of TiO2 particles in the capsule shell [6]. However, only few works are related to incorporation of carbon nanostructures (nanotubes) into the polymer capsule shell [7-8]. The interest of nanocarbon application for the capsule fictionalization is related to possibility of their triggering by remote microwave treatment. To the best of our knowledge, there are no reports on microwave-induced rupture of the polyelectrolyte capsule with carbon nanostructures in the shell.

Among the new carbon nanostructures, NDs are currently produced on an industrial scale and commercially available. The current achievements in the NDs synthesis and understanding of their possible applications led to the fact that they are considered as one of the most attractive carbon materials for nanotechnology. NDs can be successfully used in nanocomposite materials, nanoelectronics elements, selective adsorbents and catalysts. The ND use significantly improves the quality of microabrasive and polishing compounds, lubricating oils, rubbers, magnetic recording systems and their use in biology and medicine as biomarkers and for drug delivery systems.

The main difficulty associated with the use of NDs is their pronounced tendency to coagulation, which results in the formation of aggregates with sizes of several hundreds of nanometers [9]. However, even the use of ND aggregates as additives for polymer composites can significantly improve the characteristics of polymeric materials by forming additional bonds between the polymer molecules and NDs, which is largely determined by the surface activity of the ND particles.

In the present paper, we propose application of NDs as one of the components of the polyelectrolyte capsule shell for remotely triggered of their shells by microwave irradiation. Microwave absorption by NDs, most likely, occurs mainly due to dielectric relaxation. The dielectric properties of NDs particles have been sparsely studied due to the difficulty of contact electrode approaches as well as percolation issues when measuring nanoparticles [10, 11]. Many unique properties of NDs are attributed to the presence of sp2 hybridization in their structure [12]. Previously, it was demonstrated that dielectric polarisation and loss increased with increase of the sp2 hybridization; therefore, effective microwave absorption can be expected in the case of NDs [13, 14]. Additionally, microwave absorption in the composite systems increases owing to multiple scattering due to the large specific surface area of nanoparticles.

**2. Experimental section**

## The polyelectrolyte capsules were obtained by electrostatic self-assembly of positively charged poly(allylamine hydrochloride) (PAH, 50 kDa, Sigma-Aldrich) and poly(sodium styrene sulfonate) (PSS, 70 kDa, Sigma-Aldrich) according procedure described in [15]. The CaCO3 microparticles were used as sacrificial template for the capsule formation. The carbonate particles were synthesized by mixture of CaCl2 and Na2CO3 under stirring as described in [16]. The layer of NDs (carboxylated, 5 nm, Sigma-Aldrich) was formed by simultaneous adsorption of PAH and NDs solution (3.3. mg/ml).

## The microwave triggering was performed by treatment of the capsule water suspension by microwave irradiation (2.45 GHz, 800 W, 10 min) in the ice bath. The sample was placed in ice bath to prevent heating before irradiation.

## The microcapsules were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), confocal laser scanning microscopy (CLSM) and dynamic light scattering (DLS) methods.

**3. Results and discussion**

The capsules were fabricated by LbL adsorption of oppositely charged polyelectrolytes from their water solution. PAH and PSS were used as a polycation and polyanion, respectively. NDs cannot be directly adsorbed on the carbonate template due to their hydrophobic nature. However, they can form coacervates with the polyelectrolytes used in this work. The most stable coacervate was formed between NDs and PSS due to the contribution of hydrophobic interactions between NDs and PSS benzene ring, which was further used for NDs electrostatic deposition in the capsule shell

