MXenes for Plasmonic and Metamaterial Devices

Zhuoxian Wang,[1] Krishnakali Chaudhuri,[1] Mohamed Alhabeb,[2] Xiangeng Meng,[1] Shaimaa I Azzam,[1] Alexander Kildishev,[1] Young L. Kim,[3] Vladimir M. Shalaev,[1] Yury Gogotsi,[2] and Alexandra Boltasseva[1]

[1]*School of Electrical and Computer Engineering, and Birck Nanotechnology Center, Purdue University, West Lafayette, IN 47907, USA*
[2]*Department of Materials Science and Engineering, and A. J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, PA 19104, USA*
[3]*Weldon School of Biomedical Engineering, Purdue University, West Lafayette, IN 47907, USA*
Author e-mail address: aeb@purdue.edu

Abstract We explore the applications of MXenes, a new material class of growing interest, in the area of nanophotonics and plasmonics. A broadband plasmonic metamaterial absorber and a random laser device have thus been demonstrated. © 2018 The Author(s)

OCIS codes: (160.3918) Metamaterials; (250.5403) Plasmonics; (140.3460) Lasers

1. Introduction

MXenes are a new family of two-dimensional (2D) nanomaterials formed of transition metal carbides and carbon nitrides that shows high metallic conductivity, surface hydrophilicity and excellent mechanical properties [1-2]. They are derived from layered ternary carbides and nitrides known as MAX ($M_{n+1}AX_n$) phases by selective chemical etching of the 'A' layers and addition of surface functional groups 'T' (=O, -OH or -F), making the final composition of $M_{n+1}X_nT_x$ [3]. MXenes have been explored in a variety of applications [3]; however, investigations of MXenes in the context of nanophotonics and plasmonics have been limited [4-5]. This motivates the current study of MXenes as building blocks for plasmonic and metamaterial devices.

2. Results and discussion

For the purpose of this work, we focus on one of the most well studied MXene, titanium carbide ($Ti_3C_2T_x$). Single to few layer sheets of $Ti_3C_2T_x$ (in a solution dispersed form) were synthesized from the parent MAX phase of Ti_3AlC_2 by selective chemical etching of the Al layer [3]. This dispersion of the sheets is then used to create a continuous film on a desired substrate by using spin coating technique followed by drying in an inert ambient. The spectral dependence of the real and imaginary parts of the dielectric permittivity (ε) was measured for the spin coated $Ti_3C_2T_x$ film, using a variable angle spectroscopic ellipsometry set up. A dielectric to metallic crossover at ~1.07 µm corroborates the existence of surface plasmon polaritons (SPPs) at the MXene interface in the near- and mid- infrared (IR) frequencies (Fig. 1a). A large imaginary part of the relative dielectric permittivity (Im(ε)) is observed for the film which is attributed in parts to the intrinsic absorption and to losses stemming from surface roughness and bulk disorder related scattering of carriers [6].
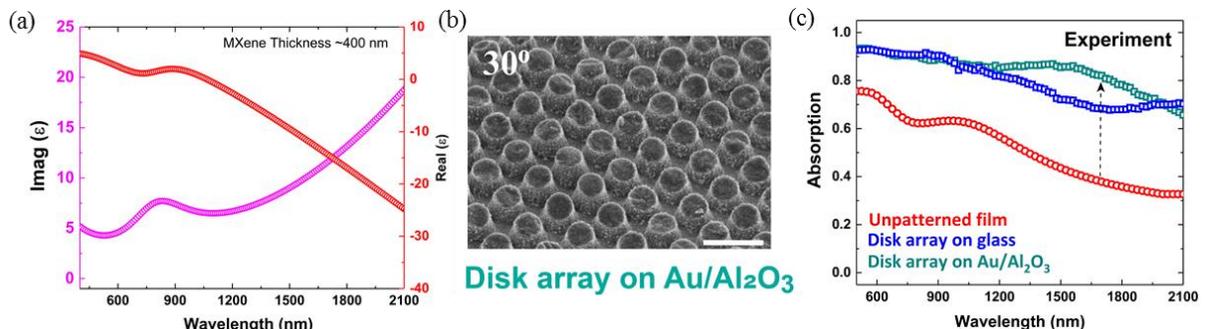

Fig. 1. Broadband plasmonic metamaterial absorber based on $Ti_3C_2T_x$ MXene. (a) The real and imaginary parts of the dielectric permittivity. (b) The scanning electron microscope image of the fabricated disk array on Au/alumina substrate (the scale bar indicates 1 µm). (c) Measured absorption spectra comparison for the two types of disk arrays and unpatterned MXene film (incident light is TE polarized, angle of incidence is 20º).

Losses inherent to the bulk MXene and existence of LSP resonances in nanostructures led us to investigate the potential of nano-patterned MXene as an absorber metamaterial. Using the measured optical data for these spin-coated films, we perform finite element method simulations of $Ti_3C_2T_x$ disks/pillar-like structures showing strong signatures of surface plasmon resonances in the NIR. These resonances are then optimized for the design of the absorber with maximum efficiency in the NIR. Our experiment shows that the simple disk array (Fig.1b) enables ~80% absorption across ~0.5-1.6 µm (Fig 1c). To further increase the performance of this broadband absorber design, we add a thin mirror (Au) and dielectric spacer layer (Al_2O_3) underneath the disk array. This geometrical configuration supports gap surface plasmon resonance which stretches the bandwidth further to ~1.55 µm and with efficiency ~ 85-90%.

