CSIRO PUBLISHING

Aust. J. Chem. **2012**, *65*, 1223–1227
http://dx.doi.org/10.1071/CH12119

Ag Nanoparticle-Poly(acrylic acid) Composite Film with Dynamic Plasmonic Properties

Volodymyr Chegel,[A,D] *Andrii Lopatynskyi,*[A] *Shinsuke Ishihara,*[B,D]
Jonathan P. Hill,[B,C] *and Katsuhiko Ariga*[B,C]

[A]V. E. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences (NAS) of Ukraine, 41 Nauky Ave., 03028, Kyiv, Ukraine.
[B]World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.
[C]Japan Science and Technology Agency, Core Research for Evolutional Science and Technology, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.
[D]Corresponding authors. Email: vche111@yahoo.com; ISHIHARA.Shinsuke@nims.go.jp

Poly(acrylic acid) (PAA) thin films with embedded Ag nanoparticles (AgNPs) prepared by UV photoreduction exhibited cyclically changeable optical absorbance properties during variation of ambient aqueous medium. The observed phenomenon is due to conformational changes in the polymer matrix which leads to variation in the 3D configuration of the AgNPs ensemble. Reversible variation of the distance between nanoparticles during swelling and shrinking processes within the PAA matrix changes the optical parameters of these plasmonic metamaterials and can be considered a useful feature for optoelectronic devices and sensors. The finite-difference time-domain method was used for modelling of light extinction of developed matrix structures in their swollen and shrunken states.

Manuscript received: 25 February 2012.
Manuscript accepted: 28 March 2012.

Introduction

The development of nano-structured materials[1–5] with dynamic properties[6–10] may lead to various innovative functions. In particular, metamaterials with unique optical properties have attracted great interest over the last 10 years because of the wide-ranging possibilities for practical applications in laser optics, optoelectronics, chemical and biosensing, etc.[11–14] The most important contributions to the creation of such metamaterials have been obtained by using plasmonic nanostructures, such as gold and silver nanoparticles, nanorods, nanodiscs and nanoholes.[15–19] Most works describe metamaterials developed having static physical characteristics and only a few articles have been devoted to preparations of metamaterials that permit tuning of physical properties or, in other words, exhibit so-called ‘dynamic plasmonic’ behaviour.[20–23] This discrepancy is due to difficulties related to physical and technological limitations especially when different types of thin composite films are considered. It is obvious that tuning of physical characteristics of plasmonic colloidal solutions can be achieved more easily than for plasmonic nanostructures embedded in polymer matrices or, moreover, within solid materials due to the limited possible variation in the distance between nanoparticles. Unfortunately, only thin matrix structures can be used for preparation of chip-based formats, which are most suitable for practical applications. The physical aspect of this problem might be overcome if shape-anisotropic nanoparticles that are sensitive to polarization of light are used. However, only exclusive and expensive methods such as nanoimprint lithography using specially constructed two-dimensional nanostructure array (nanoblock) moulds derived from one-dimensional gratings can be used.[24]

In the present work, we propose a quick and simple method to prepare a plasmonic nanocomposite matrix film using features of the ‘dynamic interface’. To prepare the nanocomposite matrix we use the known properties of some polymers to reduce the ions of plasmonic metals (Ag, Au). Gradess et al.[25] used polyvinyl alcohol (PVA) to reduce Ag^+ ions at high temperature. In our case, we used poly(acrylic acid) (PAA) since polyacrylate films exhibit stronger pH-dependent swelling and shrinking in the liquid phase. We have also used UV irradiation instead of heating as a more effective and rapid process. It is possible to vary the distance between Ag nanoparticles embedded in PAA matrices in 3 dimensions while the PAA network fixes their relative positions within the matrix. The Ag nanocomposite matrix developed after immersion in liquids of different pH showed reversible spectral properties both in localized surface plasmon resonance (LSPR) and surface plasmon resonance (SPR) measurements. pH-induced swelling and shrinking activity of the composite polymer structures is proposed and theoretically simulated to explain this phenomenon.

The results presented suggest the possibility of exploiting such composite films as nanoplasmonic sensor elements or as a pH-actuated dynamic system.

