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Communication

Polyelectrolyte - Graphene Oxide Multilayer Composites for Array of Microchambers Which Are Mechanically Robust and Responsive to NIR Light^a

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Development of composite polymer/graphene oxide (GO) materials attracts significant attention due to their unique properties. In this work a highly ordered arrays of hollow microchambers made of composite polyelectrolyte/GO multilayers (PEGOMs) are successfully fabricated via Layer-by-Layer assembly on sacrificial or sustainable templates having imprinted patterns of microwells on their surface. Mechanical and optical properties of PEGOMs are studied by nanoindentation and NIR absorption spectroscopy. Incorporation of three GO layers in between the polyelectrolyte multilayer stacks increases Young's modulus and critical stress of the microchambers by a factor of 5.6 and 2.6, respectively. Optical density of this PEGOM film is found to decrease gradually from 0.14 at $\lambda = 800$ nm to 0.06 at $\lambda = 1500$ nm. Remote opening of PEGOM microchambers with NIR laser beam is also demonstrated. One of the possible applications of the developed structures includes micropackaging & delivery systems in biological tissues with remote triggering.

1. Introduction

Nanostructured polymer-based composites inclusive carbon-based materials, such as graphene, GO or carbon nanotubes, are especially advantageous for various fields due to their unique optical, mechanical, electrical and other properties.^[1,2] Incorporation of high-modulus species in a low modulus polymer matrix in order to fabricate mechanically strong composite materials was inspired by biocomposites, such as bones and nacre,^[3,4] while graphene is the strongest ever tested material with a Young's modulus of 1.0 TPa.^[5] Compared to graphene, GO has inferior mechanical properties due to disruption of the structure through oxidation,^[6] e.g. its tensile strength decreases by a factor of two.^[7] Despite this, GO is widely applied to reinforce polymer composites because it can be chemically modified with functional groups on basal planes and edges that improves its bonding with polymer matrices and makes it easier to disperse GO in aqueous solutions.^[8]

Two types of GO-polymer composites can be designated: bulk GO-filled polymers and layered GO-polymer films. GO-filled polymers are fabricated via solution mixing,^[9-12] melt blending,^[13,14] and in situ polymerization.^[15,16] However, stress transfer from a polymer matrix to GO sheets is not effective in this type of composites due to disordered orientation of GO. Chemical cross-linking between GO sheets and polymer matrix helps to overcome this issue increasing Young's modulus of the composite by as much as 900%.^[10] GO-polymer films prepared by sequential spin-coating demonstrate more effective stress transfer.^[17,18] In this manner, polymer-enriched graphene foams exhibit high modulus and biocompatibility.^[19]

A great progress in the development of layered composites was achieved via layer-by-layer (LbL) assembly technique. The technique allows precise control over vertical composition and thickness of the films at a nanometer level.^[20,21] It has been widely applied for assembly of polyelectrolytes,^[22] proteins,^[23] metal and metal oxide nanoparticles,^[24,25] clays,^[26,27] carbon nanotubes,^[28,29] and many other materials including GO-polymer films.^[30-35] A combination of LbL assembly and Langmuir–Blodgett technique was used to

incorporate GO sheets onto the polyelectrolyte multilayer (PEM) films made of poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrenesulfonate) (PSS).^[36] PEGOM films fabricated in this way achieved Young's modulus of 20 GPa at 8 vol % of GO.

Enhanced mechanical properties of PEGOM films could be specifically advantageous for making 3D structures, e.g. an array of microchambers developed recently.^[37-40] Potential applications of these structures include micropackaging of drugs,^[41-43] or sensors for rapid diagnostics of biological fluids,^[44] where resilience of the microchambers towards external stresses is required to avoid accidental burst release, the event that could be catastrophic. Moreover, GO could be used to provide near infrared (NIR) light responsiveness, which is important for many release-on-demand applications in biological systems as NIR light penetrates into the biological tissues for up to 10 cm causing no harm.^[45]

Present study aims to develop PEGOM microchambers combining enhanced mechanical stability and high responsiveness towards NIR irradiation. In this regard, we have applied LbL assembly of PEGOM films on patterned templates to fabricate arrays of microchambers. We have studied their mechanical and optical properties. Finally, we have demonstrated selective opening of microchambers triggered by NIR light in the range of wavelengths from 800 to 1200 nm.