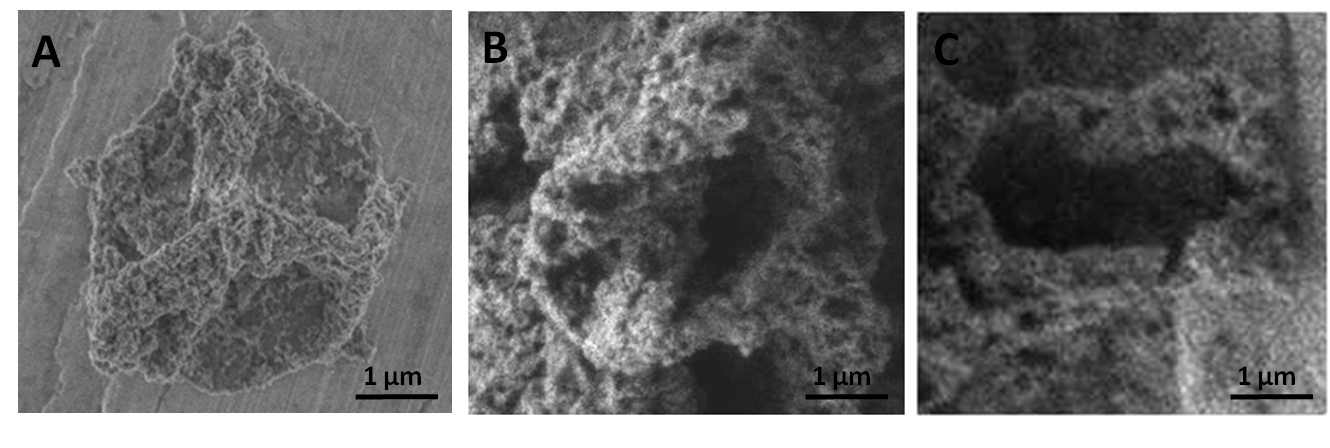
The LBL assembly of the polyelectrolyte capsule shell was monitored by measurements of the electrophoretic mobility. Figure 1A demonstrates the alternated charge of the capsule surface, which proves the successful build-up of the polymer shell on the surface of the template particles. It was shown that presence of NDs in each polymer layer has no influence on the value of ζ-potential compare to the capsules without NDs. This observation is typical for the entrapment of the nanoparticles into the polyelectrolyte multilayer wall [16]. The same observation was described by Kolesnikova et al. in [6].

Figure 1.tif

**Figure 1**. A. The ζ-potential measurements confirming the successful formation of the polymer capsule shell. B. The fluorescent confocal images of the (PSS/PAH)2(PSS/PAH+NDs)2PSS capsules. C. TEM observation of a magnified part of the polymer capsule shell with incorporated NDs.

The confocal observations confirm the successful impregnation of NDs into the shell of the polyelectrolyte capsules. Figure 1B represents fluorescence of the capsules with NDs when excited by a laser with a wavelength of 532 nm, while the control sample (without NDs) indicates no fluorescence at the same conditions. The results indicate the presence of NDs in the shell, which have luminescence due to inclusion of nitrogen atoms in the structure causing an existence of negatively charged “nitrogen-vacancy” defects in the diamond lattice.

The results of high resolution TEM demonstrate an inclusion of the nanoparticles with a crystal lattice of about 5 nm into the capsule shell, which corresponds to the size of NDs (Figures 1C). However, DLS measurements indicate the presence of aggregates in the range of 40 nm in the solution of NDs. We could suggest that the inclusion NDs/PSS coacervates in the polymer shell leads to disaggregation of the nanoparticles and their uniform distribution in the polymer matrix. The entrapment of NDs in the shell of the polyelectrolyte capsules as individual nanoparticles has many perspectives of their application as the nanocomposite systems. In particular, modification with NDs can insure the control of the thermal susceptibility of the capsule shell and increase their sensitivity to the external irradiation.



**Figure 2**. SEM images of the initial capsules with embedded NDs (A) and after microwave treatment (B, C).

We have demonstrated the influence of the microwave irradiation on the integrity of polyelectrolyte capsules modified with NDs. SEM investigations indicate the change of the polymer capsule morphology. Figure 2A shows the untreated capsule, which shell is characterized by spherical shape without any defects. The capsules after the microwave treatment changed their morphology. The SEM images reveal the damages of the polymer shell in the form of cavities and cracks (Figure 2 B, C). On the other hand, the integrity and morphology of the capsules without NDs (control experiments) were not changed (SI).

**4. Conclusions**

We successfully fabricated the polyelectrolyte capsules with embedded diamond nanoparticles in the shell and demonstrated their remote opening under the microwave irradiation. This opening can be explained by two possible mechanism of the effect of microwave exposure on the shell: thermal and oscillation [17]. The first one is attributed to the thermal effects of microwaves irradiation. NDs effectively adsorb microwaves converting electromagnetic energy to heat [13]. As a result, homogeneous heating of the polyelectrolyte layers surrounding NDs leads to the destruction of the capsule shell. The second way is related to non-heating microwaves effects. The charged groups of the polyelectrolytes from the capsule shell start to oscillate as a result of electromagnetic field in microwave region. It could be suggested that multiple scattering from the surface of the embedded NDs will enhance the non-heating microwaves effect leading to the destruction of the polymer shell integrity.

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