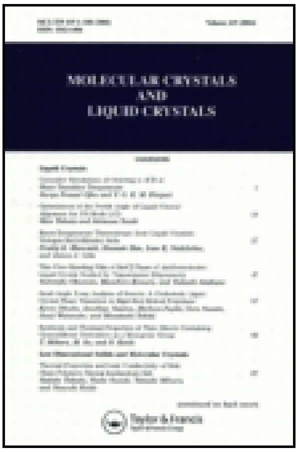
This article was downloaded by: [Siauliu University Library]
On: 17 February 2013, At: 00:29
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Fabrication and Characterization of Stretchable PDMS Structures Doped With Au Nanoparticles

U. Cataldi [a], P. Cerminara [a], L. De Sio [a], R. Caputo [a] & C. P. Umeton [a]

[a] LICRYL (Liquid Crystals Laboratory, IPCF-CNR), and Center of Excellence CEMIF.CAL and Department of Physics University of Calabria, 87036 Arcavacata di Rende (CS), Italy

Version of record first published: 18 Apr 2012.

To cite this article: U. Cataldi, P. Cerminara, L. De Sio, R. Caputo & C. P. Umeton (2012): Fabrication and Characterization of Stretchable PDMS Structures Doped With Au Nanoparticles, Molecular Crystals and Liquid Crystals, 558:1, 22-27

To link to this article: http://dx.doi.org/10.1080/15421406.2011.653675

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., Vol. 558: pp. 22–27, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.653675

Downloaded by [Siauliu University Library] at 00:29 17 February 2013

Fabrication and Characterization of Stretchable PDMS Structures Doped With Au Nanoparticles

U. CATALDI,* P. CERMINARA, L. DE SIO, R. CAPUTO, AND C. P. UMETON

LICRYL (Liquid Crystals Laboratory, IPCF-CNR), and Center of Excellence
CEMIF.CAL and Department of Physics University of Calabria,
87036 Arcavacata di Rende (CS), Italy

Fabrication of samples showing plasmonic properties is a fundamental step towards the realization of devices that can exhibit peculiar electromagnetic properties. In this work we illustrate some fabrication techniques that can reveal useful for the realization of this kind of samples. For what concerns materials, we used polydimethylsiloxane (PDMS) combined with Au nanoparticles (NPs). A first experimental characterization of the obtained structures has been reported.

Keywords Metallic nanoparticles; optofluidics; plasmonic resonances

Introduction

Wide interest is actually devoted to the realization of structures showing metamaterial properties [1]. However, up to now, main results have been achieved in the microwave and in the far-infrared regime. In general, an electromagnetic system can be defined as a metamaterial when it gains its peculiar behaviour from structure rather than composition: the macroscopic "metamaterial" effect is the result of the collective behaviour of a large number of subunits (defined as meta-atoms), that are resonant with the probe radiation, and geometrically organised in a regular way [2]. When considering the microwave range, such units can be designed as very tiny electromagnetic circuits assembled in arrays. Fabrication of such devices is not particularly difficult because it can benefit of the silicon on-the-shelf technology. Achieving similar results in the optical range is much more difficult [3]: in this case, the typical size of the subunits needs to scale down to tens or hundreds of nanometers and the single subunit becomes a metal (generally gold or silver) nanoparticle. The choice of a top-down approach (e-beam or photo-lithography) is still valid but, due to the long processing times, the resulting useful area is way too small. A bottom-up approach is then preferable: NPs can be combined with host materials that have the ability to induce the self-organization of particles through chemical or physical mechanisms. In this case, the major effort is spent to design host materials that can exercise such an influence on NPs. In this paper, we report on our attempts to realize a system made of Au NPs embedded in an elastomeric support. There are several reasons why we chose such an approach. A first

---

*Address correspondence to U. Cataldi, LICRYL (Liquid Crystals Laboratory, IPCF-CNR), and Center of Excellence CEMIF.CAL and Department of Physics University of Calabria, 87036 Arcavacata di Rende (CS), Italy. E-mail: ugo.cataldi@fis.unical.it one is that an eventual device, being stretchable, should show tunable plasmonic features. Indeed, a stretching of the NP doped elastomer matrix should modify the relative distance between NPs and hence their electromagnetic coupling. Moreover, in case such prototype devices were successfully realized, its mass production should be straightforward: a master structure with the desired features would be easily replicated in the elastomer support. When elastomers are considered, polydimethylsiloxane (PDMS) is one of the most suitable. Indeed, it is widely used in optofluidic [4], photonic [5,6] and biomedical applications [7] In the following, we will illustrate our attempts to fabricate a PDMS substrate doped with Au nanoparticles that can eventually be shaped as needed for obtaining a device with tunable plasmonic properties.