2. Results and Discussion

2.1. Morphology and Structure of PEM and PEGOM Films Assembled on Sacrificial Patterned Templates

Microimprint lithography was employed to obtain sacrificial poly(methylmethacrylate) (PMMA) templates with patterns of microwells on the surface. Recently drop-casting was also suggested as a more readily available alternative for making the templates.^[39] Microchambers may be fabricated *via* one-step casting of a polyelectrolyte complex onto,^[40]

or LbL assembly of PEMs on a template.^[37,38] The latter approach requires significantly longer time but allows layered structures which is specifically advantageous for effective stress transfer in PEGOM nanocomposites. Therefore, in this work we used LbL assembly of PSS-PAH multilayer film on the PMMA template. Each layer was achieved upon adsorption of respective polyelectrolyte from a solution at high ionic strength of 2M driven by an entropy gain upon release of counter ions.^[46,47] A dispersion of GO sheets in DI water was used to introduce layers of GO. ζ -potential of GO sheets dispersion was measured to be -44.3 ± 1.7 mV, which is more negative than -30 mV generally considered sufficient to ensure the stability of a dispersion through electrostatic repulsion.^[48] When introduced to a PAH-terminated multilayer, electrostatic interactions drive adsorption of GO sheets. This sequence (several PSS-PAH layers followed by GO-PAH layer) was chosen because good stress transfer happens at the GO-polymer interface if there is a thicker layer of polymer matrix between GO layers.^[49]

Figure 1 shows Scanning Electron Microscopy (SEM) images of PMMA template before and after its coating with $(\text{PSS}/\text{PAH})_{42}$ and $(\text{PSS}/\text{PAH})_{12}/\text{GO}/\text{PAH})_3$ multilayer films. PEM film exactly conforms topography of the template. In contrast to bare PMMA, its surface exhibits globular morphology, as expected for PEM films assembled at high ionic strength of 2M.^[50] The film thickness is 0.57 ± 0.01 μm on top of the template and only 0.33 ± 0.01 μm in the bottom of the wells (as estimated from the difference in the wells size between bare PMMA template in Figure 1-a and the coated one in Figure 1-b). One reason behind different PEMs thickness could be depletion of PE concentration inside the wells due to reduced flux of polyanions into the well caused by repulsive potential from polyelectrolytes already adsorbed on top of the substrate. This effect was observed upon PEM assembly from solutions with low ionic strength inside nanochannels.^[51] However in our case both the size of the wells (15 μm) and ionic strength (2M) are much higher. Therefore we believe that the reason is hindered diffusion of the polymer chains from solution into the wells during

assembly suggested earlier,^[51] which makes the thickness of PEMs dependent on dipping time.

PEGOM film is much thicker and less uniform in comparison to PEM film and exhibits more coarse morphology with some debris and cracks (see Figure 1-c). Moreover, GO sheets round the sharp corners of imprinted square wells and even completely close some. The 90 % of GO sheets have diameter smaller than 1.9 μm (see Supporting information, Figures S1 and S2), therefore such closing may happen only if several GO sheets stack together onto the top edges of 15 μm -wide wells. The film thickness on top of the template is $2.6 \pm 0.5 \mu\text{m}$ while it is not possible to measure the film thickness in the bottom of the wells from these images.

SEM images of PEGOM films with different number of GO layers are shown in the Supporting information (Figures S3 and S4, respectively). $((\text{PSS}/\text{PAH})_{12}/\text{GO}/\text{PAH})_2$ film has much lower thickness of 0.08 – 0.33 μm , while $((\text{PSS}/\text{PAH})_6/\text{GO}/\text{PAH})_6$ film is very thick with many cracks, while most of the wells are completely closed.

