

Plasmonic Properties of Nanostructured Diamond Like Carbon/Silver Nanocomposite Films with Nanohole Arrays

Šarūnas MEŠKINIS^{1*}, Iryna YAREMCHUK², Viktoras GRIGALIŪNAS¹,
Andrius VASILIAUSKAS¹, Arvydas ČIEGIS¹

¹ Institute of Materials Science of Kaunas University of Technology, Baršausko 59, LT-51423 Kaunas, Lithuania

² Department of Photonics, Lviv Polytechnic National University, S. Bandera Str. 12, Lviv 79013, Ukraine

crossref <http://dx.doi.org/10.5755/j01.ms.22.4.13193>

Received 21 September 2015; accepted 01 October 2015

Plasmonic properties of the diamond like carbon nanocomposite films with embedded silver nanoparticles with patterned nanohole arrays were analyzed in this study. The films were deposited by unbalanced reactive magnetron sputtering of silver target. Nanopatterning of the films was performed by combining electron beam nanolithography and ion beam etching techniques. Modeling of plasmonic properties was done using the classical Maxwell-Garnett theory. Modeling data and experimental results were in good accordance. Formation of the nanohole pattern in diamond like carbon films doped with silver resulted in decreased intensity of the surface plasmon resonance absorbance peak. No new absorbance or transmittance peaks were observed after the nanopatterning. It was explained by extraordinary transmission effect in nanostructured DLC : Ag film films due to plasmon polariton resonance inside of the nanoholes.

Keywords: plasmon polariton resonance, diamond like carbon films, nanohole array.

1. INTRODUCTION

Nanocomposites consisting of the dielectric matrix with embedded group IB metal (Au, Ag, Cu) nanoparticles received considerable interest of the researchers [1, 2]. Particularly presence of the Au, Ag or Cu nanoparticles results in appearance of the surface plasmon resonance effect in such nanocomposite films [1, 2]. On the other hand, plasmonic properties of the nanocomposite can be additionally controlled by using dielectric matrix of the appropriate refractive index [2]. Besides that, dielectric matrix protects metal nanoparticles from the unwanted environmental effects such as oxidation. In such a way main disadvantage of the Au nanoparticles – oxidation resistance [3] – can be successfully eliminated enabling exploitation advantages of other group IB metals such as stronger surface plasmon resonance effect in the case of silver [3, 4]. Another important advantage of the plasmonic nanocomposites in comparison with nanoparticles is their compatibility with semiconductor device fabrication technology. Particularly, compatibility with nanofabrication techniques such as electron beam and UV lithography as well as ion beam and reactive ion etching can be mentioned [5]. In such a way, in principle different plasmonic nanocomposite based nanostructures (metamaterials) such as nanodots, split rings, nanoholes, gratings can be fabricated. However, there are few studies on this matter. Therefore, in this article nanohole arrays were fabricated in the plasmonic diamond like carbon nanocomposites with embedded silver nanoparticles (DLC: Ag). Optical properties of the fabricated nanostructures were investigated.

2. EXPERIMENTAL TECHNIQUES

Fabrication process of diamond like carbon nanocomposite films consists of a few steps – deposition, patterning and etching. Deposition of the silver doped diamond like carbon nanocomposite film was done by DC unbalanced reactive magnetron sputtering of silver target. The diameter of magnetron was 3 inches. Fused silica substrates were used. Mixture of the hydrocarbons (acetylene) and argon gas was used in the reactive magnetron sputtering. Ar gas flux was 80 sccm and C₂H₂ gas flux was 7.8 sccm. In all experiments substrate – target gap was set at 10 cm, magnetron target current was 0.1 A, base pressure was 5×10^{-4} Pa and work pressure was $(4 \pm 1) \times 10^{-1}$ Pa. The thickness of deposited films was about 50 nm. No additional bias was used, and substrates were grounded. Nanopatterning of the silver doped diamond like carbon nanocomposite film was done using Raith e-LiNE^{plus} e-beam nanolithography & scanning electron microscopy system that includes a column and electron source designed to provide a Gaussian beam of 2 nm size (at 20 kV with a probe current of 300 pA, current density at this smallest beam size is equal to 7500 A/cm²). Beam voltage can be selected within the range from 20 V to 30 kV in steps of 10 V, working distance and seven beam defining aperture settings can be adjusted separately. The apertures are changed electromagnetically providing a current range from 5 pA to approximately 20 nA. Micro- and nanostructures in Fig. 1–Fig. 3 were fabricated using a single layer of high molecular weight (950K) polymethyl methacrylate (PMMA) dissolved in Anisole at 4 % solids. PMMA was spin coated at 3000 rpm for 30 seconds and dried for 2 minutes at 200 °C on hotplate (the thickness of spin-coated layer was measured by laser ellipsometer Gaertner L-115 and varied from 230 to 240 nm). Electron beam