Samples Preparation

In order to obtain samples showing reproducible properties, we tried to develop a fabrication protocol. The starting point for obtaining a PDMS material is a bi-component mixture made of a base pre-polymer and a curing agent. Depending on the relative concentration of these components, the elastomer can vary from a gel-like to an almost plastic hard consistency. The polymerised structure is obtained by baking the bi-component syrup in oven for some time. Both baking time and temperature influence the mechanical properties of the final structure. Combination of this material with gold or silver NPs is not trivial: indeed, when dealing with NPs, the hardest job is to prevent their clustering. Indeed, the plasmonic resonance frequency of metal particles strongly depends on their size and on the dielectric features of the host material containing them [8]. For this reason, we first diluted Au NPs (from Harima Chemicals) in chloroform, stirred them for about one hour and then verified their good dispersion by scanning electron microscopy (SEM). Next step is to mix Au NPs diluted in chloroform with PDMS. There are, at least, three possible ways to proceed: they can be directly combined with the base pre-polymer, with the curing agent or with the two components previously mixed together. At first we thought that the very low viscosity of the curing agent should improve its miscibility with Au NPs. Unfortunately, this hypothesis was not correct: after a short time (about 1 hour), NPs phase separated from the curing agent. The combination of NPs with the base pre-polymer gave better results: the obtained mixture was quite stable and homogenously coloured. Probably, the high viscosity of this material prevents the diffusion of NPs and their aggregation in clusters. The further addition of the curing agent to the base pre-polymer doped with NPs did not influence the stability of the mixture that was ready then to be baked. The samples used for experiments have been prepared by following the steps depicted in Fig. 1. Instead of preparing a homogenous substrate made of PDMS doped with NPs, we preferred to limit the presence of this material just to a thin volume. In order to obtain such a result, we glued a glass substrate (1 × 2 cm^2, 1.1 mm thick) to the bottom of a petri dish (Fig. 1(a)) and then we poured a pure PDMS mixture (curing agent/base pre-polymer in 1/10 weight ratio) in it (Fig. 1(b),(c)). Afterwards, the petri dish has been baked in the oven (previously warmed up at 100°C, Fig. 1(d)) for about one hour. After the baking step, the hardened PDMS substrate can be just peeled off from the petri dish (Fig. 1(e)). The obtained sample contains a hollow volume corresponding to that occupied by the glass substrate glued in the Petri dish. We filled in this volume with a second mixture made of PDMS (same ratio between the two components) and Harima at 1 wt%, prepared as explained above. It is worth noting that the commercial product from Harima (NPG-J) that we used for our experiments contains an effective 56 wt% concentration of Au nanoparticles. As such, the real concentration of Au NPs in our samples corresponds to 0.56 wt%. The PDMS sample, including now Au NPs,

