Pis'ma v ZhETF, vol. 114, iss. 11, pp. 740 – 741

Enhanced nonlinear photoluminescence of Au-carbon dot nanohybrids produced by photocatalytic reduction of Au(III) ions

A. A. Astafiev[+×1)], *A. M. Shakhov*[+×], *S. A. Minayeva*[*], *V. A. Nadtochenko*[+×]

[+] *N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russia*

[*] *Federal Research Center "Crystallography and Photonics", Russian Academy of Sciences, 119991 Moscow, Russia*

[×] *Chemistry Department, Moscow State University, 119991 Moscow, Russia*

Submitted 24 October 2021
Resubmitted 27 October 2021
Accepted 27 October 2021

DOI: 10.31857/S1234567821230038

Nanosocale luminescent carbonaceous particles or carbon dots (CD) are a promising class of nanomaterials for applications in bioimaging, photocatalysis, light emitting devices and chemical sensing. Combination with gold or silver nanoparticles enhance and modulate optical properties of carbon dots due to effects of localized surface plasmon resonance (LSPR) [1]. Nonlinear optical effects are especially strongly affected by local field enhancement due to LSPR [2] and can be tailored by dimensions, shape and surface density of plasmonic particles bound to the carbon dot.

We describe production of Au-CD nanohybrids by photoreduction of Au(III) ions, where CD operate as both a photoreducing agent and a platform for controlled deposition of Au nanoparticles [1]. Carbon dots produced from acetonitrile by femtosecond laser synthesis [3] were mixed with gold precursor ($HAuCl_4$) in aqueous solution and irradiated with continuous wave light of a blue diode. Upon light absorption CD donated photoexcited electrons to Au(III) ions, which were reduced to Au^0 and assembled into Au nanoparticles decorating CD surface (Fig. 1a). Raman and energy-dispersive X-Ray spectroscopy confirmed that Au particles formed by photoreduction were bound to carbon dots. We produced a series of Au-CD hybrids with a different ratio of gold to CD volume. Analysis of extinction spectra of Au-CDs demonstrates that the mean diameters of Au nanoparticles deposited on CD are within nanometers range and their size and surface density are tuned by the ratio of concentrations of gold precursors and carbon dots.

Uncovered CD exhibited blue photoluminescence when excited by near-ultraviolet light, which was quenched upon photoreduction of gold and formation of Au-CD hybrids due to energy transfer from CD to metal. By contrast, Au-CD hybrids had strongly enhanced nonlinear photoluminescence (NPL) excited by near-infrared femtosecond laser pulses. NPL integral intensity could be two orders of magnitude larger than intensity of NPL of uncovered CD of the same concentration in aqueous solution (Fig. 1b). Integral intensity of Au-CD NPL depended nonlinearly on the volume of photodeposited gold and increased by 150 times with 6-fold increase of the gold volume.

Owing to broadband emission spectrum and very short luminescence lifetime (smaller than 50 ps) NPL of Au-CD hybrids is attributed to photoluminescence of metallic gold nanoparticles. The NPL emission spectrum of Au-CD hybrids broadened and shifted to shorter wavelengths with increase of the excitation laser power (Fig. 1c). The NPL integral intensity was approximated as a power function of the excitation power $I \sim P^{\alpha}$, where the power parameter α was non-integer and varied from 2.2 to 2.45. Similarly, NPL spectral intensity $I(\lambda)$ could be also described as power function of the excitation power $P^{\alpha(\lambda)}$, where the power parameter $\alpha(\lambda)$ monotonically increased with increase of the emitted photon energy. Peculiarities of the Au-CD NPL can be explained by a model of thermal emission of hot electrons in gold [4, 5]. Photons are emitted when electrons, excited by laser pulses above the Fermi level, relax to unoccupied levels in the conduction band. Intraband transitions within the conduction band of gold are promoted by enhanced and strongly localized electrical fields in and near plasmonic nanoparticles.

In conclusion, we demonstrated a method for controlled growth of Au nanoparticles on carbon dots and formation of Au-CD nanohybrids. These nanohybrids emit photoluminescence all over the visible range upon excitation with near-infrared ultrashort laser pulses.

