

Бионаночастицы



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МГУ имени М.В.Ломоносова

Микро- и наночастицы

Наночастицы:

- Особые физические и химические свойства (оптические, магнитные, каталитические, сенсорные, биологические...)
- Формирование сверхрешеток
- Широкое применение в научно – исследовательских и практических целях (устройства записи и отображения информации, наномедицина, сенсорика, катализ, фотокатализ, супергидрофобные поверхности, химические источники тока, ...)

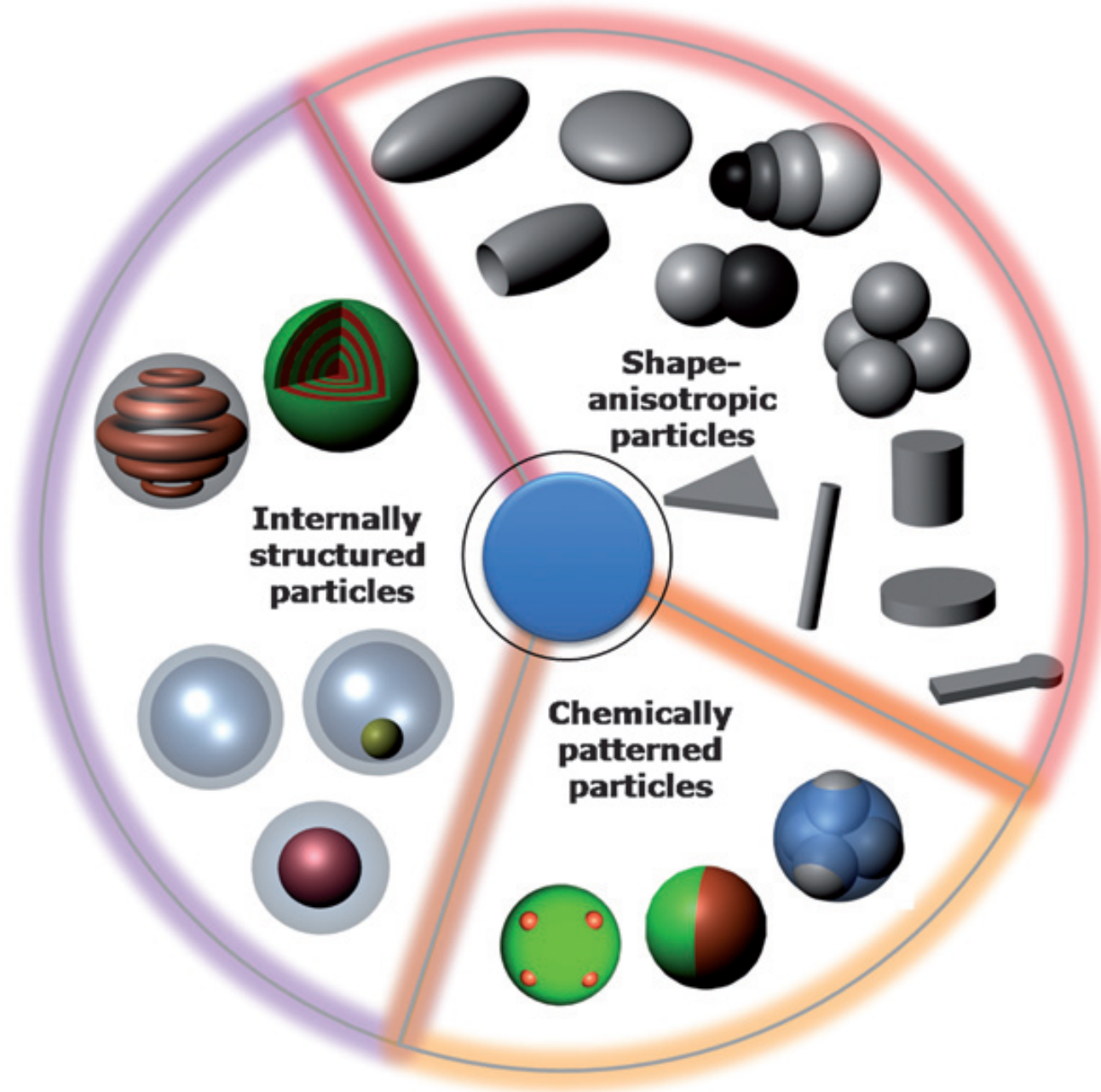
Микрочастицы:

- Строительные блоки для упорядоченных микропористых сред,
- Носители и «концентраторы» наночастиц (коллоидосомы, нанокомпозиты),
- Широкое применение в научно – исследовательских и практических целях

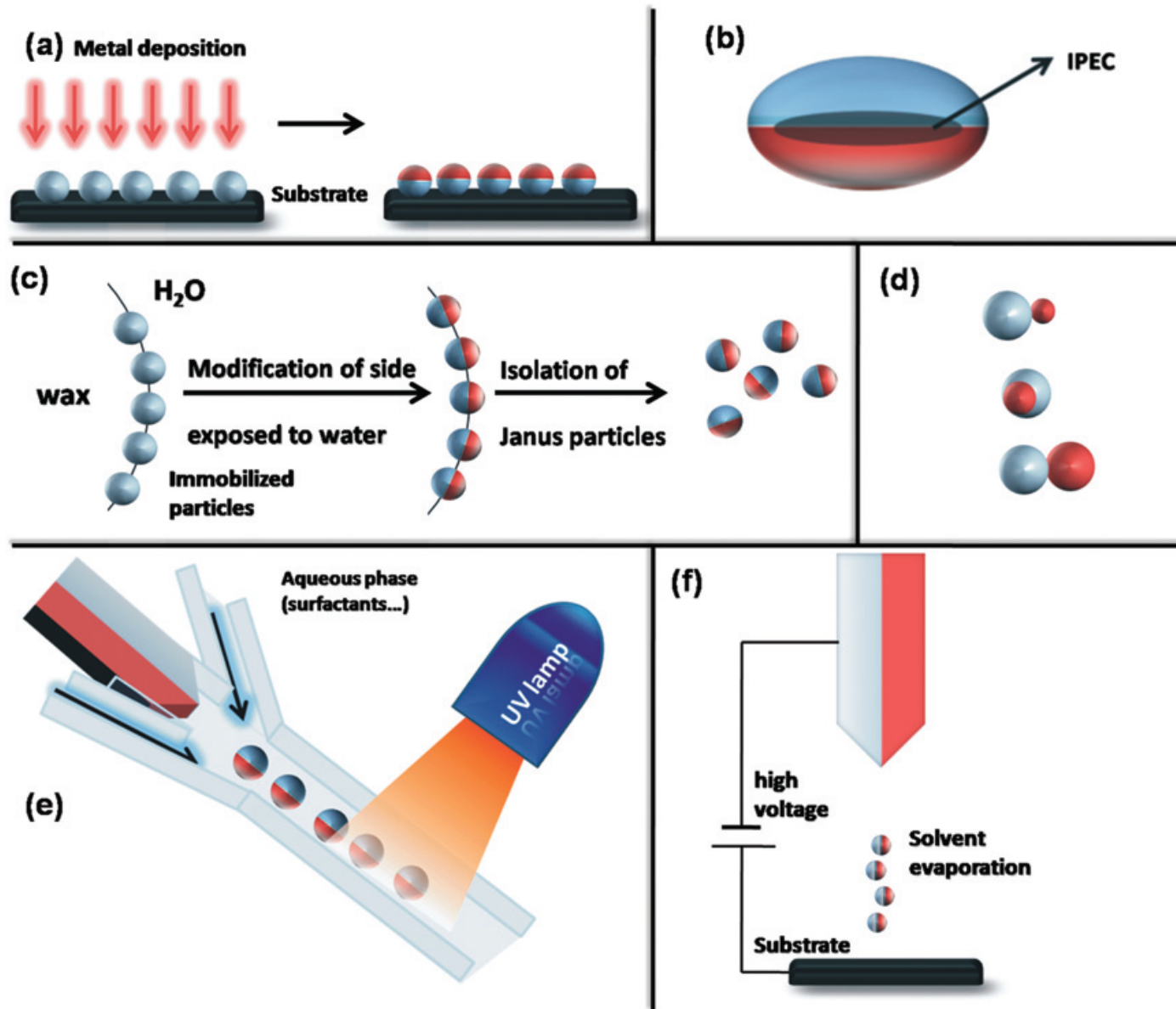
Способы получения:

- Химические методы гомогенизации
- Физические методы
- Биологические методы
- Самосборка (самоорганизация)