2.2. Fabrication of PEM and PEGOM Microchambers

Sealing the assembled films to a support followed by dissolution of sacrificial PMMA templates reveals the other side of the films which are now shaped as arrays of microchambers, corresponding SEM images are shown in **Figure 2 - a, c**. The exterior sides of both PEM and PEGOM microchambers have the same smooth morphology resembling initial PMMA template, unlike the interior side of microchambers. The microchambers look as the square pillars being a positive replica of the master mold used for PMMA template imprinting. The yield of PEGOM microchambers is higher than the yield of PEM microchambers (91% vs 55%, correspondingly), while the rest microchambers are collapsed. We should note here than 100% yield of the PEM microchambers may be achieved if 50 PSS-PAH bi-layers were assembled on PMMA template. Here we intentionally assembled 42 PSS-PAH bilayers in order to demonstrate enhanced mechanical stability of microchambers made

of PEGOM films. Cross section images show that both PEM and PEGOM microchambers are hollow inside (see Figure 2 - b, d), the thickness of chambers' roof was found to be $0.37 \pm 0.09 \mu\text{m}$ and $0.25 \pm 0.03 \mu\text{m}$ for PEM and PEGOM, respectively. Thickness of the PEM chamber roof found here is the same, within experimental error, as the thickness of PEM film formed in the bottom of imprinted wells ($0.33 \pm 0.01 \mu\text{m}$, see section 2.1). Thus both PEM and PEGOM microchambers have thinner film on top and thicker in the bottom. However this difference for PEGOM microchambers is significantly larger ($2.6 \mu\text{m}$ vs $0.25 \mu\text{m}$) than for PEM microchambers ($0.57 \mu\text{m}$ vs $0.33 \mu\text{m}$). Most probably, stacks of GO sheets formed outside of the wells obstruct diffusion of the components into the microwells and even stop it completely for some wells that become closed.

GO contains sp^2 -hybridized carbons in the aromatic network that emit fluorescence in a wide range of wavelengths from near-infrared (NIR) to visible and ultraviolet.^[52, 53] Therefore, PEGOM microchambers were analyzed by Confocal Laser Scanning Microscopy (CLSM), corresponding image is shown in the Figure 2-f demonstrating distribution of GO sheets throughout the microchambers as PEM film doesn't have any fluorescence if excited at the same wavelength of 514 nm (see Supporting Information, Figure S5).

PEGOM microchambers were also fabricated using sustainable poly(dimethylsiloxane) (PDMS) template. The template was peeled off the PEGOM film sealed towards a support, as previously described.^[43,54] Figure 2 - e shows microchambers obtained with this approach, they are notably elongated due to applied mechanical stress but still remain intact. All attempts to make PEM microchambers of this topography by peeling off the template fail as microchambers tear at the base and remain inside the template.^[54]

2.3. Mechanical Properties of PEM and PEGOM Microchambers

Mechanical properties of microchambers were investigated by nanoindentation analysis. For all measurements, individual standing microchambers were tested, while collapsed microchambers were excluded. Typical force-deformation (F - ε) profiles of PEM and PEGOM microchambers upon cycles of their loading-hold-unloading are shown in **Figure 3 - a** (F - ε profiles for all tested loading rates are available in the Supporting information, Figure S6). Here, deformation ε is the percentage ratio of displacement to the total height of microchambers (10 μm). At low deformations ($\varepsilon < \sim 12\%$), the applied force is proportional to the square root of deformation (see Figure 3-b), which is an indication of elastic deformation of the microchambers.^[55] When the load exceeds critical value, F_{cr} plastic deformation starts with buckling of the microchambers' walls, as evident from the SEM images of indented microchambers shown in Figure 3 - d-f.