Downloaded by [Siauliu University Library] at 00:29 17 February 2013

Downloaded by [Siauliu University Library] at 00:29 17 February 2013

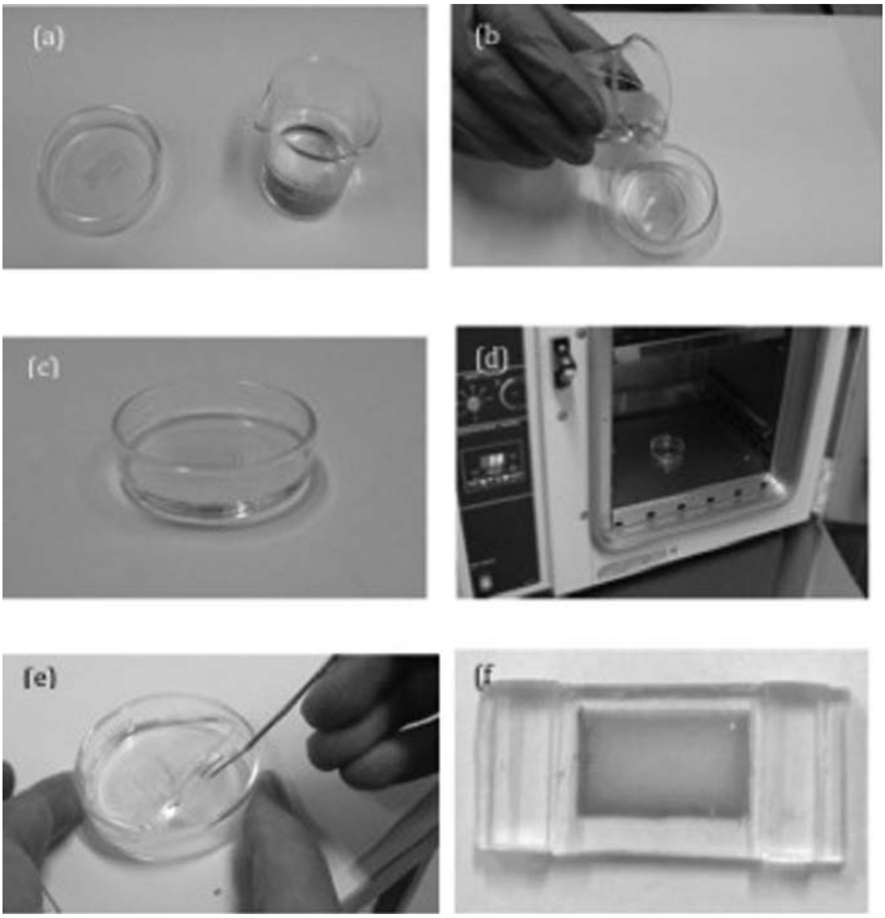


Figure 1. (a) PDMS preparation, (b) Air degassing, (c) Master covering, (d) baking process, (e) peeling off, (f) PDMS template filled with Au nanoparticles.

has been additionally baked at 200°C for about one hour. At the end of the process, we obtained ~2 mm of thickness PDMS layer that contains a thin layer (about 100 μm thick) of PDMS doped with Au NPs (Fig. 1(f)).

The choice of limiting the presence of NPs to a small volume of the sample is motivated by two reasons. First of all, by fabricating a thick layer of PDMS homogenously doped with NPs, even with low gold concentrations, the extinction coefficient of the sample would be way too high, making difficult a reliable study of the plasmonic response of the system. Moreover, in future studies it could be convenient to replicate a micro/nano structure on the surface of the pure PDMS sample. By covering afterwards this structure with NPs, it could be possible to study the influence of NPs to the optical and/or electro-optical behaviour of such a structure. Such experimental condition can be realized by using the procedure indicated above for fabricating the sample and by simply substituting the thin glass substrate in the Petri dish with one where a micro/nano structure is present.

Experimental Characterization

The prepared sample has been experimentally characterized by studying its spectroscopical response for different stretching conditions of the PDMS substrate.

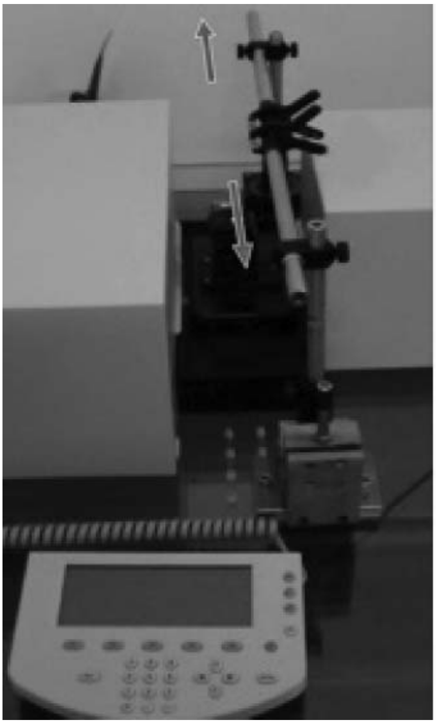


Figure 2. UV-VIS spectro-photometer and stretching setup.

In order to apply a mechanical strain to the sample, we placed it between two tweezers that could be moved apart by two micrometre mobile actuators. The set-up has been mounted between the light source and the detector of an Agilent 8453E spectro-photometer. For each elongation of the sample, the corresponding transmission spectrum has been acquired (Fig. 2). Obtained normalized spectra are reported in Fig. 3.