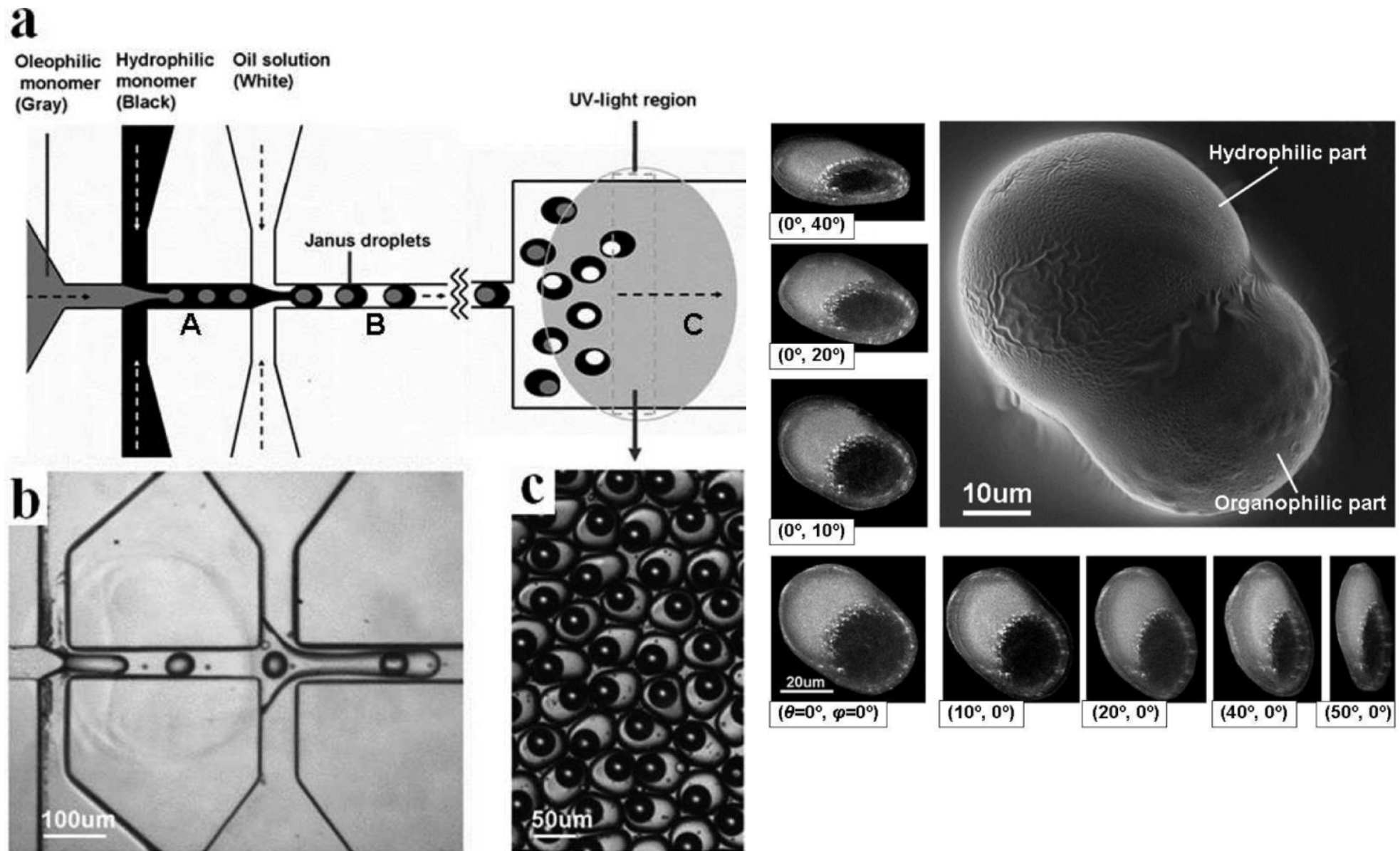
Типы частиц - янусов

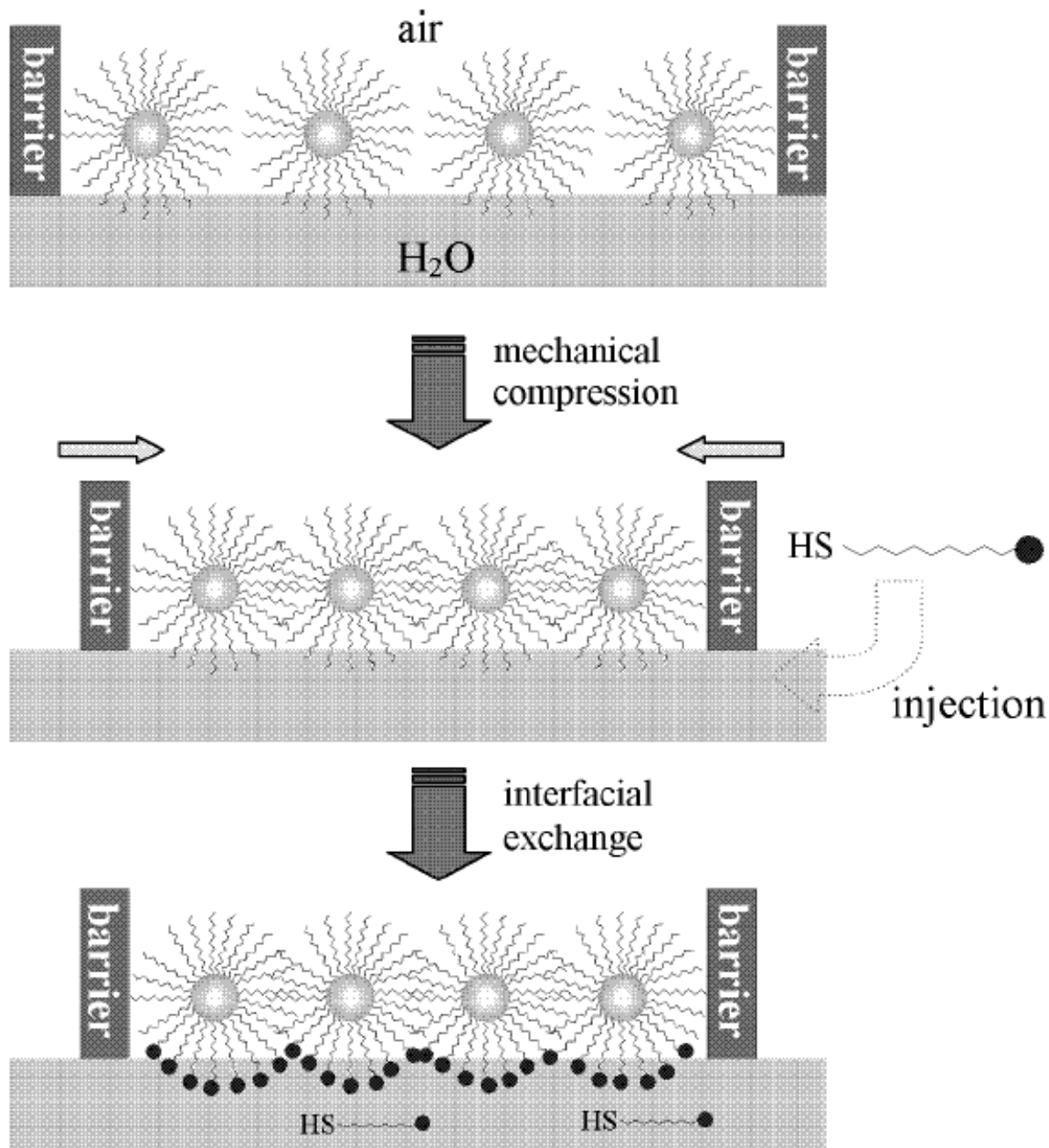


Методы получения частиц - янусов



Микрожидкостная машина

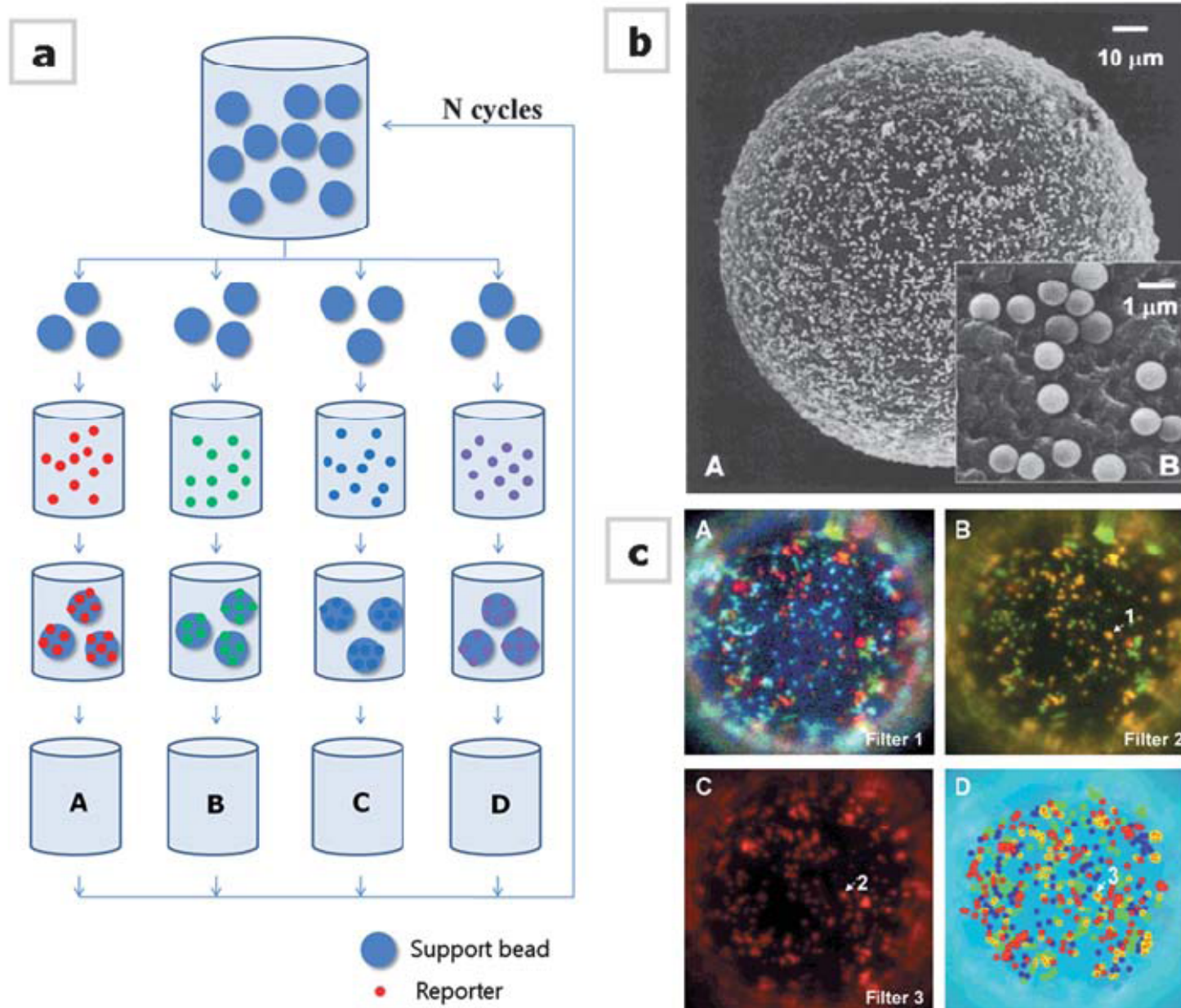