Results and Discussion

Typical absorbance spectra of composite PAA film with embedded Ag nanoparticles, deposited on a glass substrate, acquired during the UV treatment are shown in Fig. 1. The gradual increase of absorbance and redshift of absorbance peak (from 420 to 440 nm) originates from the intensifying nanoparticle LSPR response due to the increase in size and concentration of Ag nanoparticles over the course of the UV photoreduction process. These results (Fig. 1) demonstrate that it is possible to control the process of Ag nanoparticle formation by adjustment of UV exposure time.

After 15 min of exposure to UV the sample was immersed in deionized water and a blue shift of the absorbance peak to ~425 nm was observed. This change in optical properties of the composite film is explicitly related to alteration of the Ag nanoparticle's environment. It is known that LSPR of noble metal nanoparticles depends on both dielectric properties of the surrounding medium[26] and intensity of the electromagnetic interaction between adjacent nanoparticles.[27] According to these specific plasmonic properties, a blue shift in absorbance for an ensemble of Ag nanoparticles can typically be induced by a refractive index decrease of environment and a decrease in electromagnetic interaction between nanoparticles (e.g. due to increase of interparticle distance). Because of the strong adsorption of water to PAA leading to hydrogel formation,[28,29] optical evidence for the interaction of the PAA film with embedded Ag nanoparticles with deionized water can be treated as a simultaneous influence of the aforementioned mechanism. Namely, adsorption of water by the PAA polymer network leads to reduction of its average refractive index due to the difference in their refractive indices – 1.527 for PAA[30] and 1.333 for water. Additionally, water adsorption by PAA induces swelling of the polymer film due to hydrogel formation and subsequently results in an increase of average distance between Ag nanoparticles contained in the film.

Successive alternate immersion of the sample in deionized water then aqueous 0.1 M sulfuric acid led to a cyclic reversible shift of the absorbance peak (Fig. 2). Namely, the absorbance maximum switched between ~425 and ~411 nm for deionized

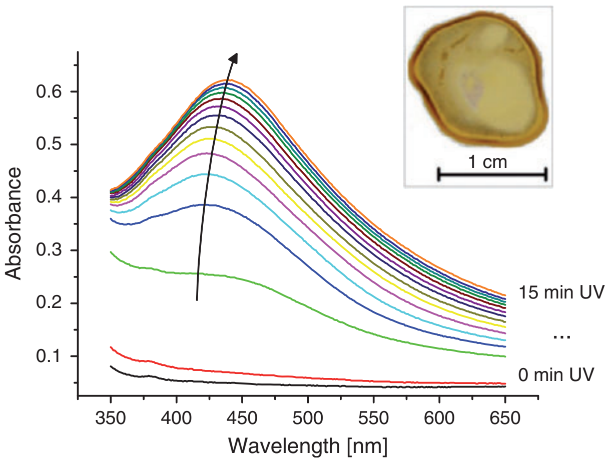

Fig. 1. Electronic absorption spectra of a PAA film during treatment with UV light that leads to formation of embedded Ag nanoparticles. Inset: Image of PAA/AgNPs matrix (in swelled state at the centre of the spot and in shrunk state around).

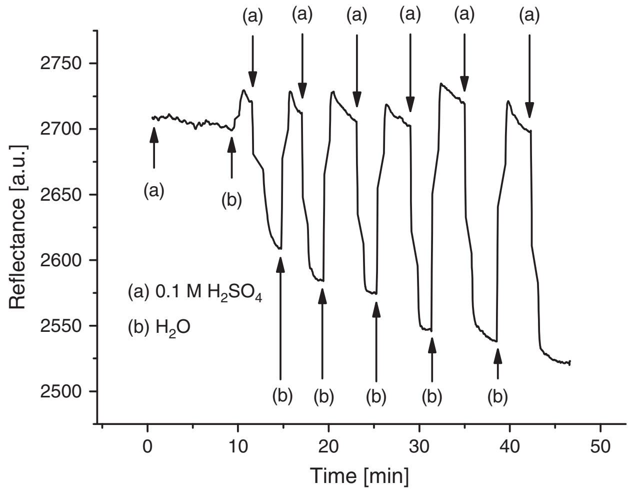

Fig. 3. SPR sensogram corresponding to the shrinking and swelling of the PAA hydrogel film containing embedded Ag nanoparticles, during successive immersions in deionized water and aqueous 0.1 M sulfuric acid, respectively.