From the graph, it can be observed that an increase of the applied strain corresponds to a red shift of the plasmon resonance wavelength of about $\Delta\lambda = 12$ nm (from $\lambda = 551$ nm, no applied strain, to $\lambda = 563$ nm, 20,4% applied strain). This result confirms the hypothesis made above that, by using a PDMS matrix doped with Au NPs, it is possible to obtain a system showing tunable plasmonic properties. Indeed, Kinnan and Chumanov have also demonstrated that, by changing the inter-distance between NPs, their electromagnetic coupling is correspondingly modified [9]. In their case, a spectroscopic analysis performed on substrates coated with Ag NPs of the same size but with different surface density also showed a red shift of the plasmon resonance wavelength. Results reported in Fig. 4, show two micrographs depicting the same area but with different magnifications.

Size and distribution of particles is quite variable but the presence of bigger aggregates of elongated shape (Fig. 4(a)) prevails. The higher magnification detail, of Fig. 4(b), allowed an estimation of the average sizes of these aggregates with a result of the short side measuring $l = 246 \pm 33$ nm and the long one, $d = 563 \pm 71$ nm. In order to theoretically explain the red-shift of the Plasmon resonance position, obtained upon stretching the sample, we can assume a quasi-static approximation, in which the wavelength of probe light is considered much larger than the typical size of the Au nanosphere [10]. Under this condition, there is a dipolar electrostatic interaction between the electromagnetic wave and

Downloaded by [Siauliu University Library] at 00:29 17 February 2013

Downloaded by [Siauliu University Library] at 00:29 17 February 2013

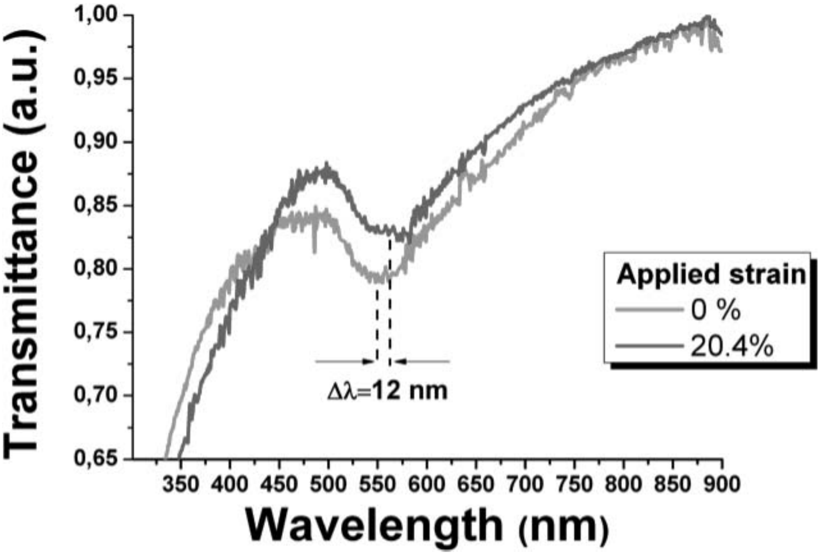


Figure 3. Wavelength of the plasmon resonances versus the applied strain; the dash lines indicate the points of minimum of the surface plasmon resonances.

the single Au particle. In this view, the contribution of the single aggregate can be seen as the sum of many dipolar terms, each of them due to the particles constituting the aggregate.

Under an applicative point of view, we can envision several possibilities for the obtained result. By reproducing the system in thin layers (100 μm) it could be possible to realize very precise pressure control sensors. A more sophisticated employment would instead result in advanced solar applications due to the ability of Au nanoparticles to harvest the electromagnetic radiation [11]. Finally, by better controlling size and distribution of Au nanoparticles, it could be even possible to realize metamaterials with functionalities in the infrared or visible spectrum.