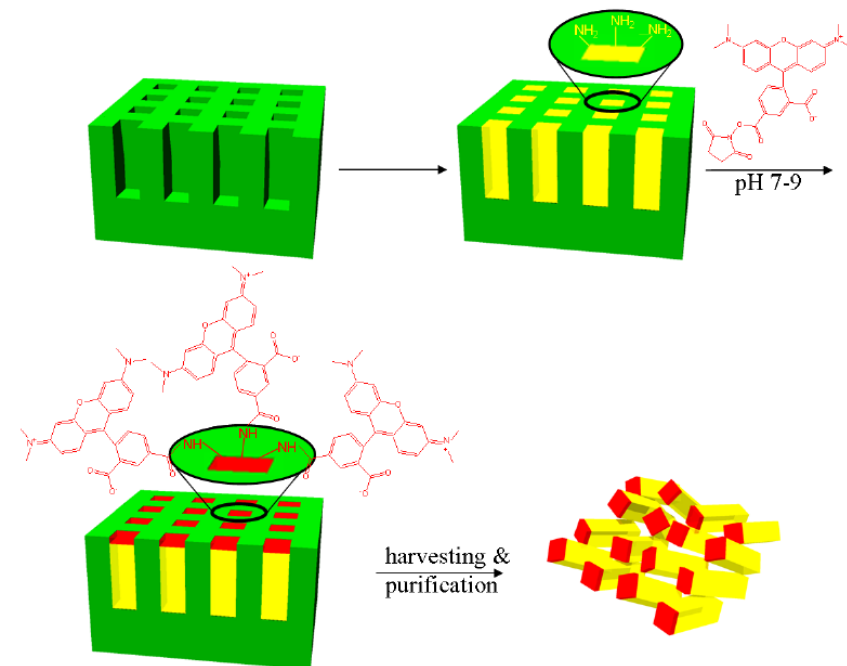
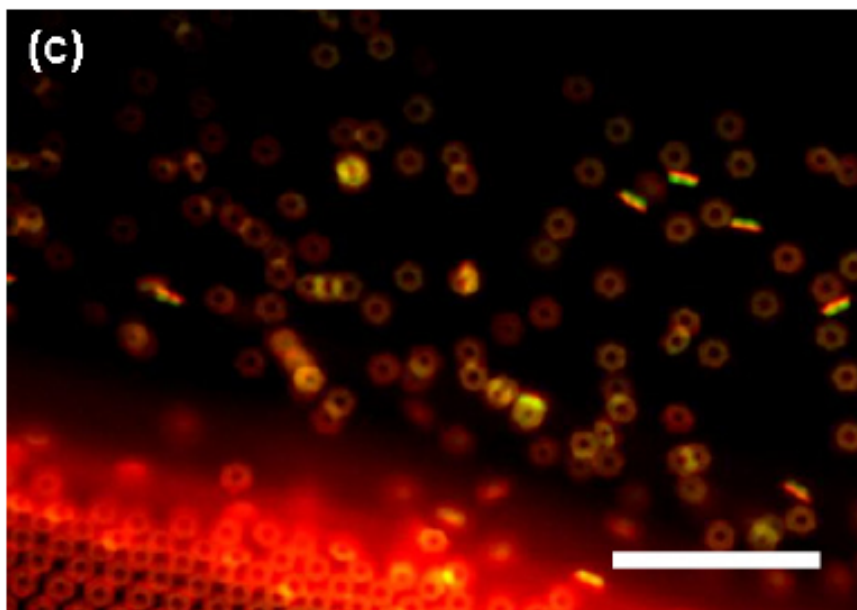
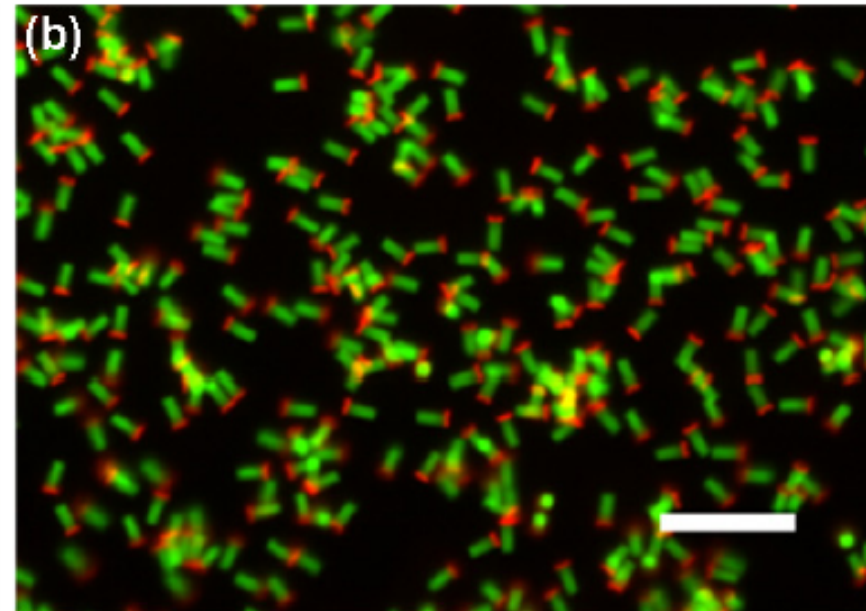
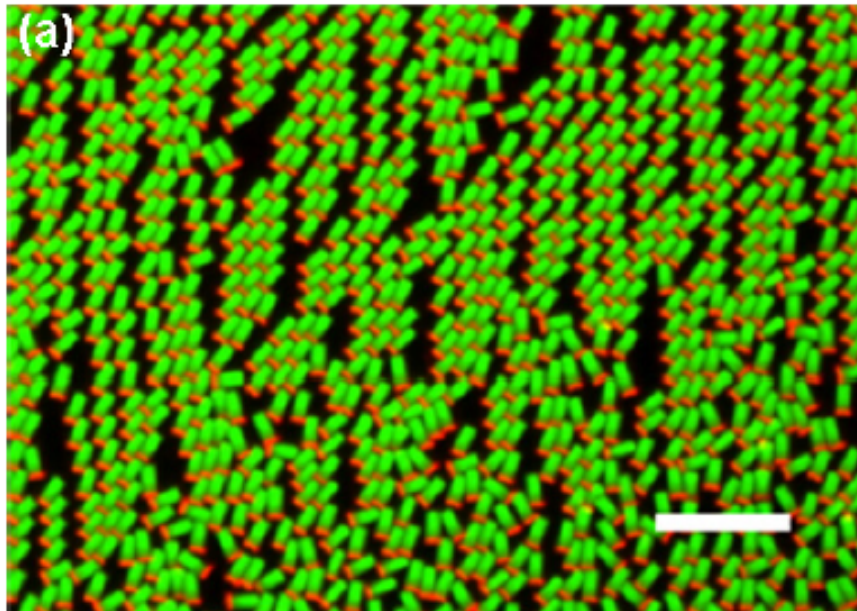
Метод Лэнгмюра - Блоджет и частицы - янусы

