Photosensitive free-standing ultra-thin carbyne–gold films

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Abstract
In the article we introduce the experiment of the photostimulation effect in the tunneling conductivity of free-standing thin carbyne-gold films. We observe a sharp increase of the conductivity of hybrid film due to the electromagnetic exciting at the frequencies which are close to the plasmon resonance of gold nanoparticles. The use of carbyne threads as a stabilizing matrix makes it possible to obtain free-standing thin films that demonstrate a good structural stability. The tunnel current–voltage measurements demonstrate a strong dependence of the current value on the intensity of green laser radiation used to photostimulate thin C–Au in area of the measuring experiment.

Keywords Thin films · Gold nanoparticle · Carbyne · Photocurrent

1 Introduction

The formation of ultrathin films containing metal nanoparticles is a promising task for applications in optoelectronics and photonics. Using such films one can significantly simplify the production of a wide class of optoelectronic devices which are based on transparent conducting metamaterials with flexible optical properties. Various methods of formation of such films based on the self-assembly of polymers, nanoparticles and molecules interacting at the air–water interface (Mueggenburg et al. 2007; He et al. 2010, 2011) or the liquid–liquid interface (Duan et al. 2004; Wang et al. 2006; Xia and Wang 2008) as well as modified
Langmuir–Blodgett methods (Zasadzinski et al. 1994; Guo et al. 2003) and other methods have been developed recently.

The sacrificial layer method is one that is used most widely. In this method, the formation of individual nanostructures occurs during the removal of the sacrificial layer situated below it (Jin et al. 2007; Wu et al. 2004; Xu et al. 2008). The sacrificial layer method is very suitable for fabrication of free-standing nanoparticles, fluorescent quantum dots, nanocomposites. (Jiang et al. 2004a, b, 2006) However, it is not the universal one. One of its valuable alternatives is the film self-assembly method that allows to obtain a great variety of structures characterized by a reliable level of stability. In order to solve the stability problem for island like structures, one can combine colloidal nanoparticles with polymers in order to produce tailored hybrid materials (Vaia and Maguire 2007; Ofir et al. 2008; Kodiyan et al. 2012). This approach not only allows to increase the stability of colloidal particles, but also improved the functional characteristics of meta- and nano-materials for applications in sensors (Zamborini et al. 2002; Nam et al. 2004), microelectronics (Wei et al. 2012), and catalysis (Huh and Kim 2010).

Nowadays, organic matrixes are extensively popular, for instance, the widespread materials such as the cellulose that contains a natural polysaccharide have been proposed for various applications in electronics (Fortunato et al. 2008). In addition, the usage of a carbon matrix for stabilization of metal nanoparticles and preventing their degradation in an environment appears to be an interesting and promising direction for the development of hybrid films with tailored optical properties (Bashouti et al. 2015). Here we shall focus specifically metal–carbon materials based on carbyne (Sladkov 1989). Carbyne is the fourth carbon allotrope that is composed by monoatomic linear chains of carbon. Carbyne is suitable for encapsulating the nanoobjects of an arbitrary shape and size, in particular, spherical nanoparticles of different metals. The distance between the atoms in a carbyne chain is of 0.133 nm for a single electron bond and 0.124 nm for a triple bond. Both these distances are less than the interatomic distance in graphite (0.142 nm). This is why, according to the theoretical estimates the robustness of carbyne based materials can be higher than one of graphene (Liu et al. 2013). Interestingly, carbyne crystals are predicted to be direct bandgap semiconductors featuring the gaps of 0.4–1.2 eV width depending on the electronic bond structure and the distortion level (Heimann et al. 2011).

