

Nanoscale investigation of two-photon polymerized microstructures with tip-enhanced Raman spectroscopy

Kazantseva A.V., Chernykh E.A., Crook C., Garcia E.P., Fishman D.A., Potma E.O., Valdevit L., Kharintsev S.S., Baldacchini T.

Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

We demonstrate the use of tip-enhanced Raman spectroscopy (TERS) on polymeric microstructures fabricated by two-photon polymerization direct laser writing (TPP-DLW). Compared to the signal intensity obtained in confocal Raman microscopy, a linear enhancement of almost two times is measured when using TERS. Because the probing volume is much smaller in TERS than in confocal Raman microscopy, the effective signal enhancement is estimated to be ca. 104. We obtain chemical maps of TPP microstructures using TERS with relatively short acquisition times and with high spatial resolution as defined by the metallic tip apex radius of curvature. We take advantage of this high resolution to study the homogeneity of the polymer network in TPP microstructures printed in an acrylic-based resin. We find that the polymer degree of conversion varies by about 30% within a distance of only 100 nm. The combination of high resolution topographical and chemical data delivered by TERS provides an effective analytical tool for studying TPP-DLW materials in a non-destructive way.

<http://dx.doi.org/10.1088/2515-7647/abdcb>

Keywords

3D nano-printing, Near-field enhancement, Raman spectroscopy, Two-photon polymerization

References

- [1] Maruo S, Nakamura O and Kawata S 1997 Three-dimensional microfabrication with two-photon-absorbed photopolymerization *Opt. Lett.* 22 132
- [2] Baldacchini T (ed) 2016 *Three-Dimensional Microfabrication Using Two-Photon Polymerization: Fundamentals, Technology, and Applications* (Oxford: William Andrew)
- [3] Stampfl J, Liska R and Ovsianikov A (ed) 2016 *Multiphoton Lithography: Techniques, Materials, and Applications* (Weinheim: Wiley-VCH)
- [4] Spiegel C S, Hippler M, Munchinger A, Bastmeywe M, Barner-Kowollik C, Wegener M and Blasco E 2020 4D printing at the microscale *Adv. Funct. Mater.* 30 1907615
- [5] Maruo S and Fourkas J T 2008 Recent progress in multiphoton microfabrication *Laser Photonics Rev.* 2 110
- [6] Malinauskas M, Farsari M, Piskarskas A and Juodkazis S 2013 Ultrafast laser nanostructuring of photopolymers: a decade of advances *Phys. Rep.* 533 1
- [7] Fischer J and Wegener M 2013 Three-dimensional optical laser lithography beyond the diffraction limit *Laser Photonics Rev.* 7 22
- [8] Juodkazis S, Mizeikis V, Seet K K, Miwa M and Misawa H 2005 Two-photon lithography of nanorods in Su-8 photoresist *Nanotechnology* 16 846