Scheme 2. Schematic of the preparation of Janus nanoparticles based on the Langmuir technique.

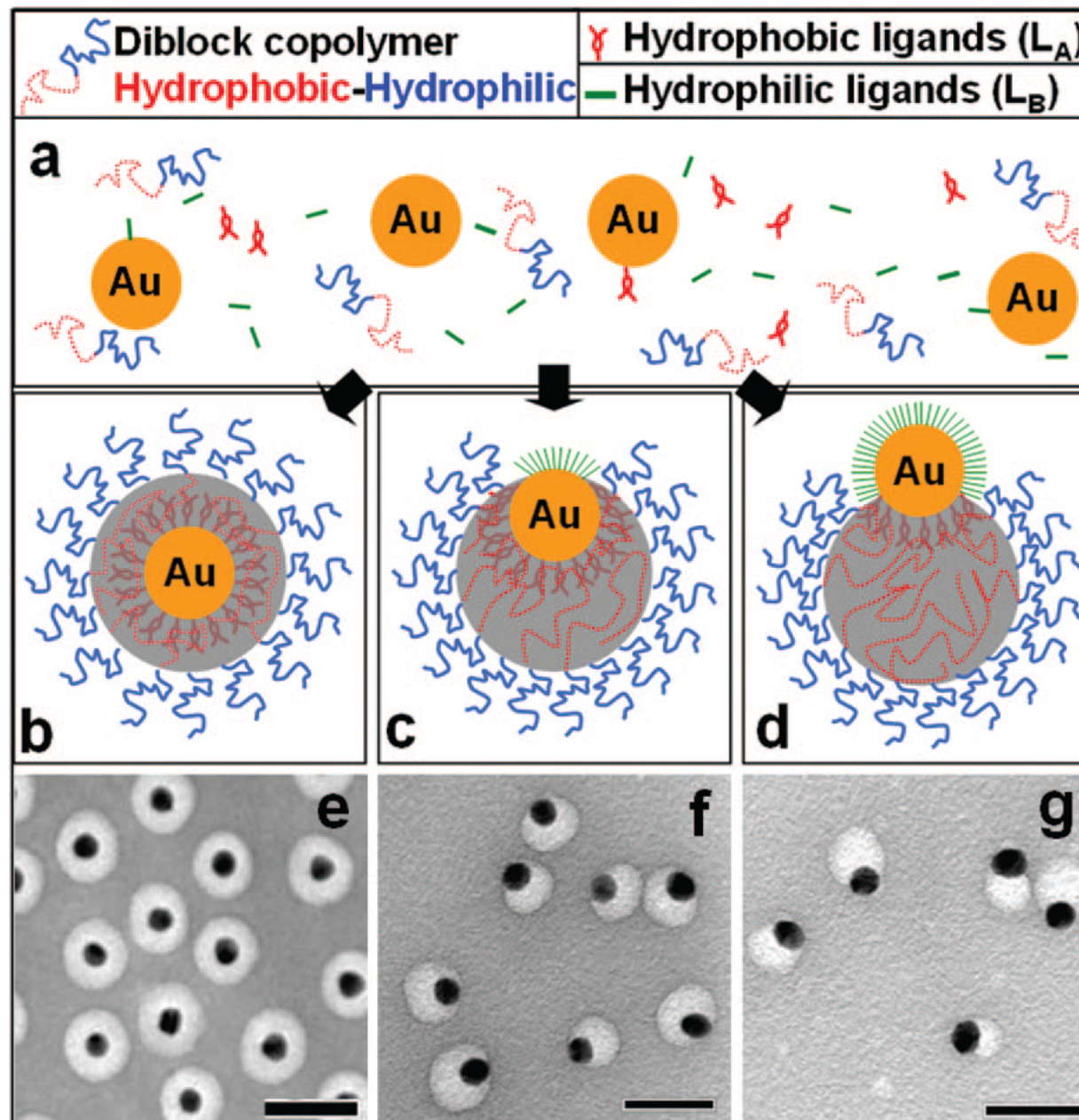
Полифункциональные коллоидосомы



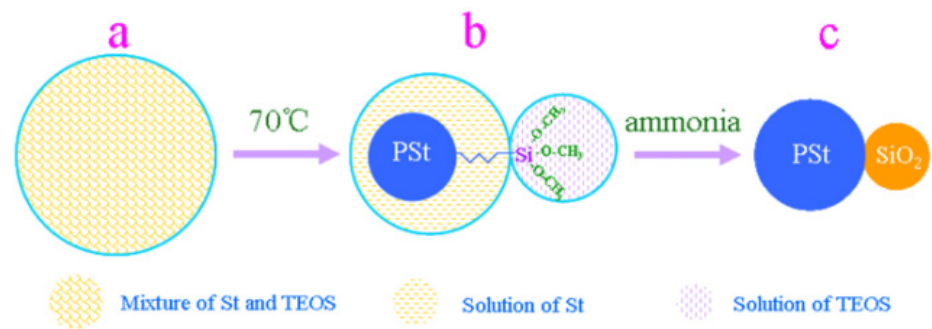
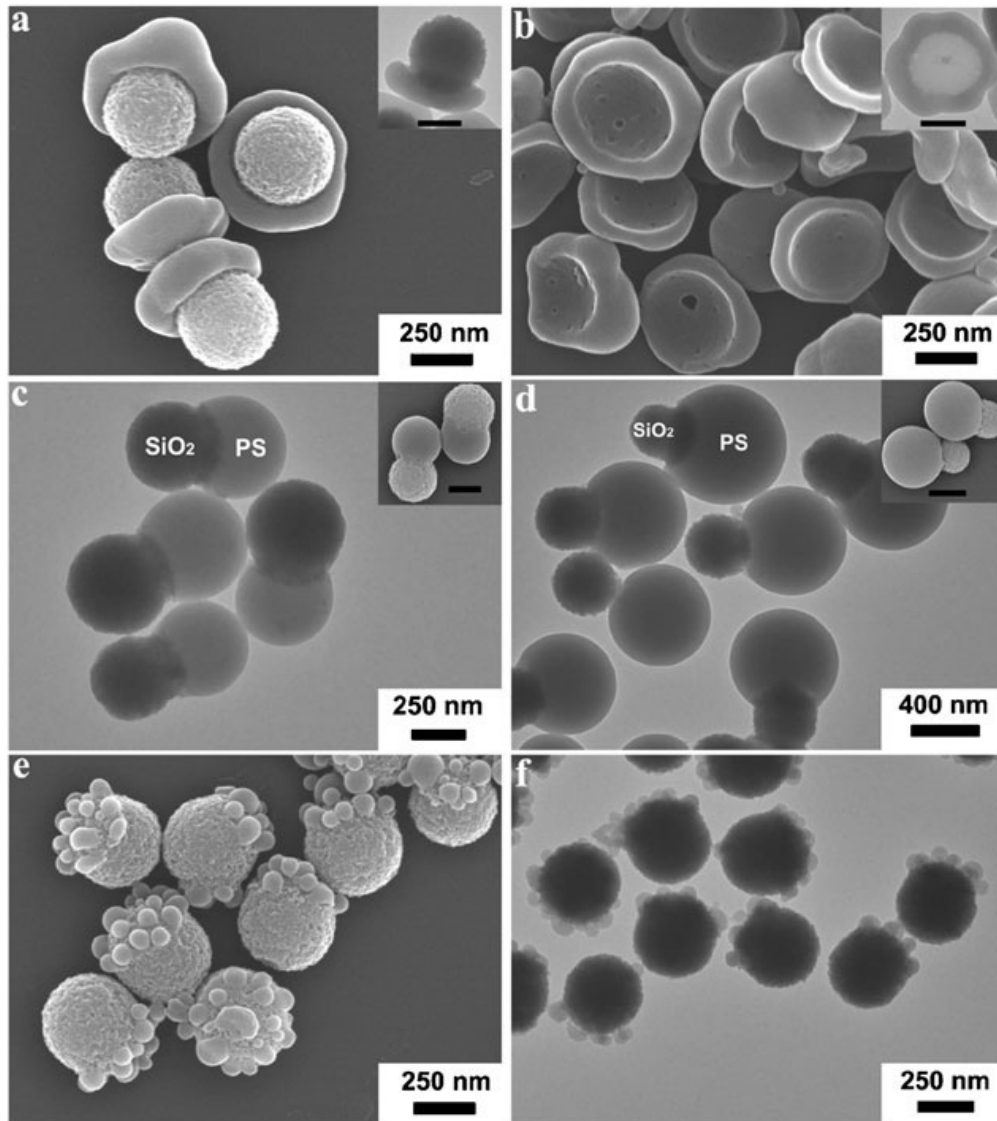
Литография и модифицирование