Here we report on the experimental study of the photostimulation effect in the tunneling conductivity of free-standing thin C–Au films. Namely, we observe a sharp increase of the conductivity of this hybrid film when optically exciting the system at the frequencies close to the plasmon resonance in gold nanoparticles. We study thin films formed by spraying under atmospheric pressure of a colloidal system containing gold nanoparticles and carbon polymers based on linear carbon chains-carbynes, synthesized according to the work (Kucherik et al. 2016). We deposited the solid constituent on an optically polished substrate for the morphology studies and on a special conductive grid for the transmission electron microscopy (TEM) studies. To measure the current–voltage characteristics as well as to examine the photosensitivity of our samples we used a scanning tunneling microscopy (STM). The characteristic features of tunneling current are nicely reproduced by our theoretical model that predicts the variation of the carrier mobility under the light action.
2 The fabrication technic for free-standing C–Au films

The colloidal system containing metal nanoparticles and linear carbon chains-(carbyne) was prepared following the method described in (Kucherik et al. 2016). The average diameter of gold nanoparticles was about 10 nm. To form a free-standing film we sputtered the colloidal solution through a nozzle of 0.3 mm diameter on a substrate placed within the distance of 10 mm. We used a single shot spray regime to prepare a sufficiently thin film in order to be able to reveal its landscape by TEM. In contrast, the multishot spray regime was used to prepare the films suitable for the studies of conductivity. The overlap area covered by the sputtering process was up to 5 cm.

As shown in Kutrovskaya et al. (2017), in the course of the sputtering process, a set of separately located droplets incorporating C–Au complexes is being formed on a substrate. These areas became growth points of islands of metal nanoparticles connected to each other by carbyne filaments that attach themselves to the substrate in the process of evaporation. We used Ntegra Aura and Ntegra Spectra devices made by NT-MDT working as the atomic-force microscopy (AFM) as well the STM regime, the Raman spectroscopy using the Senterra spectrometer, made by Bruker and the transmission electron technique by FEI Titan³ for a comprehensive investigation of the deposited films.

The Fig. 1 shows the experimental results obtained on the deposited gold-carbyne films. The AFM image allows to distinguish metal nanoparticles distributed within the stable inhomogeneous film. One can clearly see that the film is composed by several fractions. However, we detect no significant height variations (see the z-scale in Fig. 1a). The Raman

![Fig. 1](https://example.com/fig1.png)

Fig. 1 The deposited free-standing C–Au films. a The AFM-image measured in the contact mode in vacuum by the Ntegra Aura device. b The Raman spectra of a deposited layer. c The characteristic high resolution TEM images of the studied film deposited on a copper grid. The film was formed by stretching inside the grid mesh. d, e TEM-images taken with different magnifications that clearly show a fractal type of the obtained C–Au film. f The high resolution TEM image that clearly shows carbyne based bridges connecting the neighboring gold nanoparticles.
The analysis shows that the formed carbon filaments are predominantly related to the polyynes allotrope of carbyne characterized by alternating single and triple electronic bonds. Indeed, the intense peaks at the wavelengths 2150 cm\(^{-1}\) and 1050 cm\(^{-1}\) correspond to triple and single electron bonds linking carbon atoms, respectively (see Fig. 1b). The broadening of the peak corresponding to the C–C bond at 600 sm\(^{-1}\) is a result of deformation of the chains after deposition as well as of the Peierls distortion. The presence of hp2-hybridization carbon allotrope is undoubtedly visible in the spectral vicinities of 1400 and 1650 sm\(^{-1}\). These spectral features are characteristic of randomly oriented carbon threads.

For a detailed morphological analysis, we have performed the high resolution transmission electron microscopy (HR TEM) studies with a spatial resolution of up to 2 Å. The set of characteristic magnified images shown in Fig. 1c–f demonstrates the formation of free-standing thin films containing separate gold islands. Each island is formed by individual gold nanoparticles, while no uniform gold film is formed. The average diameter of the observed gold islands is about 30 nm and the distance between them is 5 nm (see Fig. 1e). Carbon filaments form a random array connecting metal islands (see Fig. 1f).

### 3 Tunneling conductivity measurements

To study the electrophysical properties of the deposited films we employed a set-up based on the Ntegra Aura device operating in the tunneling mode in vacuum. Figure 2 schematically illustrates the experimental set-up we used. Firstly, we reconstruct the landscape of the film in order to be able to put the probe directly on the surface of the carbon matrix between metallic islands, as shown in the inset of Fig. 2a. The measured current–voltage curves are shown in Fig. 2b.