*Corresponding author. Tel.: +370-37-313432; fax.: +370-37-314423.
E-mail address: sarunas.meskinis@ktu.lt (Š. Meškinis)

exposure was done at 10 kV (aperture diameter 30 μm , probe current 250 pA, write field size 100 x 100 μm) with dose variations from 120 to 140 $\mu\text{C}/\text{cm}^2$. Exposed PMMA was developed in methyl isobutyl ketone (MIBK) and isopropanol (IPA) solution (1 : 3) for 30 seconds with agitation (development was stopped in isopropyl alcohol for 15 seconds and the sample dried at room temperature with dry nitrogen flow). After the fabrication of the nanoholes array in PMMA by e-beam nanolithography, Ar ion beam etching of DLC : Ag film followed. Argon ion beam etching was performed by using ion beam etching unit “Usi-ionic” (LPA Industry) equipped with a multi-cell closed drift Hall-current ion source. The following technological process parameters were used: ion beam energy 300 eV, ion current density 0.25 mA/cm^2 , work pressure 1×10^{-1} Pa, substrate temperature 20 $^\circ\text{C}$. After etching, PMMA mask was removed in Remover PG (Micro Resist Technology GmbH), as shown in Fig. 5.

Optical properties of the nanopatterned DLC : Ag film were evaluated by AvaSpec-2048 spectrometer in the ultraviolet and visible (UV-VIS) region. Spectrometer is based on the AvaBench-75 symmetrical Czerny-Turner design and is equipped with 2048 pixel CCD detector array (resolution – 1.4 nm).

Volume filling factor was calculated as a ratio between the volume of the nanoholes and overall volume of the film.

3. EXPERIMENTAL RESULTS

Electron beam lithography presents the smallest writing tool known and is the preferred technology when the highest resolution is required to fabricate nanometer-scale structures. Unfortunately, due to extremely small beam spot, electron beam lithography technique is up to 10 million times slower than optical lithography and this is a serious limitation, especially when writing many small patterns over a large area. Efficient nanoscale patterning requires precise focusing and alignment procedures and system parameters shall be customized for specific applications, e.g. exposing different parts of one design and changing column and other parameters in between [6]. Resolution of electron beam lithography is determined not only by the focused beam size, but also very much depends on electron beam resist thickness, electron scattering and proximity effects (it is almost impossible to fabricate structures of size less than electron beam resist thickness). Having resist thickness of 230–240 nm, we have chosen four patterning dimensions of plasmonic nanoholes array, varying patterned area from 100 x 100 to 400 x 400 nm, and varying spacing between patterned holes from 300 to 600 nm. Dimensions of the plasmonic nanoholes array are listed in Table 1.

Table 1. Dimensions of the plasmonic nanoholes array

Title	Patterned hole dimension, nm	Spacing between patterned holes, nm	Period, nm	Volume filling factor f
E100_T300	100 x 100	300	400	0.07
E200_T400	200 x 200	400	600	0.27
E300_T300	300 x 300	300	600	0.44
E400_T600	400 x 400	600	1000	0.28

Micrographs of plasmonic nanoholes array fabricated in the PMMA coated onto the silver doped diamond like carbon nanocomposite films are shown in Fig. 1 and Fig. 2. Fig. 1 illustrates array with patterning dimensions of 200 x 200 nm. Nanohole diameter expands here to 350 nm, respectively spacing between patterned holes shrinks to 250 nm. Fig. 2 illustrates array with patterning dimensions of 300 x 300 nm. Actual nanohole diameter here is equal to 450 nm, and actual spacing between patterned holes is 150 nm. There is good accordance between dimensions of the nanoholes fabricated in PMMA layer and dimension of the nanoholes fabricated in DLC:Ag film (Fig. 2, Fig. 3).