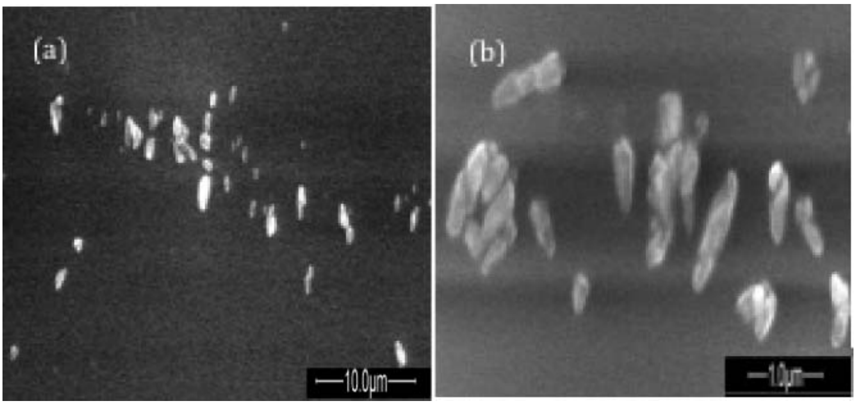


Figure 4. Electron microscopy images of (a) typical ensemble vision, (b) particular of nanoparticles shape.

Conclusions

In this paper, we have reported on our first attempts to fabricate a template structure made of PDMS and partially coated with a mixture of the same elastomer and Au nanoparticles. A spectroscopic characterization of the obtained samples has shown that it is possible to tune their plasmon resonance wavelength through application of a mechanical strain. In particular, it has been observed that a red-shift of this resonance wavelength corresponds to a longitudinal elongation of the sample, This behaviour is probably due to an increase of particle interdistance occurred because of the applied mechanical stretching. These preliminary results represent, in our opinion, the first steps towards the realization of metamaterial devices with tunable properties.

Downloaded by [Siauliu University Library] at 00:29 17 February 2013

Acknowledgments

The research leading to these results has received funding from the European Union's Seven Framework Programme (FP7/2007-2013) under grant agreement n°228455.

The present communication is co-funded by the European Commission, European Social Fund and Calabria Region. Authors are the only responsible of this communication and the European Commission and Calabria region decline every responsibility on the use that will be done with the contained information.

Authors are grateful to Dr. Giovanni Desiderio for the valuable help provided performing the SEM analysis of our samples.

References

[1] Veselago, G. (1968). The electrodynamics of substances with simultaneously negative values of ε and μ. *Sov. Phys. Usp.*, *10*(4), 509.

[2] Rockstuhl, C., Lederer, F., Etrich, C., Pertsch, T., & Scharf, T. (2007). *Phys. Rev. Lett.*, *99*, 017401.

[3] Valentine, J., Zhang, S., Zentgraf, T., Ulin-Avila, E., Genov, D. A., Bartal, G., & Zhang, X. (2008). Three dimensional optical metamaterial exhibiting negative refractive index. *Nature*, *455*, 376.

[4] Fainman, Y., Lee, L. P., Psaltis, D., & Yang, C. (2010). *Optofluidics: Fundamental, Devices, and Application*. McGraw-Hill.

[5] Merola, F., Paturzo, M., Coppola, S., Vespini, V., & Ferraro, P. (2009). Self-patterning of a polydimethylsiloxane microlens array on functionalized substrates and characterization by digital holography. *J. Micromech. Microeng.*, *19*, 125006.

[6] Cuennet, J. G., Vasdekis, A. E., De Sio, L., & Psaltis, D. (2011). Optofluidic modulator based on peristaltic nematogen microflows. *Nature Photonics*, *5*, 234.

[7] Mata, Fleischman, A. J., & Roy, S. (2005). Characterization of polydimethylsiloxane (PDMS) properties for biomedical micro/nanosystems. *Biomed. Microdev.*, *7*(4), 281.

[8] Kreibig, U., & Vollmer, M. (1995). *Optical Properties of Metal Clusters*. Springer: Berlin, New York.

[9] Kinnan, Mark K., & Chumanov, George. (2010). Plasmon coupling in two-dimensional array of silver nanoparticles: II effect of the particle size and interparticle distance. *J. Phys. Chem. C*, *114*, 7496.

[10] Zhao, L. L., Kelly, K. L., & Schatz, G. C. (2003). The extinction spectra of silver nanoparticle arrays: Influence of array Structure on plasmon resonance wavelength and width. *J. Phys. Chem. B*, *107*, 7343.

[11] Atwater, H. A., & Polman, A. (2010). Plasmonics for improved photovoltaic devices. *Nature Materials*, *9*, 205.