The blue and red curves in Fig. 2b correspond to the voltage-current dependences of the thin deposited film placed on a pure aluminum substrate. These are to be compared with black curve containing only the data for a pure substrate. The thickness of film was enough to neglect the substrate contribution into the collecting data of the tunneling current. It demonstrates a nearly linear behavior in the selected voltage range from −1 to 1 V. The presence of a nonzero current at zero voltage can be ascribed to the formation of an electron cloud near the metal surface. The I/V curve for a thin hybrid C–Au film looks similar to the black curve. It is also essentially linear. However, the value of the locking voltage is increased up to 0.27 V (see Fig. 2c) in the latter case as compared to the former case. We detect a significant increase of the tunneling current in the case of the laser illumination of the tunneling probe area.

As a consequence, the I/V curve does not deviate from the linear behavior even in the small voltage region (see the blue curve in Fig. 2b). The observed current amplification may be caused by the increase of the free charge carrier concentration due to the resonant absorption of the laser radiation of the 532 nm wavelength by gold nanoparticles.

The tunneling current spectroscopy results (see Fig. 3) confirm this assumption. The increase of the distance between the STM probe and the thin film surface in the absence of laser irradiation results in a typical exponential decay of the tunneling current (see the black curve in the Fig. 3). In contrast, the laser action leads to the appearance of steps in the current reduction curve that becomes nonmonotonous.

This can be interpreted as a manifestation of two effects: first, the decrease of the electron work function in gold nanoparticles due to the absorption of light (Wood 1981), second, the discontinuous topological structure of the studied hybrid films. The conductivity
Fig. 2  The tunneling current as a function of the voltage applied to the deposited free-standing C–Au films: a schematically illustrates the layout of the main elements of the STM set-up. b The current–voltage curves measured at various samples: the black line corresponds to the I/U curve of a pure aluminum substrate, the red curve corresponds to the C–Au thin film and the blue curve shows the I/U dependence of the C–Au thin film subjected to the excitation at the wavelength of 532 nm. c The inset presents the behavior of the tunneling at a low applied voltage level. (Color figure online)

Fig. 3  a The positive branch of the experimentally measured current–voltage curve shown in Fig. 2b compared to the predictions of the model marked by black points. b The dependence of the tunneling current on the distance between the STM probe and the thin film surface: the red curve is measured under laser stimulation, the black curve is measured with the laser switched off. The results of the theoretical calculation are shown by black points. (Color figure online)
in disordered metal–semiconductor structures is governed by the interplay between hopping and tunneling of electrons (Kavokin et al. 2017). Abrupt features in the current dependence on the distance between STM probe and the surface may be attributed to the thresholds between tunneling and hoping mechanisms of conductivity. Indeed, the electric current rapidly decreases at the distances of over than 2 nm that is in good agreement with the anticipated collapse of the tunneling conductivity at the distances of 2–3 nm between islands (depending on the shape of the islands).

4 Analytical model describing the current–voltage dependence of the tunnel current

To describe the STM data, we have used the low voltage \( U \) model which takes into account only the electron tunneling between the conducting probe and the sample surface directly under the probe. The width of the tunnel junction is given by the distance between the probe and the sample surface. This way, the bias current \( I \) can be described as (Fishelson et al. 2001):

\[
I(U) = A \ast U \ast e^{-k \ast d},
\]

where \( k = \frac{4\pi\sqrt{2m\varphi}}{\hbar} \) is the damping constant of the wave function in the potential barrier region, \( m = 9.1 \ast 10^{-31} \) kg is the electron, \( \varphi = 6.5689 \ast 10^{-19} \) J is the electron work function for gold, \( \hbar = 6.6 \ast 10^{-34} \) J/s is the Planck constant, \( d \) is the probe—sample surface distance, \( A = 10^{-9} \) m is the scaling factor.