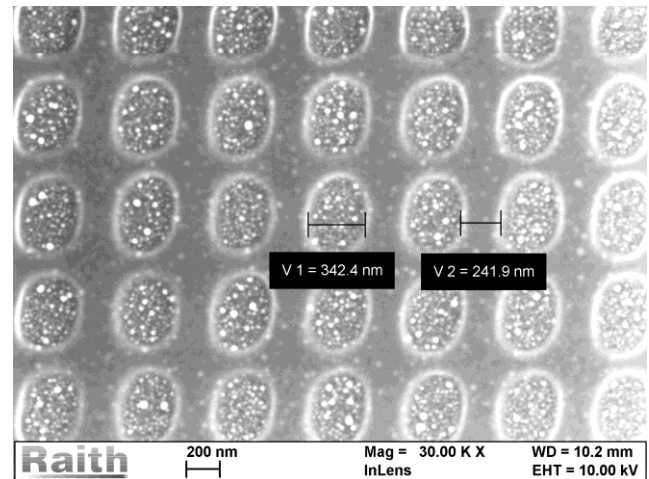


Fig. 1. SEM micrograph illustrates patterned hole array (patterning dimensions 200 x 200 nm, spacing 400 nm) fabricated in PMMA layer, spin coated on the silver doped diamond like carbon nanocomposite film

Absorbance spectra of the patterned silver doped diamond like carbon nanocomposite films in the ultraviolet and visible range are presented in Fig. 4. Original surface plasmon resonance peak is seen at 455 nm in all patterning cases, except the smallest holes’ case of 100 x 100 nm. This case can be attributed to the ion beam over-etching and PMMA mask destroying.

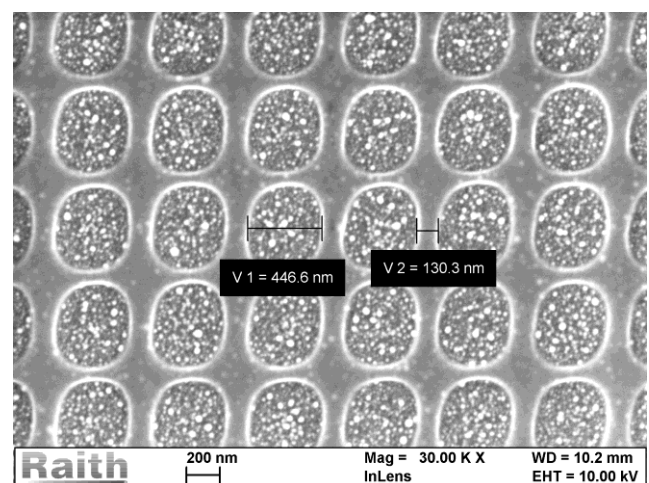


Fig. 2. SEM micrograph illustrates patterned hole array (patterning dimensions 300 x 300 nm, spacing 300 nm) fabricated in PMMA layer, spin-coated on the silver doped diamond like carbon nanocomposite film

The smallest and the most broadened peak can be seen in the case of patterning 200 x 200 nm with spacing between holes of 400 nm (after ion beam etching hole diameter is expanded about to 350 nm, and spacing shrunk to 250 nm, see Fig. 1).

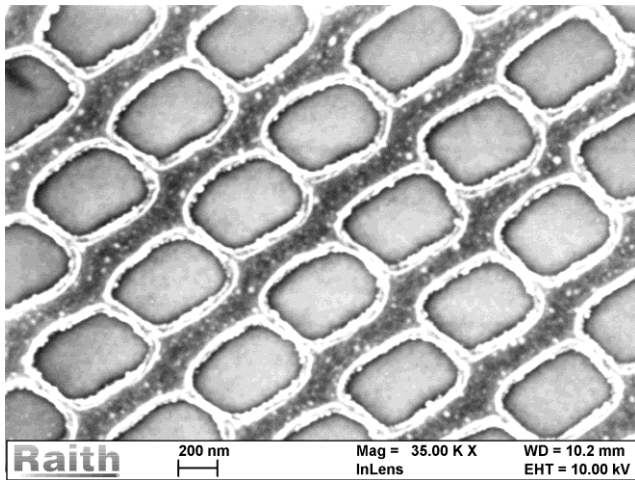


Fig. 3. SEM micrograph illustrates patterned silver doped diamond like carbon nanocomposite film after removal of PMMA

