Carbyne Based Metasurfaces Stabilized with Metallic Nanoparticles

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Abstract

Carbyne is a linear carbon polymer. In a carbyne molecule, the carbon atoms are joined in chains by either triple or single bonds such as in polyene structure, or by constant double bonds such as in polycoumoulene structure. Here, we develop a metasurface deposition procedure in which we align carbyne structures on a surface. Our novel metasurface based on linear carbon chains is expected to provide a solid platform for chip-scale devices.

1. Introduction

Linear carbon chains are inherently unstable. One-dimensional carbon-based structures cannot maintain their state of matter. Therefore, to keep the chains stable during the deposition process, we applied an external electric field within the deposition area, which prevented the structures from curling up. This method allowed us to successfully deposit the carbyne on the substrate while maintaining the linearity of the chains.

2. Synthesis of carbyne in the liquid

A colloidal solution was obtained by laser-ablating the target immersed in a liquid. Shungite was used as the basis for the solution. For irradiation of the colloidal systems, a Ytterbium (Yb) fiber laser was used with a central frequency of 1.06 μm, pulse duration of 100 ns, repetition rate of 20 KHz and pulse energy up to 1 mJ. The laser radiation was focused into the volume of the colloid with a spot diameter of 50 μm, the scan rate varied from 1 to 10 mm/s. The irradiation time varied from 5 to 15 minutes. During the laser exposure, we observed the colloidal systems clearing up and lighten as shown in Figure 1. Characterization by a laser particle size analyzer (Horiba LB-550) shows the particle diameter variation with the exposure time. We found that the particle size distribution becomes bimodal with time. This indicates that particle aggregation occurs in addition to the particle fragmentation. However, the average particle diameter in a colloidal system decreases with increasing the exposure time. In general, this behavior of colloidal systems is consistent with typical mechanisms of laser fragmentation of liquid systems [1, 2].

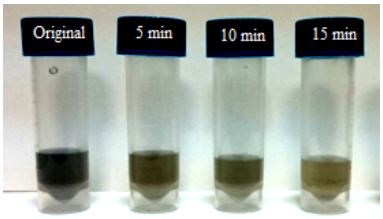

Figure 1: Colloidal systems before and after the laser exposure. Left to right: the original system, after irradiation for: 5, 10 and 15 minutes, respectively.

To obtain the carbyne-based structures, we first prepared a gold-based colloidal solution that was mixed with the carbon-based colloidal solution. The second step was to irradiate the mixture for 15 minutes.

We analyzed the colloidal solution using Raman spectroscopy as shown in Figure 2. The carbyne structure is most clearly isolated in the spectral range of 4690-5200 nm [3, 4]. The valence vibrations of the triple carbon bonds ($C \equiv C$) corresponding to the polyinic carbyne structure are reflected by bands in the range of 4750-5250 nm [5, 6]. In accordance with ref. [7], the band of nm corresponds to the vibrational modes of ideal poly-linear chains, hence the shift of this peak to the short-wave region is explained by the change in the length of the chain.

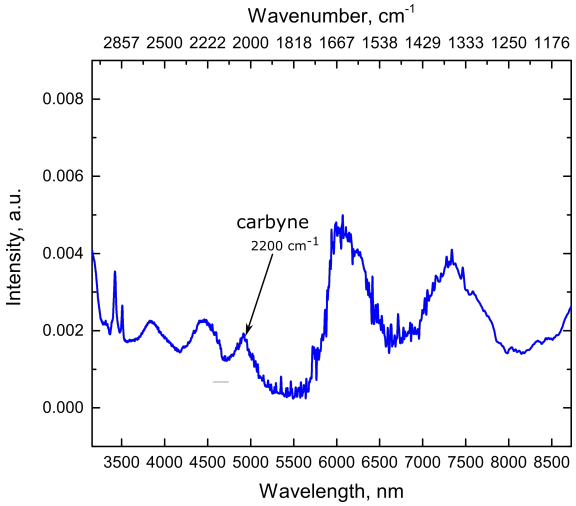

Figure 2: Raman spectrum of carbyne.

3. Surface deposition of carbon chains

To implement the deposition of linear carbon chains, we have constructed a special experimental apparatus shown in Figure 3. A lithium 9V battery was used as the source of electric field formation. The copper mesh was placed on a negatively charged anode. Then, using a micropipette, we placed a droplet of carbyne solution on its surface. This scheme with the use of an external field allows us to stabilize linear carbon chains on the surface. This is due to the fact that gold particles have a negative charge and interact with each other, stretching the chains of the carbyne and not allowing them to twist. A positively charged cathode attracts gold particles. The combination of electrical and gravitational forces cause the gold particles to pass through the copper mesh and precipitate on it.