Ones the voltage increases and raises over 1 V, the tunneling current starts exhibiting a nonlinear growth as a function of the voltage (see Fig. 2) (Fishelson et al. 2001). The conductivity changes under the effect of light excitation of the deposited layer are likely to be caused by the change in the effective mobility of the carriers (Valverde-Aguilar et al. 2011). To account for this effect, we include the stationary photocurrent that emerges under the effect of laser irradiation into the model:

\[
I = qG\Phi,
\]

where \( q \) is an electron charge, \( G \) is the photoelectric gain, \( \Phi \) is the luminous flux density (Chen et al. 2011).

In its turn, the photoelectric gain can be defined as

\[
G = \frac{\tau \mu U}{L^2},
\]

where \( \tau \) is the lifetime of photocarriers, \( \mu \) is their mobility, \( U \) is the voltage applied to the sample, \( L \) is the distance between electrodes, for our case it is equal to the distance between the sample and the STM probe (Tanabe 2016).

According to this approach, the current–voltage curve was calculated for the low voltage range (from 0 to 1 V) using the following parameters \( \tau = 10^{-6} \) s, \( L = 0.1 \) nm, \( f = 10^3 \) W/sm\(^2\), \( \mu = 0.41 \ast 10^{-8} \) s. The calculation results are in a good agreement with the experimental data as Fig. 3 shows. One can clearly see that in the absence of the optical stimulation the current–voltage curve demonstrates the linear behavior at the low voltage region (see Fig. 3a). To reproduce the nonlinear dependence of the photocurrent, we have assumed the quadratic dependence of the carrier mobility on the light intensity that is typical for semiconductor crystals. Generally, the calculation results are in a good qualitative agreement.
with the experimental data. The present model can be applied to assess the electrical properties of the hybrid thin films containing metallic islands. The model calculation of the tunneling current shown in Fig. 3b correctly reproduces the decrease of the tunneling current with the increase of the distance between the STM probe and the surface. We note that the proposed approach only accounts for the carrier mobility directly in the measurement area of the tunneling current. The model neglects the electron hopping between metal islands (Kavokin et al. 2017), that leads to the supplementary variation of the carrier concentration. This effect will be a subject to our next studies.

5 Conclusions

We have studied morphological and electrophysical properties of hybrid C–Au thin films. The use of carbyne threads as a stabilizing matrix makes it possible to obtain free-standing thin films that demonstrate a good structural stability. The effect of green laser light illumination on tunnel current–voltage measurements in the thin films has been shown. The observed phenomena are described within the theoretical model that ascribes the variations of the tunneling current to the variation of the carrier mobility. Clearly, the introduction of metal nanoparticles characterized by a variety of plasmon frequencies enables one to strongly improve the tunneling current for applications in nanoelectronic and photonic devices.