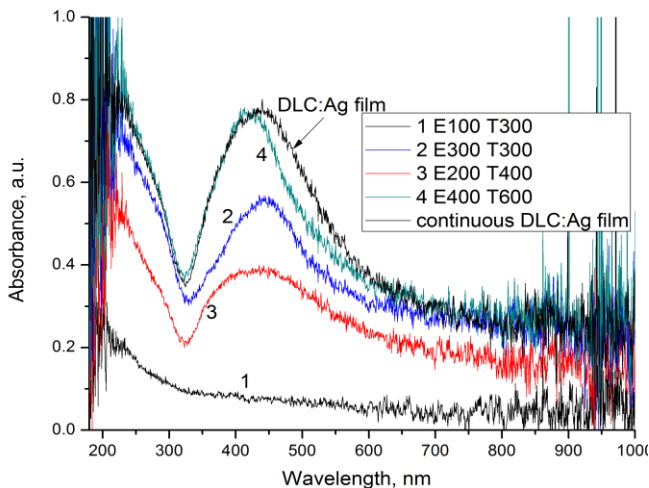


Fig. 4. Absorption spectra of the patterned silver doped diamond like carbon nanocomposite films

The peak intensity is about twice less than in the case of the unpatterned silver doped diamond like carbon film. Increasing (see Fig. 2) the hole diameter and shrinking spacing between holes (the period is kept the same – 600 nm) plasmon resonance peak intensity apparently increases. In the case of hole diameter 400 x 400 nm with spacing between the holes of 600 nm plasmon resonance peak intensity is almost the same, as in the case of unpatterned silver doped diamond like carbon film, but the peak location is slightly shifted to shorter wavelengths (blue-shift). It is obvious, that variations of silver doped diamond like carbon film patterning dimensions has strong impact on plasmon resonance peak intensity and also can effect peak wavelength. However, no additional absorbance peaks appear as a result of the nanopatterning.

Ratio between absorbance of the nanostructures DLC : Ag with nanohole pattern and absorbance of the continuous DLC:Ag film for more thorough analysis of the absorbance spectra is presented in Fig. 5. It can be seen that in the case of the nanostructured DLC : Ag film containing 400 nm diameter nanoholes absorbance decreases only in the region of the surface plasmon resonance peak. In other cases, absorbance decrease in all analyzed range of the spectra.

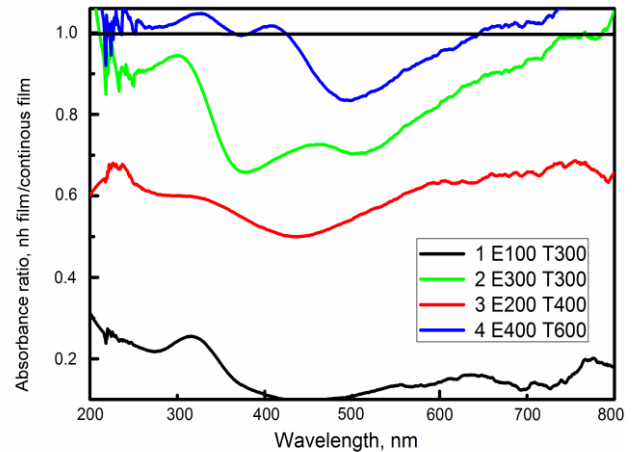


Fig. 5. Ratio of absorbance of the patterned and continuous silver doped diamond like carbon nanocomposite film

However, in all cases the highest decrease of the absorbance takes place in the region of the surface plasmon resonance peak. Nanohole nanopatterning of DLC : Ag films can result in decreased absorbance due to the two reasons. If light transmission is increased due to the geometric effect, absorbance should decrease in all spectral range [7]. Such decrease is seen for 3 samples. It seems that geometric effect is absent only in the case of the nanopatterned film containing largest nanoholes. The second reason can be extraordinary transmission effect already reported for nanostructured plasmonic metal films with nanohole arrays [8, 9]. Extraordinary transmission effect occurs due to plasmon polariton resonance inside of nanoholes for TM polarization. In our case this resonance occurs in addition to the local plasmon resonance in Ag nanoparticles. It seems that due to the high concentration of silver particles and interactions between them plasmon polariton wave occurs in the holes of the nanocomposite. In all cases extraordinary transmission effect occurs in all samples.