Young's modulus, E was measured using the following equation: $E = F/(\varepsilon S)$, where S is the contact area of the tip with chamber's roof. Figure 3 - c shows the modulus of microchambers at the elastic deformations regime, and the critical stress, $\sigma_{\text{cr}} = F_{\text{cr}}/S$ microchambers can withstand without buckling. Both E and σ_{cr} increase by a factor of 5.6 and 2.6, respectively, as the number of GO layers, n is increasing from 0 to 3. Microchambers with 6 GO layers demonstrate the same modulus and critical stress as microchambers with 3 GO layers but the measurements error increases dramatically. As it was discussed in the section 2.1, in this sample many of the wells were completely closed upon LbL assembly. Once closed, further deposition of GO sheets inside the wells is blocked leading to a lower actual number of GO layers in microchamber's walls and higher non-uniformity. In this regard, PEGOM composition of $((\text{PSS}/\text{PAH})_{12}/\text{GO}/\text{PAH})_3$ is considered as optimal for the formation of microchambers of given geometry.

In the plastic deformation regime, microchambers' buckling first leads to a degradation of Young's modulus, as shown in the supporting information (Figure S7). However, Young's

modulus increases again at deformations of 30 % and higher because incision of microchamber's roof by the indenter tip happens, as shown in Figure 3-f.

2.4. Optical Properties of PEGOM Microchambers and their Opening Triggered by NIR Light

For controlled release applications in biological tissues, remote triggering with NIR light has tremendous importance. With this regards, GO could be a cost-effective alternative to gold nanorods or agglomerates of gold nanoparticles widely used to achieve NIR responsiveness.^[39,56,57] Optical density of PEGOM film is 0.14 at $\lambda = 800$ nm, and then it decreases gradually with the wavelength reaching 0.06 at $\lambda = 1500$ nm, corresponding NIR absorption spectrum is shown in the Supporting Information, Figure S8.

To demonstrate possibility of remote opening of PEGOM microchambers using NIR light, they were irradiated with focused laser light at 800, 1000, 1200, and 1500 nm. The SEM images of irradiated samples are shown on **Figure 4**. Laser light at 800 nm ablates the PEGOM film completely; at 1000 nm isolated islands of 10-15 microchambers are ablated; at 1200 nm laser light opens random individual microchambers along its path, while at 1500 nm it doesn't induce any changes to PEGOM microchambers. In the wavelengths range 800 - 1500 nm, power of the laser radiation decreases five times (from 100 to 20 mW) while optical density of PEGOM film decreases two times from (0.14 to 0.06). Therefore, responsiveness of PEGOM films towards laser radiation also decreases. Possible reason for the observed opening of only few random microchambers in the array upon their irradiation with the laser at 1000 nm, and even more profoundly at 1200 nm, is a variation in the number of GO sheets incorporated in different microchambers. Those with higher GO content remain responsive while the rest are not.

3. Conclusions

Nanocomposite PEGOM microchambers were successfully fabricated *via* LbL assembly using PMMA as well as PDMS templates. Morphologies of PEM and PEGOM films assembled on PMMA template are drastically different. Upon GO adsorption, the edges of square wells become rounded, thickness of the film assembled on top of PMMA template increases and some wells become completely closed.

A remarkable reinforcement of nanocomposite films by GO allows to increase the yield of microchambers from 55 % for PEM films to 91% for PEGOM films. Young's modulus and critical stress increase by a factor of 5.6 and 2.6, respectively, as the number of GO layers in microchambers is increasing from 0 to 3. Moreover, PEGOM microchambers with 3 GO layers are robust enough to withstand peeling off the PDMS template. This allows multiple usage of the same PDMS template for microchambers fabrication contributing to more sustainable process.

NIR laser radiation at the wavelength of 800 nm ablates the PEGOM microchambers, while laser radiation at 1000 and 1200 nm allows gentler opening of random individual microchambers or groups of microchambers with higher GO content. These results show the possibility to fabricate mechanically robust array of microchambers for encapsulation and storage of substances followed by their remote release triggered by NIR light. This approach opens up opportunities for remote control over drug delivery in biological tissues.