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References

Bashouti, M.Y., Manshina, A., Povolotckaia, A., Povolotskiy, A., Kireev, A., Petrov, Y., Mačković, M., Spiecker, E., Koshevoy, I., Tunik, S., Christiansen, S.: Direct laser writing of μ-chips based on hybrid C–Au–Ag nanoparticles for express analysis of hazardous and biological substances. Lab Chip 15, 1742–1747 (2015). https://doi.org/10.1039/c4lc01376j
Chen, C., Wu, F., Geng, H., Shen, W., Wang, M.: Analytical model for the photocurrent-voltage characteristics of bilayer MEH-PPV/TiO2 photovoltaic devices. Analytical model for the photocurrent-voltage characteristics of bilayer MEH-PPV/TiO2 photovoltaic devices. Nanoscale Res. Lett. 6, 350 (2011). https://doi.org/10.1186/1556-276X-6-350
Duan, H., Wang, D., Kurth, D.G., Möhwald, H.: Directing self assembly of nanoparticles at water/oil interfaces. Angew. Chem. Int. Ed. 43, 5639–5642 (2004). https://doi.org/10.1002/anie.200460920
Fishelson, N., Shkrob, I., Lev, O., Gun, J., Modestov, A.D.: Studies on charge transport in self-assembled gold-dithiol films: conductivity, photoconductivity, and photoelectrochemical measurements. Langmuir 17, 403–412 (2001). https://doi.org/10.1021/la000830q
Fortunato, E., Correia, N., Barquinha, P., Pereira, L., Gonçalves, G., Martins, R.: High-performance flexible hybrid field-effect transistors based on cellulose fiber paper. IEEE Electron Device Lett. 29, 988–990 (2008). https://doi.org/10.1109/LED.2008.2001549
Guo, Q., Teng, X., Rahman, S., Yang, H.: Patterned Langmuir-blodgett films of monodisperse nanoparticles of iron oxide using soft lithography. J. Am. Chem. Soc. 125, 630–631 (2003). https://doi.org/10.1021/ja0275764
He, J., Kanjanaboos, P., Frazer, N.L., Weis, A., Lin, X.-M., Jaeger, H.M.: Fabrication and mechanical properties of large scale freestanding nanoparticle membranes. Small 6, 1449–1456 (2010). https://doi.org/10.1002/smll.201000114
He, J., Lin, X.-M., Chan, H., Vukovic, L., Jaeger, H.M.: Diffusion and filtration properties of self-assembled gold nanocrystal membranes. Nano Lett. 11, 2430–2435 (2011). https://doi.org/10.1021/nl200841a
Heimann, R.B., Evsyukov, S.E., Kavan, L.: Carbyne and Carbynoid Structures. Physics and Chemistry of Materials with Low-Dimensional Structures. Springer, Dordrecht (2011)

Huh, S., Kim, S.B.: Fabrication of conducting polymer films containing gold nanoparticles with photo-induced patterning. J. Phys. Chem. C 114, 2880–2885 (2010). https://doi.org/10.1021/jp908743y

Jiang, C., Markutysa, S., Pikus, Y., Tsukruk, V.V.: Freely suspended nanocomposite membranes as highly sensitive sensors. Nat. Mater. 3, 721 (2004a). https://doi.org/10.1038/nmat1212

Jiang, C., Markutysa, S., Tsukruk, V.V.: Compliant, robust, and truly nanoscale free standing multilayer films fabricated using spin assisted layer by layer assembly. Adv. Mater. 16, 157–161 (2004b). https://doi.org/10.1002/adma.200306010

Jiang, C., Singamaneni, S., Merrick, E., Tsukruk, V.V.: Complex buckling instability patterns of nanomembranes with encapsulated gold nanoparticle arrays. Nano Lett. 6, 2254–2259 (2006). https://doi.org/10.1021/nl061630n

Jin, J., Wakayama, Y., Peng, X., Ichinose, I.: Surfactant-assisted fabrication of free-standing inorganic sheets covering an array of micrometre-sized holes. Nat. Mater. 6, 686 (2007). https://doi.org/10.1038/nmat1980

Kavokin, A., Kutrovskaya, S., Kucherik, A., Osipov, A., Vartanyan, T., Arakelian, S.: The crossover between tunnel and hopping conductivity in granulated films of noble metals. Superlattice Microst. 111, 335–339 (2017). https://doi.org/10.1016/j.spmi.2017.06.050

Kodiyan, A., Silva, E.A., Kim, J., Aizenberg, M., Mooney, D.J.: Surface modification with alginate-derived polymers for stable, protein-repellent, long-circulating gold nanoparticles. ACS Nano 6, 4796–4805 (2012). https://doi.org/10.1021/nn205073n

Kucherik, A.O., Arakelyan, S.M., Vartanyan, T.A., Kutrovskaya, C.V., Osipov, A.V., Povolotckaia, A.V., Povolotskiy, A.V., Manshina, A.A.: Laser-induced synthesis of metal–carbon materials for implementing surface-enhanced Raman scattering. Opt. Spectrosc. 121, 263–270 (2016). https://doi.org/10.1134/S0030400X16080105