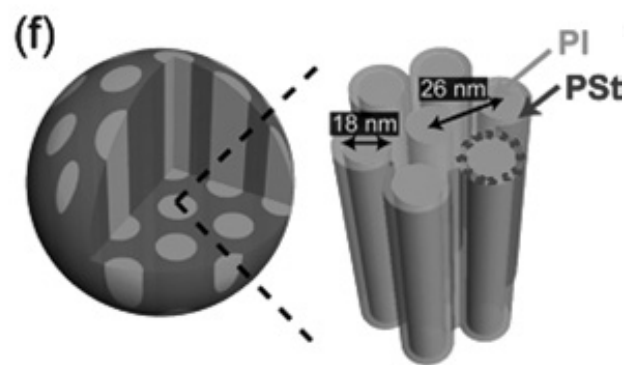
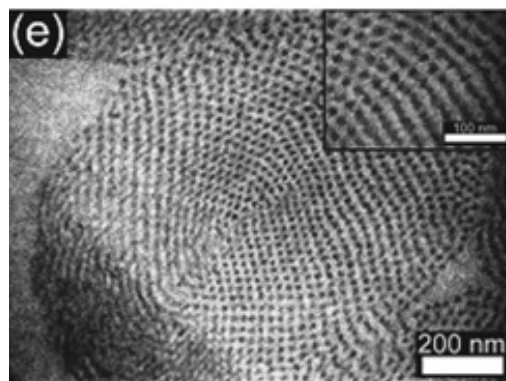
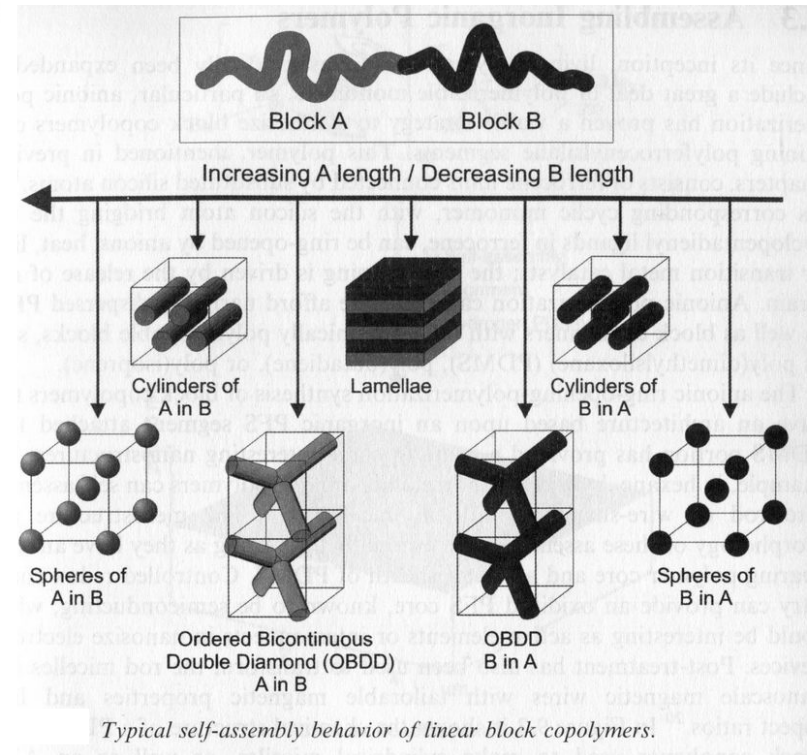
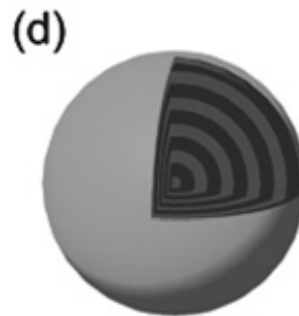
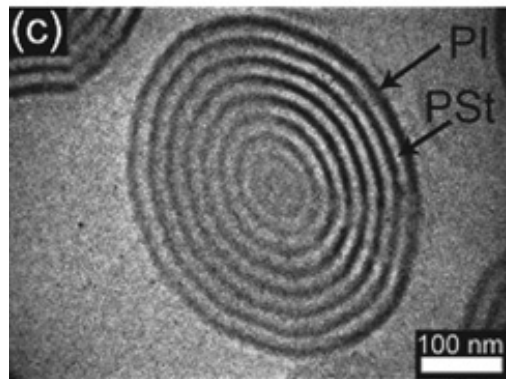
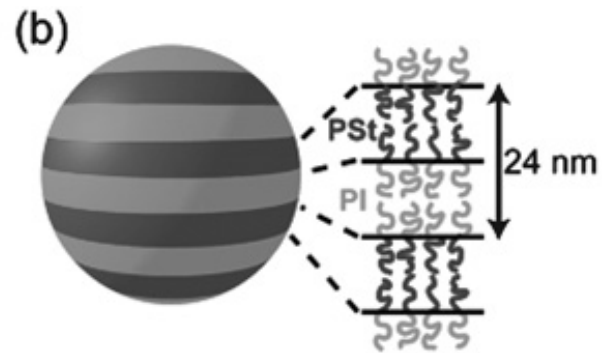
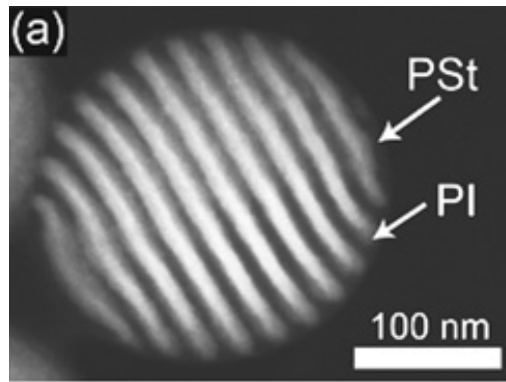
Золотые частицы - янусы