1) e-mail: astafiev.artyom@gmail.com

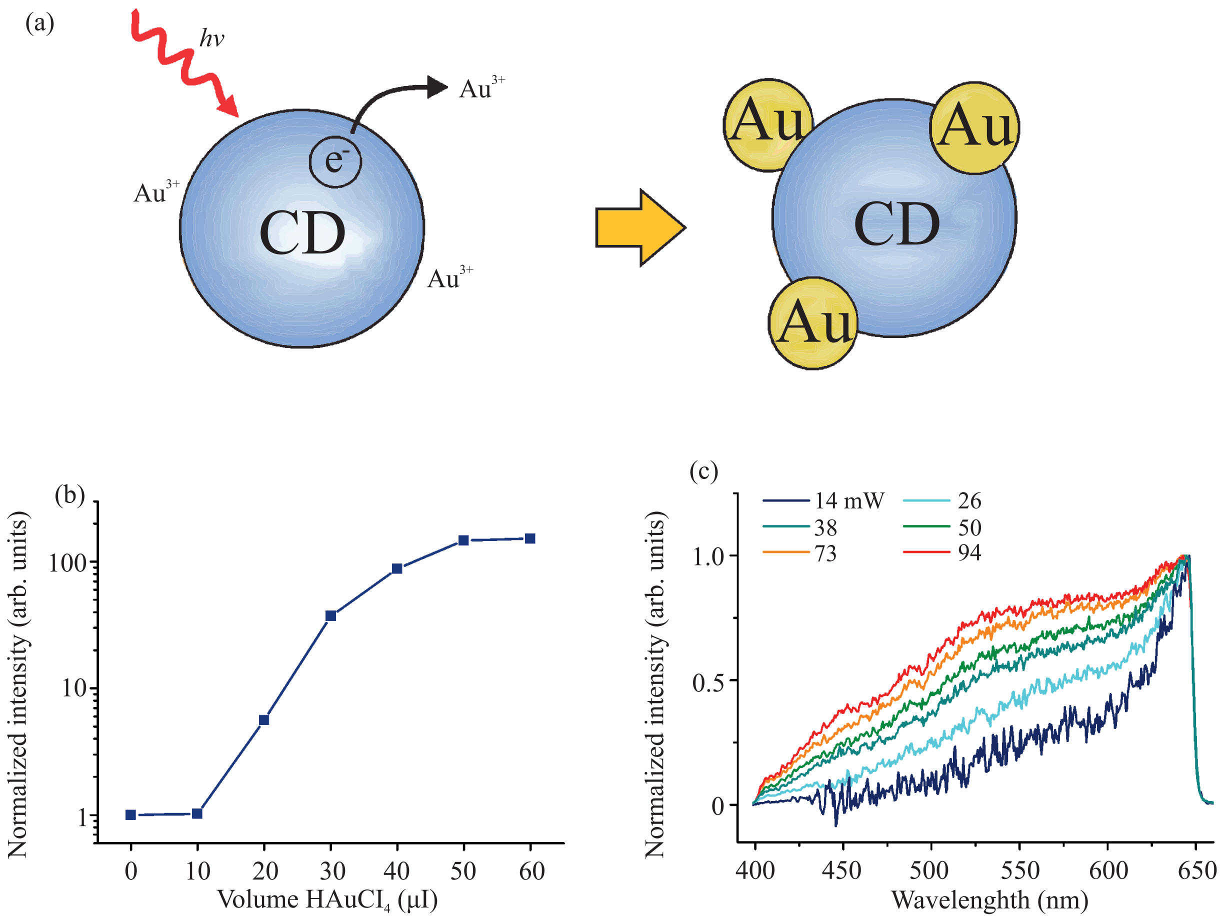

Fig. 1. (Color online) (a) – Schematic representation of Au-CD hybrid formation by photoreduction of Au(III) ions. (b) – Integral NPL intensity of Au-CD hybrids at the same concentration in water excited by femtosecond laser pulses as a function of the volume of gold precursor used to obtain the hybrids. Zero volume corresponds to CD without decorating gold nanoparticles. (c) – Comparison of normalized NPL spectra of Au-CD registered at different excitation laser powers

Broadband emission spectrum and short luminescence lifetimes are attractive properties for nonlinear luminescence imaging with Au-CD nanohybrids.

The work has financial support from the Russian Scientific Foundation grant # 21-72-20169. The measurements were performed in the FRCCP shared research facilities # 506694 and large-scale research facilities # 1440743.

This is an excerpt of the article “Enhanced nonlinear photoluminescence of Au-carbon dot nanohybrids produced by photocatalytic reduction of Au(III) ions”. Full text of the paper is published in JETP Letters journal.
DOI: 10.1134/S0021364021230016

1. L. Cao, S. Sahu, P. Anilkumar, C. E. Bunker, J. Xu, K. A. S. Fernando, P. Wang, E. A. Guliants, K. N. Tackett, and Y.-P. Sun, JACS **133**, 13 (2011).
2. S. I. Kudryashov, P. A. Danilov, S. G. Bezhanov, A. A. Rudenko, A. A. Ionin, S. A. Uryupin, S. F. Umanskaya, and N. A. Smirnov, JETP Lett. **109**, 6 (2019).
3. A. A. Astafiev, A. M. Shakhov, A. S. Kritchenkov, V. N. Khrustalev, D. V. Shepel, V. A. Nadtochenko, and A. G. Tskhovrebov, Dyes Pigm. **188**, 109176 (2021).
4. M. B. Agranat, S. I. Ashitkov, A. V. Ovchinnikov, D. S. Sitnikov, A. A. Yurkevich, O. V. Chefonov, L. T. Perel'man, S. I. Anisimov, and V. E. Fortov, JETP Lett. **101**, 9 (2015).
5. T. Haug, P. Klemm, S. Bange, and J. M. Lupton, Phys. Rev. Lett. **115**, 6 (2015).