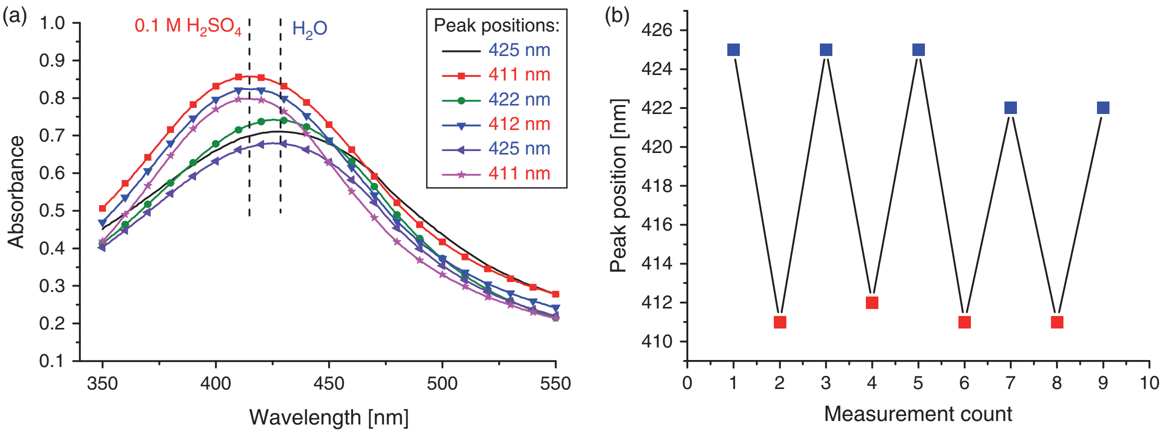

Fig. 2. (a) Electronic absorption spectra of PAA hydrogel film containing Ag nanoparticles after alternating immersion in deionized water and 0.1 M sulfuric acid aqueous solution. (b) Respective absorbance spectrum peak positions.

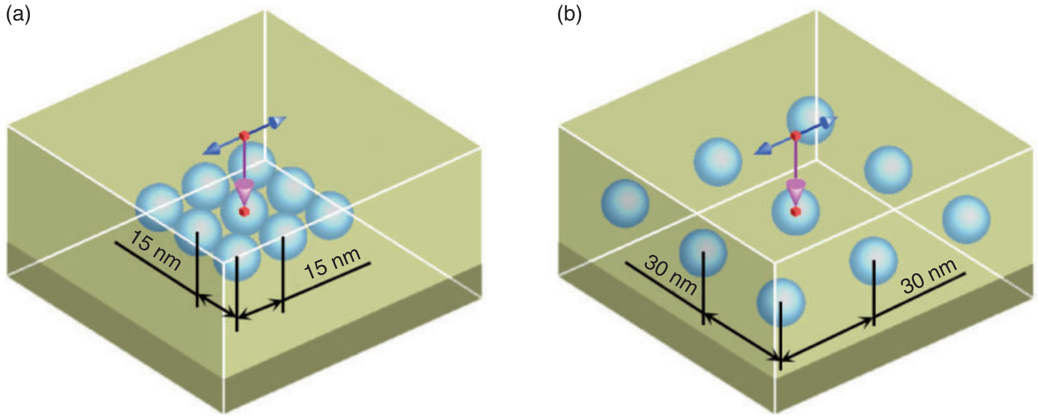

Fig. 4. Model of the (a) shrunken and (b) swollen PAA hydrogel containing Ag nanoparticles.