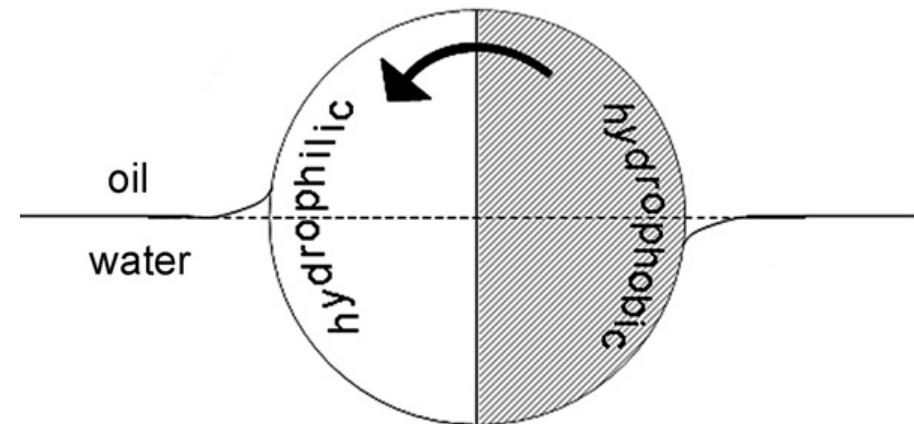
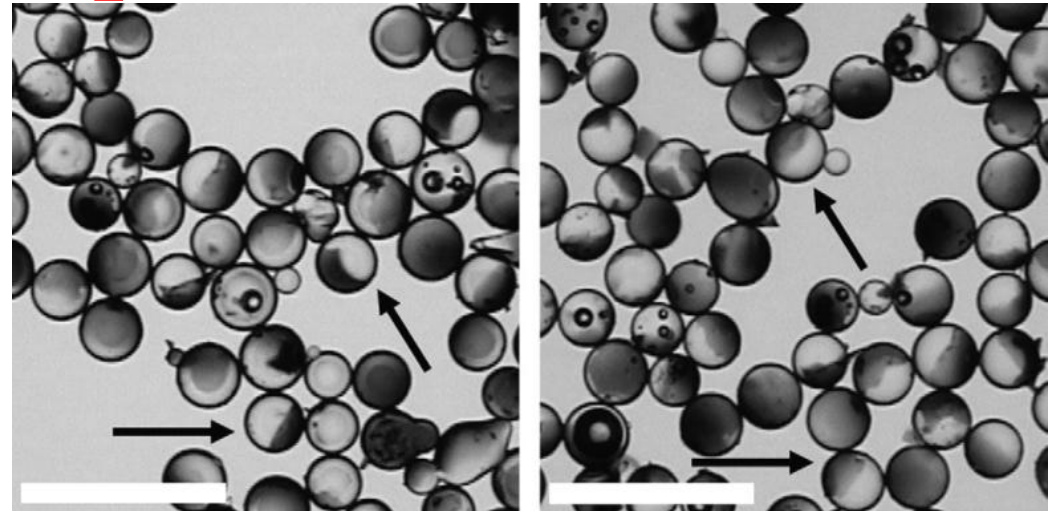
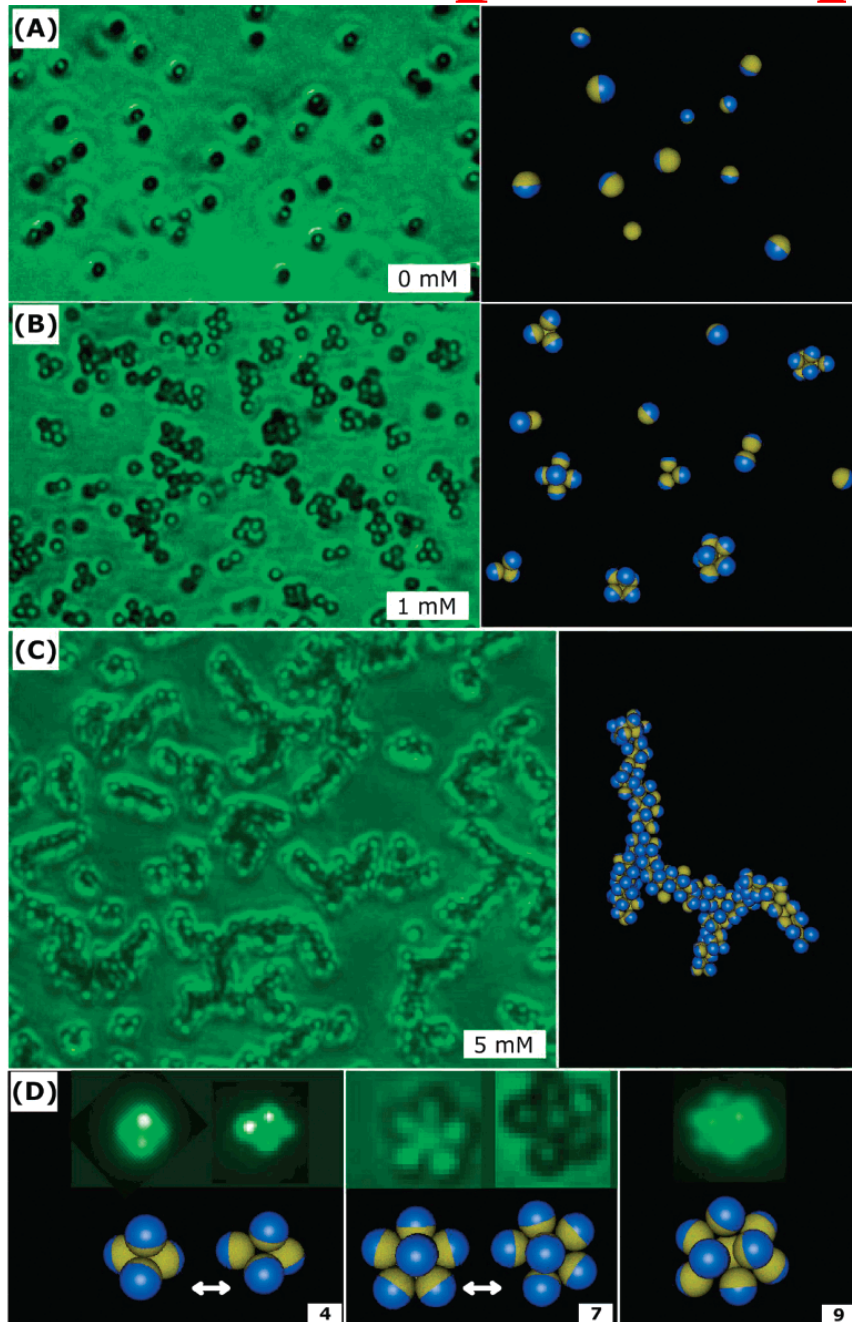
SiO₂-полистирол



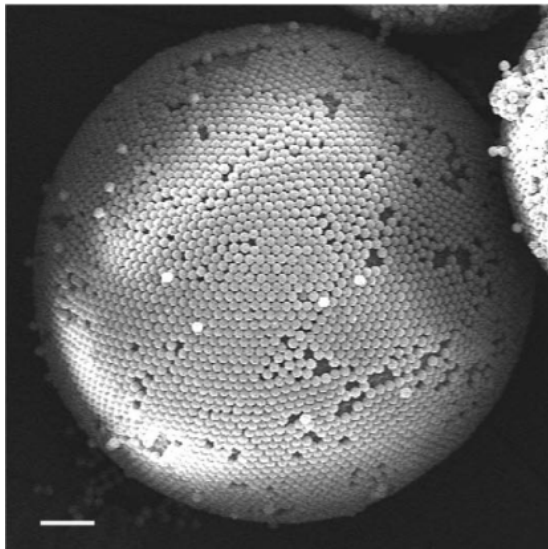
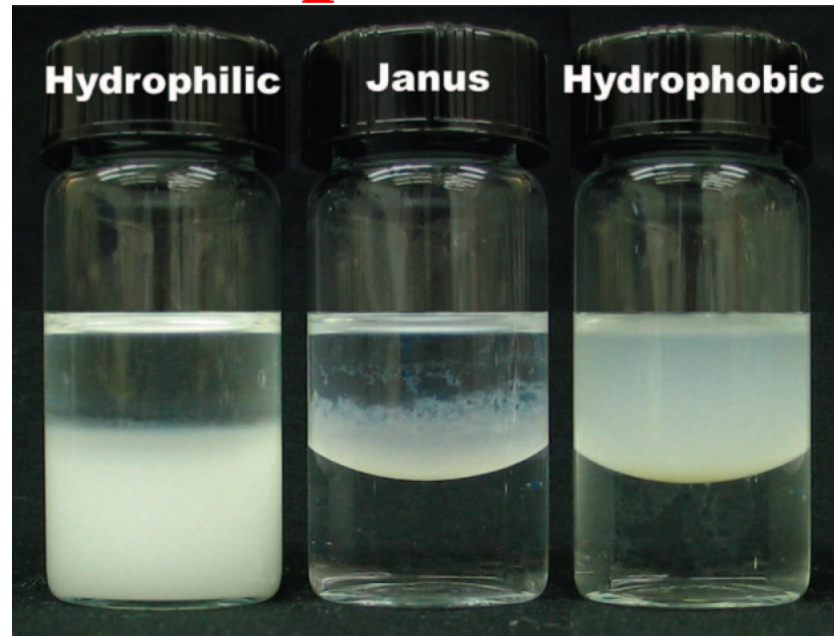
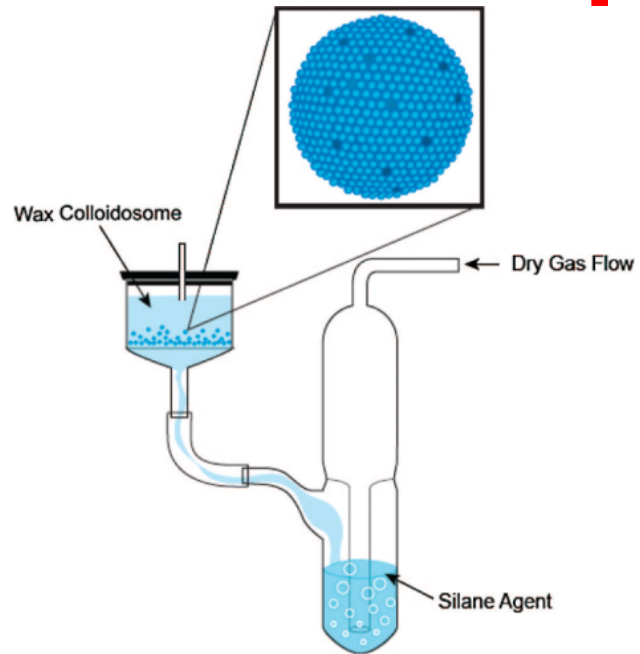
Полимеры и структуры