4. Experimental Section

Materials, methods, analysis, and additional experimental data are supplied in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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- [1] H. Kim, A. A. Abdala, C. W. Macosko, *Macromolecules*, 2010, **43**, 6515–6530.
- [2] T. Kuilla, S. Bhadra, D. Yao, N. H. Kim, S. Bose, J. H. Lee, *Prog. Polym. Sci.*, 2010, **35**, 1350–1375.
- [3] S. P. Kotha, S. Kotha, N. Guzelsu, *Compos. Sci. Technol.*, 2000, **60**, 2147–58.
- [4] B. Chen, P. D. Wu, H. Gao, *Compos. Sci. Technol.* 2009, **69**, 1160–1164.
- [5] C. Lee, X. D. Wei, J. W. Kysar, J. Hone, *Science*, 2008, **321**, 385–388.
- [6] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko G, *Nature*, 2007, **448**, 457–460
- [7] J. T. Paci, T. Belytschko, G. C. Schatz, *J. Phys. Chem. C*, 2007, **111**, 18099–18111.
- [8] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, *Carbon*, 2007, **45**, 1558.
- [9] H. Bai, C. Li, X. Wang, G. Q. Shi, *Chem. Commun.*, 2010, **46**, 2376–2378.
- [10] D. Y. Cai, K. Yusoh, M. Song, *Nanotechnology*, 2009, **20**, 085712.
- [11] Y. X. Xu, W. J. Hong, H. Bai, C. Li, G. Q. Shi, *Carbon* 2009, **47**, 3538–3543.
- [12] W. H. Kai, Y. Hirota, L. Hua, Y. Inoue, *J. Appl. Polym. Sci.*, 2008, **107**, 1395–1400.
- [13] Y. Cao, J. Zhang, J. Feng, P. Wu, *ACS Nano*, 2011, **5**, 5920–5927.
- [14] C. Bao, L. Song, W. Xing, B. Yuan, C. A. Wilkie, J. Huang, Y. Guo, Y. Hu, *J. Mater. Chem.*, 2012, **22**, 6088–6096.
- [15] J. Y. Wang, S. Y. Yang, Y. L. Huang, H. W. Tien, W. K. Chin, C. C. M. Ma, *J. Mater. Chem.*, 2011, **21**, 13569–13575.
- [16] N. Zhang, R. Li, L. Zhang, H. Chen, W. Wang, Y. Liu, T. Wu, X. Wang, W. Wang, Y. Li, Y. Zhao, J. Gao, *Soft Matter*, 2011, **7**, 7231–7239.
- [17] S. S. Li, K. H. Tu, C. C. Lin, C. W. Chen, M. Chhowalla, *ACS Nano*, 2010, **4**, 3169–3174.

- [18] L. Gong, I. A. Kinloch, R. J. Young, I. Riaz, R. Jalil, K. S. Novoselov, *Adv. Mater.*, 2010, **22**, 2694–2697.
- [19] J. K. Wang, G. M. Xiong, M. Zhu, B. O. Zyilmaz, A. H. Castro Neto, N. S. Tan, C. Choong, *ACS Appl. Mater. Interfaces*, 2015, **7**, 8275–8283.
- [20] M. A. C. Stuart, W. T. S. Huck, J. Genzer, M. Muller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, S. Minko, *Nat. Mater.*, 2010, **9**, 101–113.
- [21] *Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials* (Eds: G. Decher, J. B. Schlenoff), 2nd Ed, Wiley-VCH, Weinheim, Germany, 2012.
- [22] G. Decher, *Science*, 1997, **277**, 1232.
- [23] G. Decher, B. Lehr, K. Lowack, Y. Lvov, J. Schmitt, *Biosens. Bioelectron.*, 1994, **9**, 677-684.
- [24] N. Malikova, I. Pastoriza-Santos, M. Schierhorn, N. A. Kotov, L. M. Liz-Marzan, *Langmuir*, 2002, **18**, 3694–3697.
- [25] M. Giersig, N. A. Kotov, L. M. Liz-Marzán, *Langmuir*, 2000, **16**, 2731–2735.
- [26] Y. Lvov, K. Ariga, I. Ichinose, T. Kunitake, *Thin Solid Films*, 1996, **284–285**, 797-801.
- [27] P. Podsiadlo, B. S. Shim, N. A. Kotov. *Coord. Chem. Rev.* 2009, **253**, 2835-2851.
- [28] M. Olek, J. Ostrander, S. Jurga, H. Mohwald, N. A. Kotov, K. Kempa, M. Giersig, *Nano Letters*, 2004, **4**, 1889–1895.
- [29] K. S. L. Chong, M. V. Kiryukhin, A. M. H. Ng. *Thin Solid Films*, 2012, **526**, 252–255.
- [30] X. Zhao, Q. Zhang, Y. Hao, Y. Li, Y. Fang, D. Chen, *Macromolecules* 2010, **43**, 9411–9416.
- [31] N. A. Kotov, I. Dekany, J. H. Fendler, *Adv. Mater.*, 1996, **8**, 637–641.