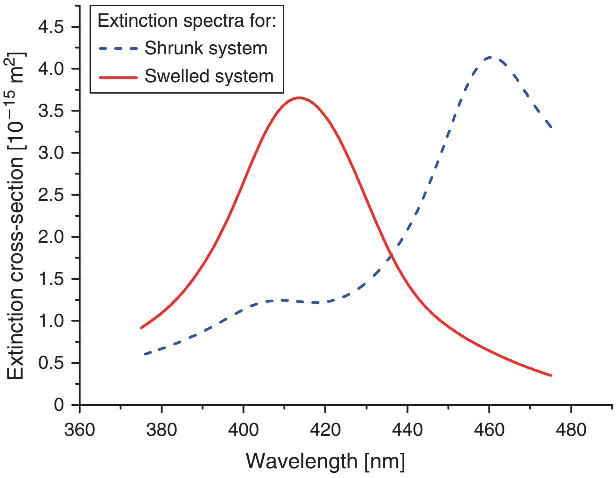

Fig. 5. Simulated absorbance spectra for shrunken and swollen PAA hydrogel film containing Ag nanoparticles.

water and 0.1 M aqueous sulfuric acid, respectively. It should be noted that the refractive index of aqueous 0.1 M sulfuric acid is almost identical to pure water,[31] and the absorption spectrum should not undergo a blue shift due to ambient refractive index change. This implies that a blue shift in absorbance under the influence of sulfuric acid solution is induced by a further swelling of the polymer due to the change of ambient medium pH. However, it is known that swelling of pure PAA usually occurs at high pH,[32] so we suppose that the presence of AgNPs in the PAA matrix drastically changes the conformation of this polymer most probably either during reduction of Ag^+ ions or by chelation of Ag atom/ions by carboxylic acid in PAA.

To verify the results of spectrophotometric measurements, SPR experiments on the same composite Ag nanoparticle-PAA film deposited on an SPR chip were carried out. The resulting observation of cyclic shifts of the SPR reflectance upon successive immersion of the sample into deionized water and aqueous 0.1 M sulfuric acid confirms the swell/shrink process (Fig. 3).

The swell/shrink process was simulated numerically as the change in ambient refractive index and interparticle distance in a layer of Ag nanoparticles (Fig. 4). Absorbance spectra (Fig. 5) and electric field intensity distributions at light wavelengths corresponding to absorbance peak maxima (Fig. 6) were calculated using the finite-difference time-domain (FDTD) method. According to modelling results, the absorbance peak undergoes a blue shift due to a decrease in the ambient medium refractive index and an increase in the interparticle distance (i.e. decrease of interparticle interaction, which is evident by a decrease of electric field intensity) during the swelling process.

Conclusion

In conclusion, PAA films containing Ag nanoparticles have been shown to exhibit optical absorbance properties controllable by the pH of the surrounding aqueous medium. Swelling and shrinking of the studied composite film inducing absorbance peak shifts was confirmed by theoretical simulations. However, optimization of preparation protocol (i.e. reagent concentrations and photoreduction process duration) is required to achieve the maximum sensitivity of optical properties due to pH changes. Hydrogels containing metal nanoparticles might be employed as pH sensors or as pH-driven dynamic systems, as well as sensor elements for substances and factors that influence LSPR properties of nanoparticles (e.g. adsorption of molecules, swelling/shrinking of polymer, changes of ambient medium, etc.).

Experimental

Poly(acrylic acid) (averaged MW = c.a. 25000) was purchased from Wako Pure Chemical Industries, Ltd (Japan). $AgNO_3$ salt was purchased from Kanto Chemical Co., Inc. (Japan). Ethanol (99.5 %), acetone, and sulfuric acid were purchased from Nacalai Tesque, Inc. (Japan). Milli-Q deionized water (type I, $R = 18.2\ M\Omega\ cm$) was used for preparation of solutions.