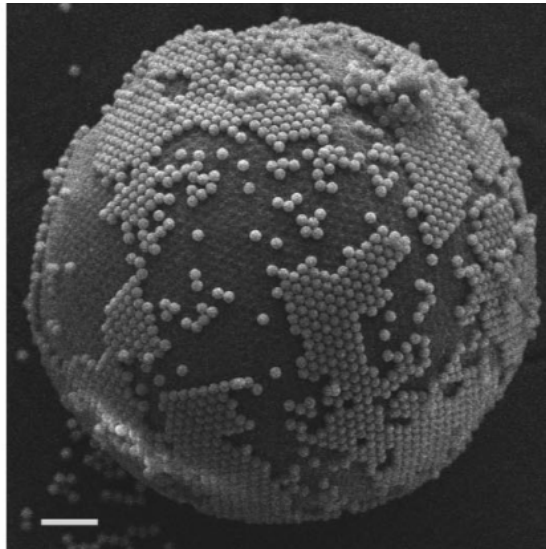
Кластеры амфифильных частиц



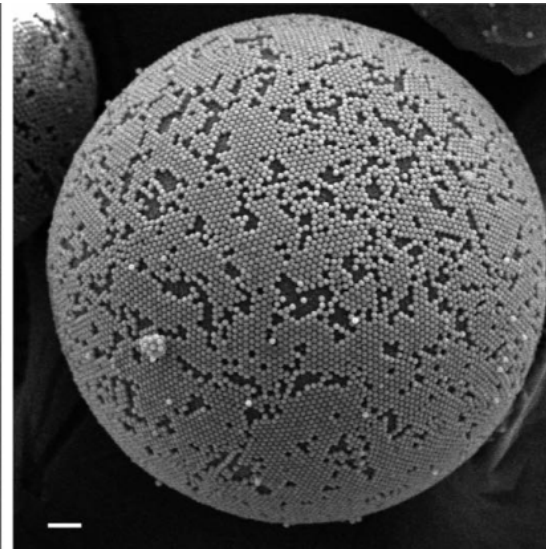
Границы раздела



(a)

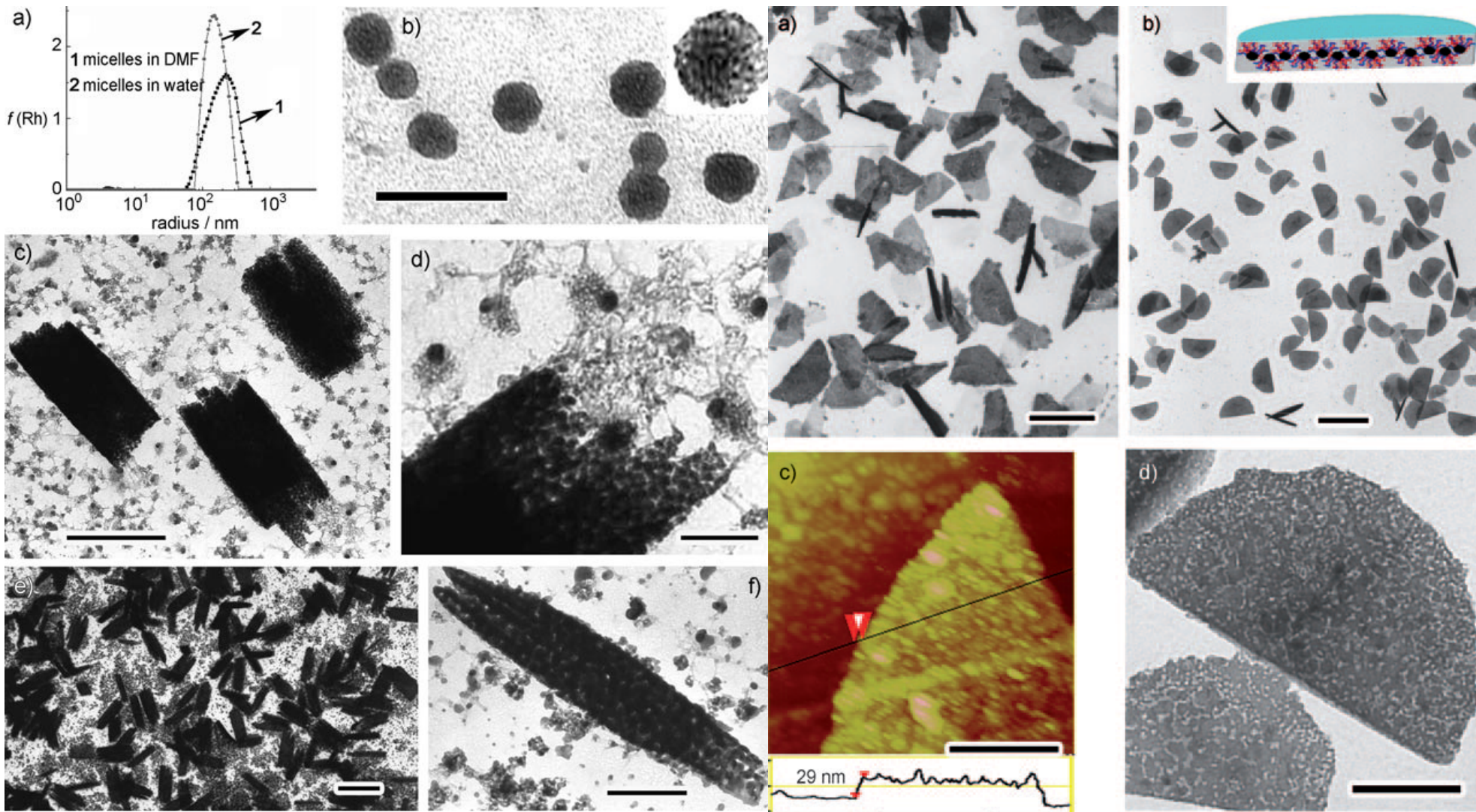


(b)