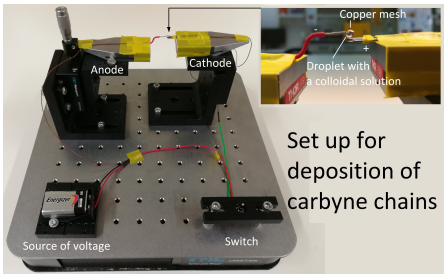

Figure 3: Experimental apparatus for deposition of carbyne chains.

4. Periodic structure formation

When exploring the sample with a transmission electron microscope (TEM Themis), we obtained the structure shown in Figure 4. These structures completely coincide with the results obtained in ref. [4].

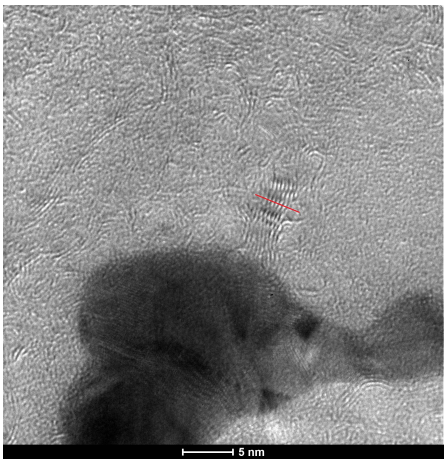

Figure 4: TEM image of the structure. The red line emphasizes the periodic carbyne chains.

Figure 5 shows histogram of the distance between the ordered carbon linear structures. The distances between the peaks of the histogram are almost identical, indicating the periodicity of the structure.

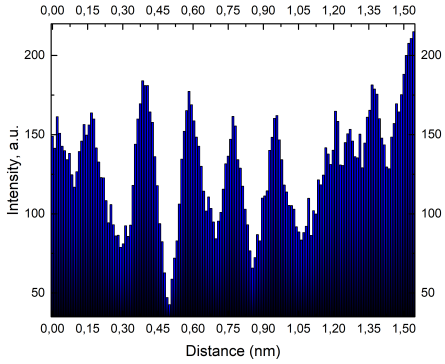

Figure 5: Histogram showing an equal distance between the linear carbon chains.

5. Conclusion

To conclude, we presented a deposition method of linear carbyne structures on a surface. Our deposition procedure is based on applying an external electric field on negatively charged free carbyne chains in a liquid for stabilization. This method is relatively simple and effective, yet the results allow us to form metasurfaces with special optical properties.

References

[1] N. A. Kirichenko, M. E. Shcherbina, A. A. Serkov, and I. I. Rakov, "Transport equation in the problem of the distribution function of nanoparticles in a colloidal solution exposed to laser pulses," *Quantum Electronics*, vol. 45, no. 12, p. 1161, 2015.

[2] K. Maximova, A. Aristov, M. Sentis, and A. V. Kabashin, "Size-controllable synthesis of bare gold nanoparticles by femtosecond laser fragmentation in water," *Nanotechnology*, vol. 26, no. 6, p. 065601, 2015.

[3] D. Y. Parashuk and V. M. Kobryansky, "Synchronous electron-nuclear oscillations in a π-conjugate chain of nano-polyacetylene," *Letters to the Journal of Experimental and Theoretical Physics*, vol. 73, no. 3, pp. 170–174, 2001, published in Russian.

[4] L. Shi, P. Rohringer, K. Suenaga, Y. Niimi, J. Kotakoski, J. C. Meyer, H. Peterlik, M. Wanko, S. Cahangirov, A. Rubio *et al.*, "Confined linear carbon chains as a route to bulk carbyne," *Nature materials*, vol. 15, no. 6, p. 634, 2016.

[5] F. Cataldo, *Polyynes: synthesis, properties, and applications*. CRC Press, 2005.

[6] M. Kijima, I. Kinoshita, and H. Shirakawa, "Spectroscopic study of soluble poly (2, 5-dialkoxy-1, 4-phenylene-alt-oligoethynylene) s$\star$," *Journal of Molecular Structure*, vol. 521, no. 1-3, pp. 279–283, 2000.

[7] K. Akagi, M. Nishiguchi, H. Shirakawa, Y. Furukawa, and I. Harada, "One-dimensional conjugated carbyne-synthesis and properties," *Synthetic Metals*, vol. 17, no. 1-3, pp. 557–562, 1987.