Synthesis of Ag nanoparticles in PAA-based hydrogel was carried out according to the following procedure: 4 wt.-% of powdered poly(acrylic acid) was dissolved in a 1 : 1 mixture of deionized water and ethanol under vigorous stirring. $AgNO_3$ was dissolved in the resulting PAA solution under vigorous stirring to obtain a 0.2 M final concentration. Standard microscope glass substrates (for spectrophotometric measurements) and SPR chips based on thin Au film (for SPR measurements) were thoroughly rinsed with acetone and ethanol then dried. The $AgNO_3$-PAA solution was spin-coated onto the prepared substrates for 30 s at 500 rpm. The thin polymer films obtained were dried in air for 3 min followed by 15 min exposure to UV light from a 150 W mercury-xenon lamp in a Hamamatsu E7536 lamp housing (Hamamatsu, Japan). The colourless polymer film changed colour to yellow (which was clearly evident on the transparent glass substrates) after exposure to UV light due to

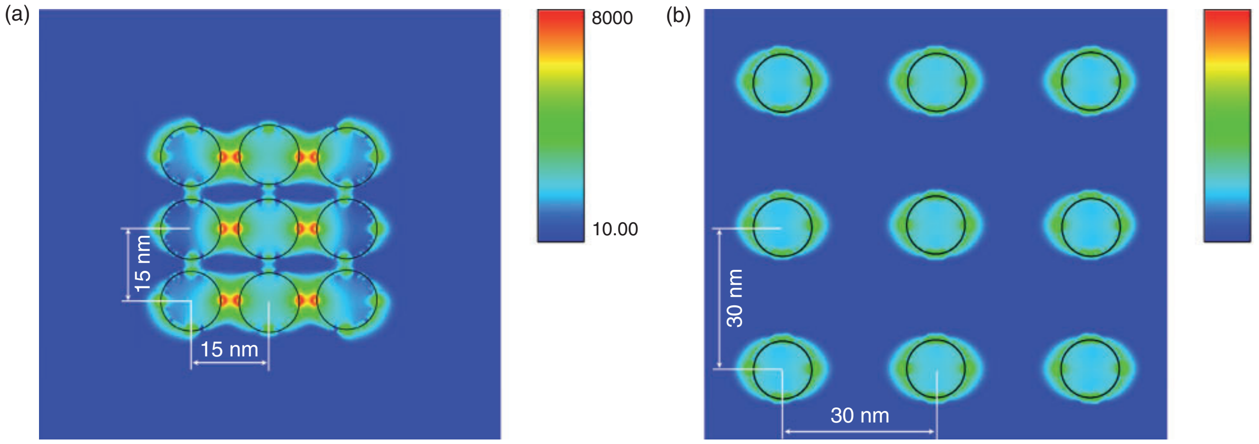

Fig. 6. Simulated electric field intensity distributions for (a) shrunken and (b) swollen PAA hydrogel film containing Ag nanoparticles at light wavelengths corresponding to absorbance peak maxima.

formation of light-absorbing Ag nanoparticles by photoreduction. To study swelling and shrinking behaviour of the composite films, they were successively immersed in deionized water then aqueous 0.1 M sulfuric acid for 1 min during spectrophotometric measurements or until SPR response stabilisation during SPR measurements. Spectrophotometric measurements of composite PAA hydrogel films containing embedded Ag nanoparticles were carried out on a Shimadzu UV-3600 UV-vis-NIR spectrophotometer (Shimadzu, Japan). SPR measurements were carried out on a NanoSPR 6 (Model 321) device (NanoSPR, USA).

Computational Methods

Simulation of optical properties was performed using the FDTD Solutions package (Lumerical Solutions, Inc.). The model of composite film that was used consisted of nine spherical Ag nanoparticles with a diameter of 12 nm located in a 3 × 3 square grid embedded into a polymer medium at a distance of 12 nm from a flat glass surface (refractive index $n_g = 1.46$). The diameter of nanoparticles was fixed at 12 nm taking into consideration the experimentally measured electronic absorption spectrum of a PAA/AgNP matrix in air (Fig. 1) that peaks at 440 nm. Shrunken and swollen composite films were designed by adjusting the polymer medium refractive index n_p and interparticle distance d in the following way: $n_p = 1.527$ and $d = 15$ nm for a shrunken system and $n_p = 1.43$ and $d = 30$ nm for a swollen system. It should be noted that the chosen parameters n_p and d differ significantly for shrunken and swollen films, and their values as well as a value of nanoparticle diameter most probably do not reflect exact experimental parameters. These values were introduced intentionally in order to obtain more pronounced differences in the simulated optical properties and to determine the direction of absorption peak shift. However, we have estimated the inter-particle distance in a shrunken state based on the composite film preparation procedure to be equal to ~22 nm, which is near to the value of 15 nm used in modelling. After obtaining absorption spectra, 2D electric field intensity distributions at light wavelengths corresponding to the absorbance peak maxima were simulated.