4. THEORETICAL CONSIDERATIONS

Pendry et al [10] have shown that for a surface wave that propagates along a perforated metal film one is able to introduce an effective permittivity. The effective dielectric permittivity of 2D arrays of nanoapertures in opaque metal films has the form identical to that of plasmonic materials. Thus, we can consider the silver doped nanocomposite diamond like carbon (DLC-Ag) films with the holes' array as plasmonic crystal with its period much smaller than the operating wavelength. Such structure behaves as an

effective medium with its optical parameters dependent on its design.

The classical effective Maxwell-Garnett theory [11] was used for calculation of the optical characteristics of DLC-Ag film with nanoholes array:

$$\varepsilon_{eff_2D} = \varepsilon_{air} \frac{\varepsilon_{DLC-Ag}(1+2f) + 2\varepsilon_{air}(1-f)}{\varepsilon_{DLC-Ag}(1-f) + \varepsilon_{air}(2+f)}. \quad (1)$$

Volume filling factor (f) of the air inclusions was calculated by analogy to diffraction 1D gratings. The optical constants of the nanocomposite film (ε_{DLC-Ag}) were modeled using the renormalized Maxwell-Garnett theory [12] by taking into account the dipole-dipole interactions between particles. The optical properties of silver are obtained from the experimental data by Johnson and Christy [13]. The refractive index (n) and extinction coefficient (k) dispersion curves of DLC film are used from [14]. The average particle size of silver nanoparticles is 10 nm according to [15]. Application of this effective theory provides good fit of the experimental refractive index and absorption spectra of the DLC-Ag films with the silver nanoparticle concentration up to 22 % [15].

Fig. 8 shows modelled and experimental absorption spectra of the various nanoholes arrays patterned silver doped diamond like carbon nanocomposite films. Comparison of the modelled and experimental curves shows good agreement between the theoretical and experimental data, consequently, this model can be used to predict plasmonic behaviour of patterned medium.

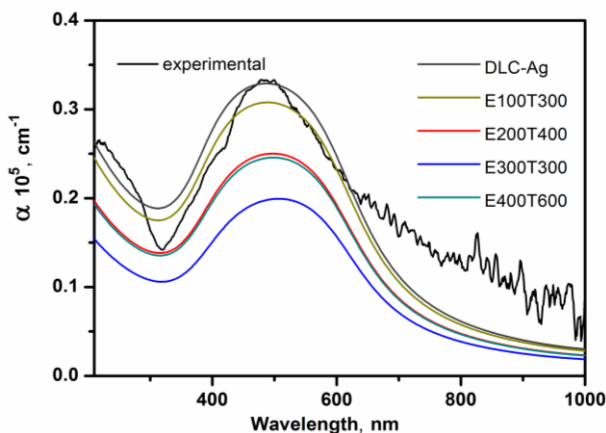


Fig. 8. Modelled and experimental absorption spectra of the patterned silver doped diamond like carbon nanocomposite films

It can be seen that overall tendencies are the same both for modelled and experimentally measured absorbance spectra of nanopatterned DLC : Ag films. In all cases extraordinary transmittance effect related decrease of the intensity of plasmonic peak can be seen (Fig. 6–Fig. 8). Similarly, to the experimental data modeling shows presence of the geometric effect, too.

5. CONCLUSIONS

Silver doped diamond like carbon nanocomposite films were patterned by micro- and nanosize hole arrays

using e-beam nanolithography and argon ion beam etching system. Formation of the nanohole pattern in DLC : Ag films resulted in decreased intensity of the plasmonic peak. In some cases, small shift of the peak position as well as some changes of the peak width was observed. No new absorbance or transmittance peaks were detected. It was explained by appearance of the extraordinary transmission effect in nanostructured films due to plasmon polariton resonance inside of the nanoholes fabricated in the plasmonic DLC : Ag film. Competition between to plasmon polariton resonance in nanoholes and local plasmon resonance in Ag nanoparticles results in decreased intensity of the surface plasmon resonance related absorbance peak.

For part of the samples overall decrease of the absorbance in all investigated wavelength range was observed. It was explained by geometric effect related with nanostructuring of DLC : Ag films.

Simulation performed using classical effective Maxwell-Garnett theory and modelling test structures were in good accordance with the experimental results and supported presence of the extraordinary transmittance effect in all samples investigated.

Acknowledgement

This research was funded by the European Social Fund under the Global Grant measure (project No. VP1-3.1-ŠMM-07-K-03-057). Support of the Research Council of Lithuania in the frames of the Lithuania-Ukraine research collaboration program should be acknowledged (grant TAP LU 04/2014).