- [32] N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva, A. D. Gorchinskiy, *Chem. Mater.* 1999, **11**, 771–778.
- [33] R. Rajasekar, N. H. Kim, D. Jung, T. Kuila, J. K. Lim, M. J. Park, J. H. Lee, *Compos. Sci. Technol.*, 2013, **89**, 167–174.
- [34] L. Zhao, H. Sun, N. Kim, J. Lee, Y. Kong, P. Li, *J. Appl. Polym. Sci.*, 2015, **132**, 41973-41984.
- [35] L. Zhao, B. Yuan, Y. Geng, C. Yu, N. H. Kim, J. H. Lee, P. Li, *Compos. A Appl. Sci. Manuf.*, 2015, **78**, 60–69.
- [36] D. D. Kulkarni, I. Choi, S. S. Singamaneni, V. V. Tsukruk, *ACS Nano*, 2010, **4**, 4667–4676.
- [37] M. V. Kiryukhin, S. M. Man, S. R. Gorelik, G. S. Subramanian, H. Y. Low, G. B. Sukhorukov, *Soft Matter*, 2011, **7**, 6550-6556.
- [38] M. V. Kiryukhin, S. R. Gorelik, S. M. Man, G. S. Subramanian, M. N. Antipina, H. Y. Low, G. B. Sukhorukov, *Macromol. Rapid Commun.*, 2013, **34**, 87–93.
- [39] M. Gai, V. L. Kudryavtseva, G. B. Sukhorukov, J. Frueh, *Bionanoscience*, 2017, 1-15.
- [40] M. Gai, J. Frueh, V. L. Kudryavtseva, R. Mao, M. V. Kiryukhin, G. B. Sukhorukov, *Sci. Rep.* 2016, 6, 37000.
- [41] M. V. Kiryukhin, *Curr. Opin. Pharmacol.*, 2014, **18**, 69-75.
- [42] M. Gai, J. Frueh, T. Tao, A. V. Petrov, V. V. Petrov, E. V. Shesterikov, S. I. Tverdokhlebov, G. B. Sukhorukov, *Nanoscale*, 2017, **9**, 7063-7070.
- [43] M. Gai, J. Frueh, V. L. Kudryavtseva, A. M. Yashchenok, G. B. Sukhorukov, *ACS Appl. Mater. Interfaces.*, 2017, **9**.
- [44] M. V. Kiryukhin, H. H. Lau, S. H. Goh, C. Teh, V. Korzh, A. Sadovoy. *Talanta*, 2018, doi.org/10.1016/j.talanta.2018.01.085
- [45] R. Weissleder, *Nat. Biotechnol.*, 2001, **19**, 316–317.