Acknowledgements

This work was partly supported by World Premier International Research Center Initiative (WPI Initiative); MEXT, Japan; the Core Research for Evolutional Science and Technology (CREST) program of Japan Science and Technology Agency (JST), Japan; and the National Academy of Science of Ukraine in the frame of the national program 'Nanotechnology and Nanomaterials' and complex program of National Academy of Sciences of Ukraine 'Sensor systems for medical, ecological and industrial purposes'.

References

[1] K. Ariga, J. P. Hill, M. V. Lee, A. Vinu, R. Charvet, S. Acharya, *Sci. Technol. Adv. Mater.* **2008**, *9*, 014109. doi:10.1088/1468-6996/9/1/014109

[2] K. Ariga, A. Vinu, Y. Yamauchi, Q. Ji, J. P. Hill, *Bull. Chem. Soc. Jpn.* **2012**, *85*, 1. doi:10.1246/BCSJ.20110162

[3] M. Li, S. Ishihara, M. Akada, M. Liao, L. Sang, J. P. Hill, V. Krishnan, Y. Ma, K. Ariga, *J. Am. Chem. Soc.* **2011**, *133*, 7348. doi:10.1021/JA202768K

[4] M. Mashimo, Q. Ji, S. Ishihara, H. Sakai, M. Abe, J. P. Hill, K. Ariga, *Chem. Lett.* **2011**, *40*, 840. doi:10.1246/CL.2011.840

[5] K. Ariga, S. Ishihara, H. Abe, M. Li, J. P. Hill, *J. Mater. Chem.* **2012**, *22*, 2369. doi:10.1039/C1JM14101E

[6] K. Ariga, S. Ishihara, J. Labuta, J. P. Hill, *Curr. Org. Chem.* **2011**, *15*, 3719. doi:10.1021/JP209251Y

[7] S. Ishihara, J. P. Hill, A. Shundo, G. J. Richards, J. Labuta, K. Ohkubo, S. Fukuzumi, A. Sato, M. R. J. Elsegood, S. J. Teat, K. Ariga, *J. Am. Chem. Soc.* **2011**, *133*, 16119. doi:10.1021/JA2056165

[8] K. Ariga, S. Ishihara, H. Izawa, H. Xia, J. P. Hill, *Phys. Chem. Chem. Phys.* **2011**, *13*, 4802. doi:10.1039/C0CP02040K

[9] K. Ariga, T. Mori, J. P. Hill, *Adv. Mater.* **2012**, *24*, 158. doi:10.1002/ADMA.201102617

[10] V. Chegel, O. Rachkov, A. Lopatynskyi, S. Ishihara, I. Yanchuk, Y. Nemoto, J. P. Hill, K. Ariga, *J. Phys. Chem. C* **2012**, *116*, 2683. doi:10.2174/138527211797884629

[11] D. Austin, N. Mullin, A. Bismuto, I. Luxmoore, A. M. Adawi, D. G. Revin, M. Soulby, J. W. Cockburn, Q. Jiang, A. B. Krysa, A. G. Cullis, J. Faist, J. K. Hobbs, L. R. Wilson, *IEEE Photon. Technol. Lett.* **2010**, *22*, 1217. doi:10.1109/LPT.2010.2052595

[12] M. Ren, B. Jia, J.-Y. Ou, E. Plum, J. Zhang, K. F. MacDonald, A. E. Nikolaenko, J. Xu, M. Gu, N. I. Zheludev, *Adv. Mater.* **2011**, *23*, 5540. doi:10.1002/ADMA.201103162

[13] Y. Gu, Q. Li, J. Xiao, K. Wu, G. P. Wang, *J. Appl. Phys.* **2011**, *109*, 023104. doi:10.1063/1.3533953