REFERENCES

1. **Etrich, Ch., Fahr, S., Hedayati Mehdi, K., Faupel, F., Elbahri, M., Rockstuhl, C.** Effective Optical Properties of Plasmonic Nanocomposites *Materials* 7 2014: pp. 727–741.
2. **Hedayati, M.K., Faupel, F., Elbahri, M.** Review of Plasmonic Nanocomposite Metamaterial Absorber *Materials* 7 (2) 2014: pp. 1221–1248.
3. **Pena-Rodríguez, O., Pal, U.** Enhanced Plasmonic Behavior of Bimetallic (Ag–Au) Multilayered Spheres *Nanoscale Research Letters* 6 2011: pp. 279–284. <http://dx.doi.org/10.1186/1556-276X-6-279>
4. **Kyeong-Seok L., El-Sayed, M.A.** Gold and Silver Nanoparticles in Sensing and Imaging: Sensitivity of Plasmon Response to Size, Shape, and Metal Composition *Journal of Physical Chemistry B* 110 (39) 2006: pp. 19220–19225.
5. **Tamulevičius, T., Tamulevičienė, A., Virganavičius, D., Vasiliauskas, A., Kopustinskis, V., Meškiniš, Š., Tamulevičius, S.** Structuring of DLC : Ag Nanocomposite Thin Films Employing Plasma Chemical Etching And Ion Sputtering *Nuclear Instruments and Methods in Physics Research (B)* 341 2014: pp. 1–6.
6. **Højlund-Nielsen, E., Greibe, T., Asger Mortensen, N., Kristensen, A.** Single-spot E-beam Lithography for Defining Large Arrays of Nano-holes *Microelectronic Engineering* 121 2014: pp. 104–107.
7. **Chih, W., Hsuan, I.W., Chih-Wei, L., Jihperng, L.** Anisotropic Optical Transmission of Femtosecond Laser Induced Periodic Surface Nanostructures on

- Indium-Tin-Oxide Films *Applied Physics Letters* 101 (10) 2012: pp. 1–5.
8. **Reilly, T.H., Tenent, R.C., Barnes, T.M., Rowlen, K.L., van de Lagemaat, J.** Controlling the Optical Properties of Plasmonic Disordered Nanohole Silver Films *ACS Nano* 4 (2) 2010: pp. 615–624.
 9. **Gordon, R.** Bethe's Theory for Aperture Arrays *Physical Review A* 76 2007: pp. 1–5.
 10. **Pendry, J.B., Martín-Moreno, L., Garcia-Vidal, F.J.** Mimicking Surface Plasmons with Structured Surfaces *Science* 305 5685 2004: pp. 847–848.
 11. **Maxwell Garnett, J.C.** Colours in Metal Glasses, in Metallic Films, And in Metallic Solutions II *Philosophical Transactions Royal Society London Seria A* 1904: pp. 237–288.
 12. **Vasilevskiy, M.** Effective Dielectric Response of Composites Containing Uniaxial Inclusions *Physica Status Solidi (b)* 219 2000: pp. 197–204.
 13. **Johnson, P, Christy, R.** Optical Constants of the Noble Metals *Physical Review B* 6 1972: pp. 4370–4380.
 14. **Yaremchuk, I., Tamulevičienė, A., Tamulevičius, T., Šlapikas, K., Balevičius, Z., Tamulevičius, S.** Modeling of the Plasmonic Properties of DLC-Ag Nanocomposite Films *Physica Status Solidi (a)* 211 2014: pp. 329–335.
 15. **Yaremchuk, I., Meškiniš, Š., Fitio, V., Bobitski, Y., Šlapikas, K., Čiegis, A., Balevičius, Z., Selskis, A., Tamulevičius, S.** Spectroellipsometric Characterization and Modeling of Plasmonic Diamond-Like Carbon Nanocomposite Films with Embedded Ag Nanoparticles *Nanoscale Research Letters* 2015:10:157, published online 2015 Apr 1.
<http://dx.doi.org/10.1186/s11671-015-0854-y>
- [http://dx.doi.org/10.1002/1521-3951\(200005\)219:1<197::AID-PSSB197>3.0.CO;2-5](http://dx.doi.org/10.1002/1521-3951(200005)219:1<197::AID-PSSB197>3.0.CO;2-5)