- [9] Fischer J and Wegener M 2011 Three-dimensional direct laser writing inspired by stimulated-emission-depletion microscopy *Opt. Mater. Express* 1 614
- [10] Li L, Gattass R R, Gershgoren E and Fourkas J T 2009 Achieving $\lambda/20$ resolution by one-color initiation and deactivation of polymerization *Science* 324 910
- [11] Fischer J, von Freymann G and Wegener M 2010 The materials challenge in diffraction-unlimited direct-laser-writing optical lithography *Adv. Mater.* 22 3578
- [12] Wollhofen R, Katzmann J, Hrelescu C, Jacak J and Klar T A 2013 120 nm resolution and 55 nm structure size in STED-lithography *Opt. Express* 21 10831
- [13] Gan Z, Cao Y, Evans R A and Gu M 2013 Three-dimensional deep sub-diffraction optical beam lithography with 9 nm feature size *Nat. Commun.* 4 1
- [14] Sakellari I, Kabouraki E, Gray D, Purlys V, Fotakis C, Pikulin A, Bityurin N, Vamvakaki M and Farsari M 2011 Diffusion-assisted high-resolution direct femtosecond laser writing *ACS Nano* 6 2302
- [15] Sharma R, Singh M and Sharma R 2020 Recent advances in STED and RESOLFT super-resolution imaging techniques *Spectrochim. Acta A* 231 117715
- [16] Jiang L J, Zhou Y S, Xiong W, Gao Y, Huang X, Jiang L, Baldacchini T, Silvain J-F and Lu Y F 2014 Two-photon polymerization: investigation of chemical and mechanical properties of resins using Raman microspectroscopy *Opt. Lett.* 39 3034
- [17] Pettinger B, Schambach P, Villagomez C J and Scott N 2012 Tip-enhanced Raman spectroscopy: near fields acting on a few molecules *Annu. Rev. Phys. Chem.* 63 379
- [18] Verma P 2017 Tip-enhanced Raman spectroscopy: technique and recent advances *Chem. Rev.* 117 6447
- [19] Kumar N, Mignuzzi S, Su W and Roy D, 2015 Tip-enhanced Raman spectroscopy: principles and applications *EPJ Tech. Instrum.* 2 9
- [20] Taguchi A, Yu J, Verma P and Kawata S 2015 Optical antennas multiple plasmonic nanoparticles for tip-enhanced Raman microscopy *Nanoscale* 7 17424
- [21] Yano T, Ichimura T, Kuwahara S, H'dhili F, Uetsuki K, Okuno Y, Verma P and Kawata S 2013 Tip-enhanced nano-Raman analytical imaging of locally induced strain distribution in carbon nanotubes *Nat. Commun.* 4 2592
- [22] Kumar N, Stephanidis B, Zenobi R, Wain A J and Roy D 2015 Nanoscale mapping of catalytic activity using tip-enhanced Raman spectroscopy *Nanoscale* 7 7133
- [23] Krebs F C and Norman K 2007 Analysis of the failure mechanism for a stable organic photovoltaic during 10000 h of testing *Prog. Photovolt., Res. Appl.* 15 697
- [24] Lee N, Hartschuh R D, Mehtani D, Kisliuk A, Maguire J, Green M, Foster M D and Sokolov A P 2007 High contrast scanning nano-Raman spectroscopy of silicon *J. Raman Spectrosc.* 38 789
- [25] Neugebauer U, Rosch P, Schmitt M, Popp J, Julien C, Rasmussen A, Budich C and Deckert V 2006 On the way to nanometer-sized information of the bacterial surface by tip-enhanced Raman spectroscopy *Chem. Phys. Chem.* 7 1428
- [26] Cialla D, Deckert-Gaudug T, Buddich C, Laue M, Moller R, Naumann D, Deckert V and Popp J 2009 Raman to the limit: tip enhanced Raman spectroscopy investigations of a single tobacco mosaic virus *J. Raman Spectrosc.* 40 240
- [27] Wood B R, Bailo E, Khiavi M A, Tilley L, Deed S, Deckert-Gaudug T, McNaughton D and Tip-enhanced D V 2011 Raman scattering from hemozoin crystals within a sectioned erythrocyte *Nano Lett.* 11 1868
- [28] Bailo E and Deckert V 2008 Tip-enhanced Raman spectroscopy of single RNA strands: towards a novel direct-sequencing method *Angew. Chem., Int. Ed.* 47 1658
- [29] Boon-Siang Y, Amstad E, Schmid T, Stadler J and Zenobi R 2009 Nanoscale probing of a polymer-blend thin film with tip-enhanced Raman spectroscopy *Small* 5 952
- [30] Xue L, Li W, Hoffmann G G, Goossens J G P, Loos J and de With G 2011 High-resolution chemical identification of polymer blend thin films using tip-enhanced Raman imaging *Macromolecules* 44 2852
- [31] Ober C K 2020 Materials systems for 2-photon lithography *Three-Dimensional Microfabrication Using Two-Photon Polymerization* 2nd edn, ed T Baldacchini (Oxford: William Andrew) pp 143-74
- [32] Kharintsev S S, Rogov A M and Kazarian S G 2013 Nanopatterning an tuning of optical taper antenna apex for tip-enhanced Raman scattering performance *Rev. Sci. Instrum.* 84 093106
- [33] Kharintsev S, Alekseev A, Valsilchenko V, Kharitonov A and Salakhov M 2015 Electrochemical design of plasmonic nanoantennas for tip-enhanced optical spectroscopy and imaging performance *Opt. Mater. Express* 5 2225
- [34] Kharintsev S S, Noskov A I, Hoffman G G and Loos J 2011 Near-field optical taper antennas fabricated with a highly replicable ac electrochemical etching method *Nanotechnology* 22 025202
- [35] Kharintsev S S, Hoffmann G G, Dorozhkin P S, de With G and Loos J 2007 Atomic force and shear force-based tip-enhanced Raman spectroscopy and imaging *Nanotechnology* 18 315502

- [36] Baldacchini T, Zimmerley M, Potma E O and Zadoyan R 2009 Characterization of microstructures fabricated by two-photon polymerization using coherent anti-Stokes Raman scattering microscopy *J. Phys. Chem. B* 113 12663
- [37] Bauer J, Izard A G, Zhang Y, Baldacchini T and Valdevit L 2019 Programmable mechanical properties of two-photon polymerized materials: from nanowires to bulk *Adv. Mater. Technol.* 4 1900146
- [38] Žukauskas A, Matulaitiene L, Paipulas D, Niaura G, Malinauskas M and Gadonas R 2015 Tuning the refractive index in 3D direct laser writing lithography: towards GRIN microoptics *Laser Photonics Rev.* 9 706
- [39] Kumar N, Rae A and Roy D 2014 Accurate measurement of enhancement factor in tip-enhanced Raman spectroscopy through elimination of far-field artefacts *Appl. Phys. Lett.* 104 123106
- [40] Ossikovski R, Nguyen Q and Picardi G 2007 Simple model for the polarization effect in tip-enhanced Raman spectroscopy *Phys. Rev. B* 75 045412
- [41] Liu Z et al 2011 Revealing the molecular structure of single-molecule junctions in different conductance states by fishing-mode tip-enhanced Raman spectroscopy *Nat. Commun.* 2 305
- [42] Di Lorenzo F and Seiffert S 2015 Nanostructural heterogeneity in polymer networks and gels *Polym. Chem.* 6 5515
- [43] Aoki H, Tanaka S, Ito S and Yamamoto M 2000 Nanometric inhomogeneity of polymer network investigated by scanning near-field optical microscopy *Macromolecules* 33 9650
- [44] Bauer J, Meza L R, Schaedler T A, Schwaiger R, Zheng X and Valdevit L 2017 Nanolattices: an emerging class of mechanical metamaterials *Adv. Mater.* 29 1701850
- [45] Izard A G, Bauer J, Crook C, Turlo V and Valdevit L 2019 Ultrahigh energy absorption multifunctional spinodal nanoarchitectures *Small* 15 1903834