[14] A. V. Kabashin, P. Evans, S. Pastkovsky, W. Hendren, G. A. Wurtz, R. Atkinson, R. Pollard, V. A. Podolskiy, A. V. Zayats, *Nat. Mater.* **2009**, *8*, 867. doi:10.1038/NMAT2546

[15] X. Zhang, B. Sun, R. Friend, H. Guo, D. Nau, H. Giessen, *Nano Lett.* **2006**, *6*, 651. doi:10.1021/NL052361O

[16] S. Malynych, G. Chumanov, *J. Am. Chem. Soc.* **2003**, *125*, 2896. doi:10.1021/JA029453P

[17] K. Aslan, Z. Leonenko, J. R. Lakowicz, C. D. Geddes, *J. Phys. Chem. B* **2005**, *109*, 3157. doi:10.1021/JP045186T

[18] Y. B. Zheng, Y.-W. Yang, L. Jensen, L. Fang, B. K. Juluri, A. H. Flood, P. S. Weiss, J. F. Stoddart, T. J. Huang, *Nano Lett.* **2009**, *9*, 819. doi:10.1021/NL803539G

[19] M. P. Jonsson, A. B. Dahlin, L. Feuz, S. Petronis, F. Höök, *Anal. Chem.* **2010**, *82*, 2087. doi:10.1021/AC902925E

[20] V. Chegel, O. A. Raitman, O. Lioubashevski, Yu. Shirshov, E. Katz, I. Willner, *Adv. Mater.* **2002**, *14*, 1549. doi:10.1002/1521-4095(20021104)14:21<1549::AID-ADMA1549>3.0.CO;2-C

[21] J.-Y. Shim, V. K. Gupta, *J. Colloid Interface Sci.* **2007**, *316*, 977. doi:10.1016/J.JCIS.2007.08.021

[22] K. S. Iyer, B. Zdyrko, S. Malynych, G. Chumanov, I. Luzinov, *Soft Matter* **2011**, *7*, 2538. doi:10.1039/C0SM01156H

[23] H. Otsuka, Y. Akiyama, Y. Nagasaki, K. Kataoka, *J. Am. Chem. Soc.* **2001**, *123*, 8226. doi:10.1021/JA010437M

[24] B. D. Lucas, J.-S. Kim, C. Chin, L. J. Guo, *Adv. Mater.* **2008**, *20*, 1129. doi:10.1002/ADMA.200700225

[25] R. Gradess, R. Abargues, A. Habbou, J. Canet-Ferrer, E. Pedrueza, A. Russell, J. L. Valdés, J. P. Martínez-Pastor, *J. Mater. Chem.* **2009**, *19*, 9233. doi:10.1039/B910020B

[26] W. A. Murray, B. Auguie, W. L. Barnes, *J. Phys. Chem. C* **2009**, *113*, 5120. doi:10.1021/JP810322Q

[27] W. Rechberger, A. Hohenau, A. Leitner, J. R. Krenn, B. Lamprecht, F. R. Aussenegg, *Opt. Commun.* **2003**, *220*, 137. doi:10.1016/S0030-4018(03)01357-9

[28] J. E. Elliott, M. Macdonald, J. Nie, C. N. Bowman, *Polymer* **2004**, *45*, 1503. doi:10.1016/J.POLYMER.2003.12.040

[29] R. Gabai, N. Sallacan, V. Chegel, T. Bourenko, E. Katz, I. Willner, *J. Phys. Chem. B* **2001**, *105*, 8196. doi:10.1021/JP0111618

[30] J. W. Gooch, *Encyclopedic Dictionary of Polymers, 2nd Edition* **2010** (Springer: New York, NY).

[31] Refractive index n of 0.1 M (c.a. 1 wt.-%) aqueous sulphuric acid at 20°C is 1.3342, which is similar to that of pure water ($n = 1.3330$). See: http://us.mt.com/us/en/home/supportive_content/application_editorials/Sulfuric_Acid_re_e.html (accessed 21 February 2012).

[32] N. Akkilic, Z. Mustafaeva, M. Mustafaev, V. Chegel, *Macromol. Symp.* **2008**, *269*, 138. doi:10.1002/MASY.200850917