- [46] N. A. Kotov, *Nanostruct. Mater.*, 1999, **12**, 789–796.
- [47] K. Ariga, J. P. Hill, Q. Ji, *Phys. Chem. Chem. Phys.*, 2007, **9**, 2319–2340.
- [48] D. Li, M. Muller, S. Gilje, R. B. Kaner, G. G. Wallace, *Nat. Nanotechnol.* 2008, **3**, 101-105.
- [49] L. Gong, R. J. Young, I. A. Kinloch, I. Riaz, R. Jalil, K. S. Novoselov, *ACS Nano*, 2012, **6**, 2086–2095.
- [50] J. Dejeu, F. Membrey, S. Diziain, C. Bainier, M. Spajer, D. Charraut, A. Foissy, *J. Phys. Chem. C*, 2008, **112**, 10531–10537.
- [51] M. V. Kiryukhin, S. M. Man, A. V. Sadovoy, H. Y. Low, and G. B. Sukhorukov. *Langmuir*, 2011, **27**, 8430-8436.
- [52] X. Sun, Z. Liu, K. Welsher, J. T. Robinson, A. Goodwin, S. Zaric, H. Dai, *Nano Res.*, 2008, **1**, 203–212.
- [53] G. Eda, Y. Y. Lin, C. Mattevi, H. Yamaguchi, H. A. Chen, I. S. Chen, C. W. Chen, M. Chhowalla, *Adv. Mater.*, 2009, **22**, 505–509.
- [54] M. V. Kiryukhin, S. M. Man, A. Tonoyan, H. Y. Low, G. B. Sukhorukov, *Langmuir*, 2012, **28**, 5678-5686.
- [55] L. D. Landau, E. M. Lifshitz, Theory of elasticity, Vol. 7 of *Course of Theoretical Physics*, 4th ed., Nauka, Moscow, 1987, pp. 81–83. (In Russian)
- [56] A. G. Skirtach, P. Karageorgiev, B. de Geest, N. Pazos-Perez, D. Braun, G. B. Sukhorukov, *Adv. Mater.* 2008, **20**, 506–510.
- [57] S. Carregal-Romero, M. Ochs, P. Rivera-Gil, C. Ganas, A. M. Pavlov, G. B. Sukhorukov, W. J. Parak, *J. Contr. Rel.*, 2012, **159**, 120 – 127

Captions to figures

Figure 1. Scanning electron microscope images of imprinted PMMA template before (a) and after LbL assembly of (PSS/PAH)₄₂ (b) and ((PSS/PAH)₁₂/GO/PAH)₃ (c) multilayers.

Figure 2. Scanning electron microscope images of microchambers sealed towards a support after dissolution of sacrificial PMMA template (a-d) and peeling off PDMS template (e). a, b - (PSS/PAH)₄₂ microchambers; c-e - ((PSS/PAH)₁₂/GO/PAH)₃ microchambers. f – Confocal laser scanning microscope image of ((PSS/PAH)₁₂/GO/PAH)₃ microchambers (excitation 514 nm, emission in the range of 550-650 nm)

Figure 3. Force-deformation curves of (PSS/PAH)₄₂ (1), ((PSS/PAH)₁₉/GO/PAH)₂ (2), ((PSS/PAH)₁₂/GO/PAH)₃ (3) and ((PSS/PAH)₆/GO/PAH)₆ (4) microchambers measured at loading rate of 0.66 mN/s (a); the same curves in (F- $\epsilon^{1/2}$) coordinates in the region of low deformations and corresponding linear fits (b); Young's modulus (1) and critical stress (2) of the microchambers containing different number of GO layers (c); scanning electron microscope images of ((PSS/PAH)₁₂/GO/PAH)₃ microchambers after deformation at loading rate of 0.07 mN/s (d), 0.66 mN/s (e), and 13.33 mN/s (f).

Figure 4. Scanning electron microscope images of PEGOM microchambers after radiation with NIR laser at wavelength λ of 800 (a, b), 1000 (c) nm and 1200 (d) nm.

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Highly ordered arrays of hollow microchambers made of polyelectrolyte/GO multilayers withstand mechanical demolding, demonstrate enhanced Young's modulus and critical stress and allow remote opening with NIR light. One of the possible applications of the developed PEGOM microchambers includes micropackaging & delivery systems in biological tissues with remote triggering.