Kutrovskaya, S., Arakelian, S., Kucherik, A., Osipov, A., Evlyukhin, A., Kavokin, A.V.: The synthesis of hybrid goldsilicon nano particles in a liquid. Sci. Rep. 7, 10284 (2017). https://doi.org/10.1038/s41598-017-09634-y

Liu, M., Artyukhov, V.I., Lee, H., Xu, F., Yakobson, B.I.: Carbyne from first principles: chain of C atoms, a nanorod or a nanorope. ACS Nano 7, 10075–10082 (2013). https://doi.org/10.1021/nn404177r

Mueggenburg, K.E., Lin, X.M., Goldsmith, R.H., Jaeger, H.M.: Elastic membranes of close-packed nanoparticle arrays. Nat. Mater. 6, 656 (2007). https://doi.org/10.1038/nmat1965

Nam, J.-M., Stoeva, S.I., Mirkin, C.A.: Bio-bar-code-based DNA detection with PCR-like sensitivity. J. Am. Chem. Soc. 126, 5932–5933 (2004). https://doi.org/10.1021/ja049384+

Ofir, Y., Samanta, B., Rotello, V.M.: Polymer and biopolymer mediated self-assembly of gold nanoparticles. Chem. Soc. Rev. 37, 1814–1825 (2008). https://doi.org/10.1039/b712689c

Sladkov, A.M.: Polusopryajennie Polimeri. Nauka, Moscow (1989)

Tanabe, K.: A simple optical model well explains plasmonic-nanoparticle-enhanced spectral photocurrent in optically thin solar cells. Nanoscale Res. Lett. 11, 236 (2016). https://doi.org/10.1186/s11671-016-1449-y

Vaia, R.A., Maguire, J.F.: Polymer nanocomposites with prescribed morphology: going beyond nanoparticle-filled polymers. Chem. Mater. 19, 2736–2751 (2007). https://doi.org/10.1021/cm062693+

Valverde-Aguilar, G., Garcia-Macedo, J.A., Renteria-Tapia, V., Aguilar-Franco, M.: Photoconductivity studies of gold nanoparticles supported on amorphous and crystalline TiO2 matrix prepared by solution-gel method. Rev. Mex. Fis. 57, 13–18 (2011)

Wang, J., Wang, D., Sobal, N.S., Giersig, M., Jiang, M., Möhwald, H.: Stepwise directing of nanocrystals to self assemble at water/oil interfaces. Angew. Chem. Int. Ed. 45, 7963–7966 (2006). https://doi.org/10.1002/anie.200602395

Wei, Q., Lin, Y., Anderson, E.R., Briseno, A.L., Gido, S.P., Watkins, J.J.: Additive-driven assembly of block copolymer-nanoparticle hybrid materials for solution processable floating gate memory. ACS Nano 6, 1188–1194 (2012). https://doi.org/10.1021/nn203847r

Wood, D.M.: Classical size dependence of the work function of small metallic spheres. Phys. Rev. Lett. 46, 749 (1981). https://doi.org/10.1103/PhysRevLett.46.749

Xia, H., Wang, D.: Fabrication of macroscopic freestanding films of metallic nanoparticle monolayers by interfacial self assembly. Adv. Mater. 20, 4253–4256 (2008). https://doi.org/10.1002/adma.200702978
Xu, Y., Bai, H., Lu, G., Li, C., Si, G.: Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets. J. Am. Chem. Soc. 130, 5856–5857 (2008). https://doi.org/10.1021/ja800745y

Zamborini, F.P., Leopold, M.C., Hicks, J.F., Kulesza, P.J., Malik, M.A., Murray, R.W.: Electron hopping conductivity and vapor sensing properties of flexible network polymer films of metal nanoparticles. J. Am. Chem. Soc. 124, 8958–8964 (2002). https://doi.org/10.1021/ja025965s

Zasadzinski, J.A., Viswanathan, R., Madsen, L., Garnaes, J., Schwartz, D.K.: Langmuir–Blodgett films. Science 263, 1726–1733 (1994). https://doi.org/10.1126/science.8134836

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