We also experimentally explore random lasing behavior in a random metamaterial composed of 2D $Ti_3C_2T_x$ MXene. Conventionally, dielectric and metallic scatterers are employed to initiate optical feedback for random lasers (RLs); however, these RLs usually lack external tunability, reproducibility and control over the spatial pattern of the lasing emission [7]. Recently, it has been shown theoretically that the exotic optical responses of 2D materials could offer new avenues to control RLs due to the extraordinarily low threshold for saturable absorption [8].
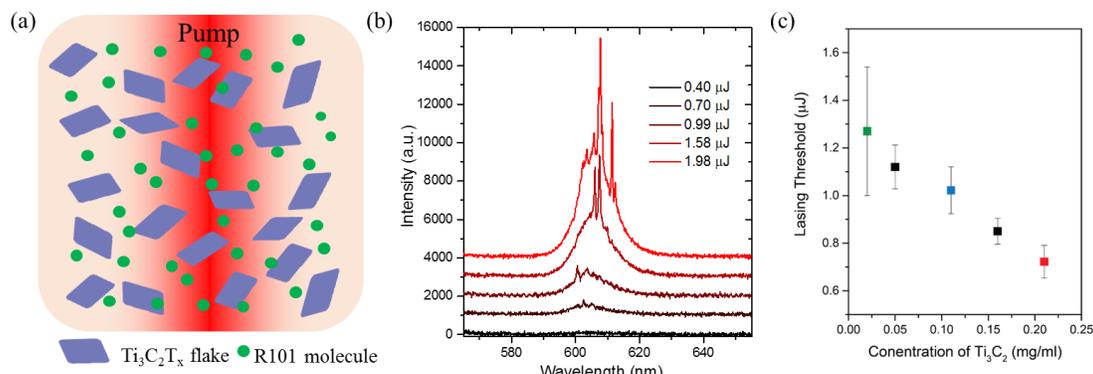

Fig. 2. Random Laser based on $Ti_3C_2T_x$ nanoflakes. (a) Schematic illustration of the RL device, which consists of a mixture of monolayer $Ti_3C_2T_x$ nanoflakes and R101 molecules. (b) Emission spectra recorded under various pump energies. An offset is applied when plotting the spectra. (c) Pump threshold as a function of the concentration of $Ti_3C_2T_x$.

Our random metamaterial device is constructed by randomly dispersing $Ti_3C_2T_x$ nanoflakes into a gain medium (rhodamine 101, R101) as illustrated in Fig. 2a. To study lasing properties, a 532 nm picosecond laser is used to pump the device. Fig. 2b depicts the evolution of the emission spectrum versus the pump energy. Sharp peaks begin to emerge from the broad-band background when the pump energy reaches the threshold value of ~ 0.70 μJ/pulse. When the pump energy is further increased, other sharp peaks subsequently appear. These results are consistent with the behavior of random lasing achieved through coherent feedback [7]. The lasing behavior in this metamaterial can be controlled by changing the density of the $Ti_3C_2T_x$ in solution, as shown in Fig. 1d. With increasing density of $Ti_3C_2T_x$ flakes in the solution, the optical response of the metamaterial is enhanced, thus making it easier to form lasing modes. This leads to a decrease of the pump threshold. This is the first experimental demonstration of random lasing behavior in metamaterials made from 2D materials. The extraordinarily low threshold for saturable absorption of 2D materials suggests that 2D materials have great potential to controlling the feedback and emission properties of lasing which is under investigation currently.

3. Conclusion

A member of the emerging class of two dimensional MXenes and its nanostructures have been explored in the realm of nanophotonics and plasmonics. A broadband plasmonic metamaterial absorber and a random laser device have thus been demonstrated. As the material class and its synthesis techniques continue to mature, applicability in optics along with device performances are also expected to improve further.

4. Acknowledgement

5. References

[1] M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M. W. Barsoum, Two-Dimensional Nanocrystals Produced by Exfoliation of Ti_3AlC_2, Adv. Mater. **23**, 4248-4253 (2011).
[2] M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall'Agnese, P. Rozier, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum, Y. Gogotsi, Cation Intercalation and High Volumetric Capacitance of Two-Dimensional Titanium Carbide, Science **341**, 1502-1505 (2013)
[3] B. Anasori, M. R. Lukatskaya, Y. Gogotsi, 2D metal carbides and nitrides (MXenes) for energy storage, Nat. Rev. Mater. **2**, 16098 (2017).
[4] Y. I. Jhon, J. Koo, B. Anasori, M. Seo, J. H. Lee, Y. Gogotsi, Y. M. Jhon, Metallic MXene Saturable Absorber for Femtosecond Mode-Locked Lasers, Adv. Mater. **29**, 1702496 (2017)
[5] X. Jiang, S. Liu, W. Liang, S. Luo, Z. He, Y. Ge, H. Wang, R. Cao, F. Zhang, Q. Wen, J. Liu, Q. Bao, D. Fan, H. Zhang, Broadband Nonlinear Photonics in Few-Layer MXene $Ti_3C_2T_x$ (T = F, O, or OH), Laser Photonics Rev., 1700229 (2017).
[6] H. Lashgari, M. R. Abolhassani, A. Boochani, S. M. Elahi, J. Khodadadi, Electronic and Optical Properties of 2D Graphene-like Compounds Titanium Carbides and Nitrides: DFT Calculations, Solid State Commun. **195**, 61-69 (2014).
[7] D. S. Wiersma, The physics and applications of random lasers, Nature Phys. **4**, 359-367 (2008).
[8] A. Marini and F. J. Garcia de Abajo, Graphene-Based Active Random Metamaterials for Cavity-Free Lasing, Phys. Rev. Lett. **116**, 217401 (2012).