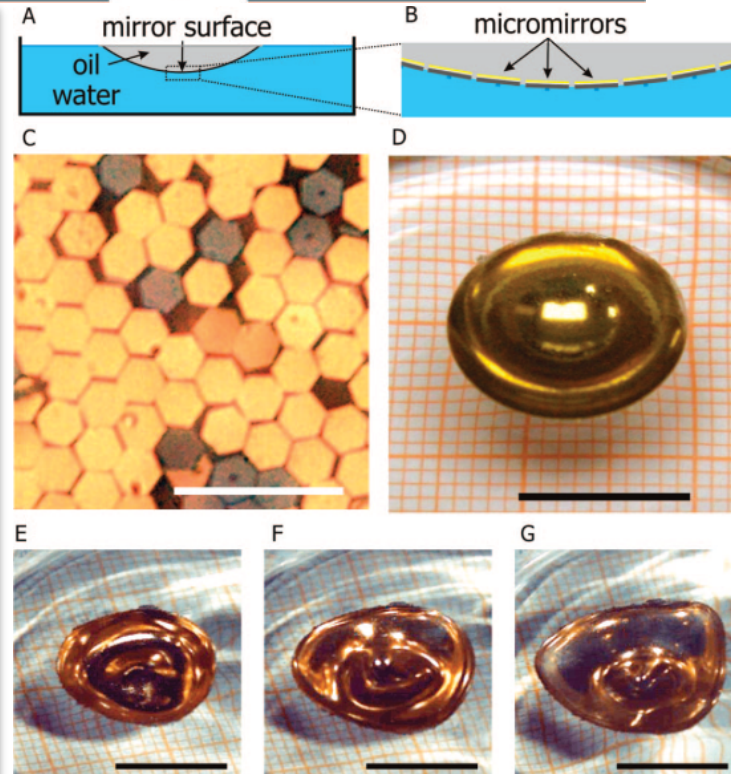
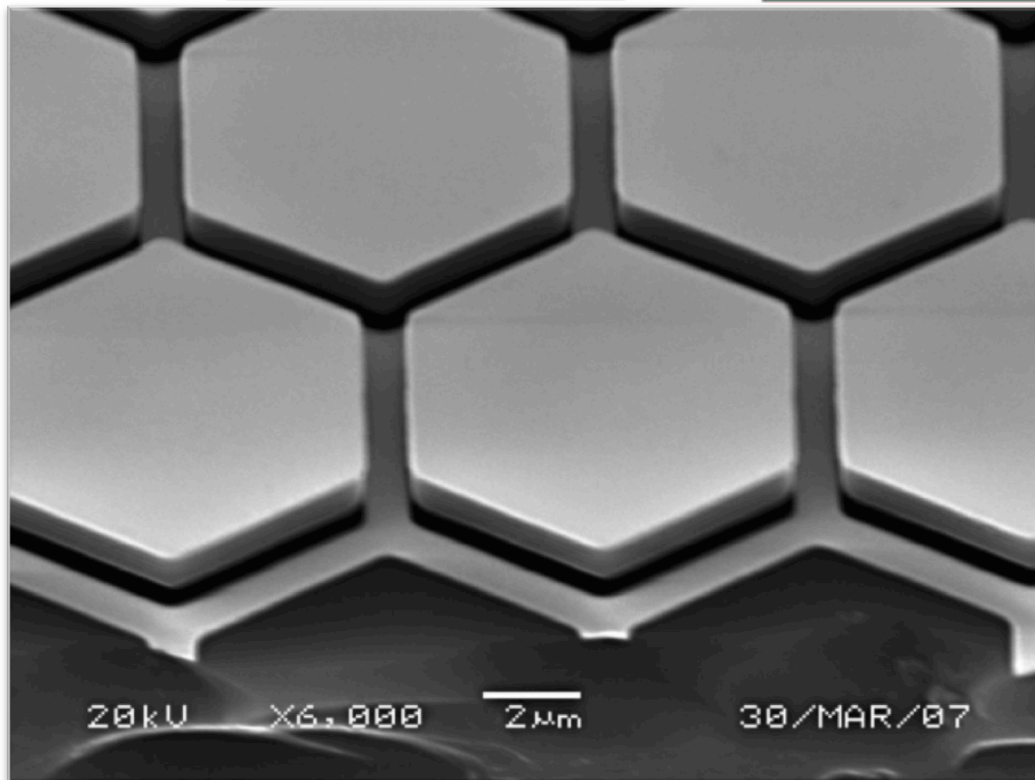
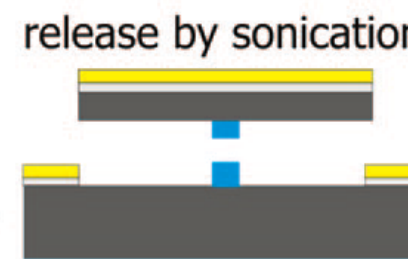
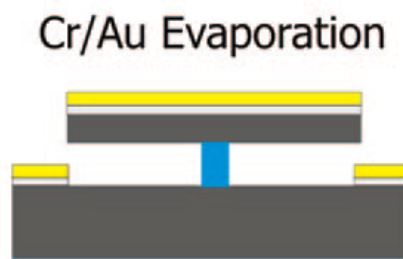
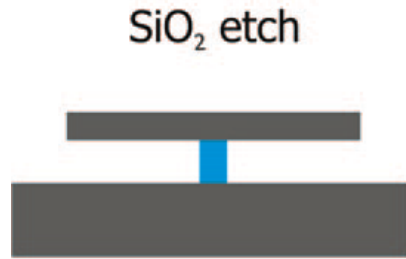
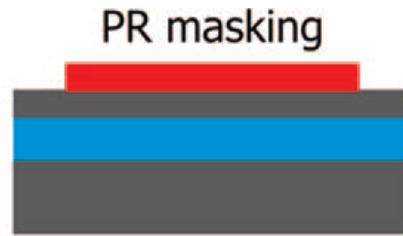
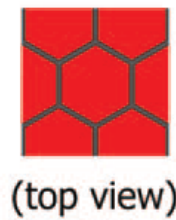
(c)

Самосборка частиц - янусов

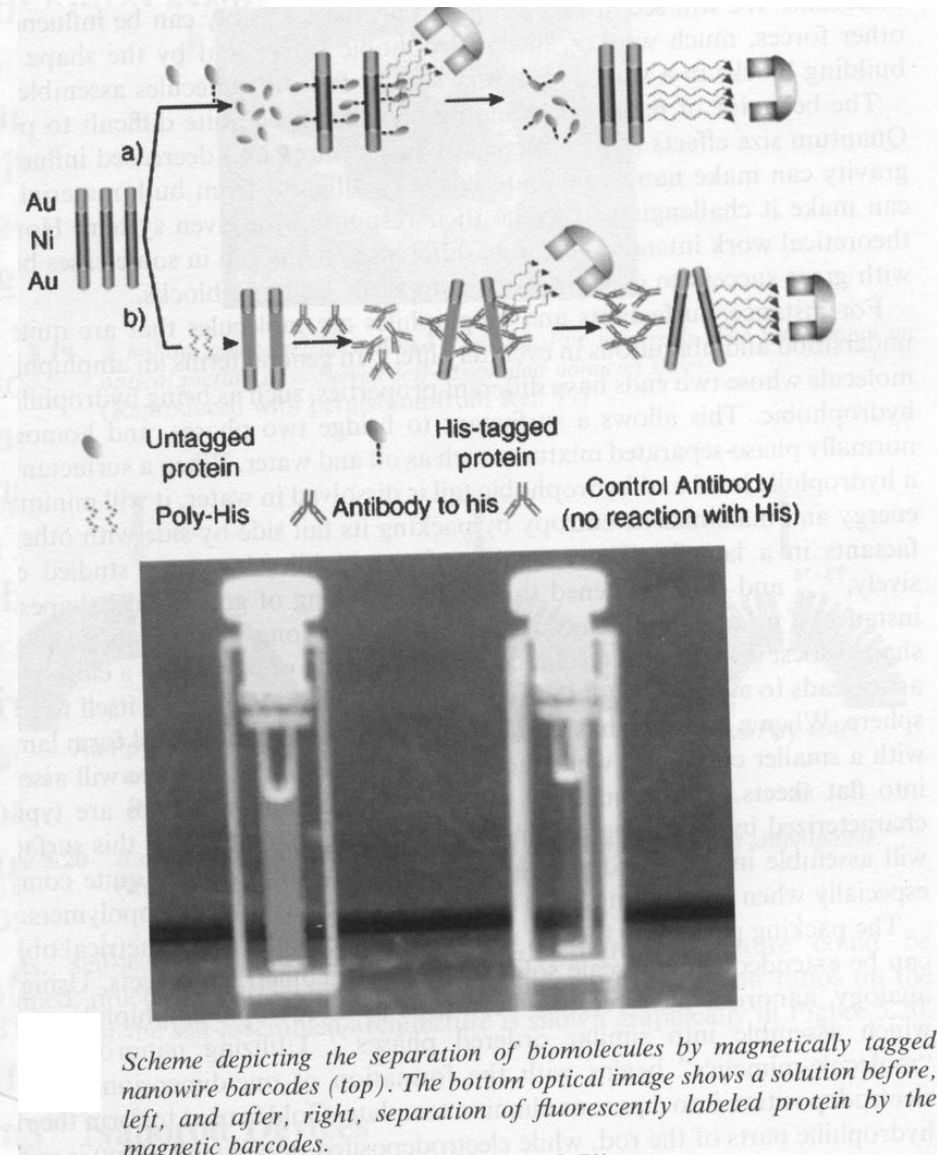
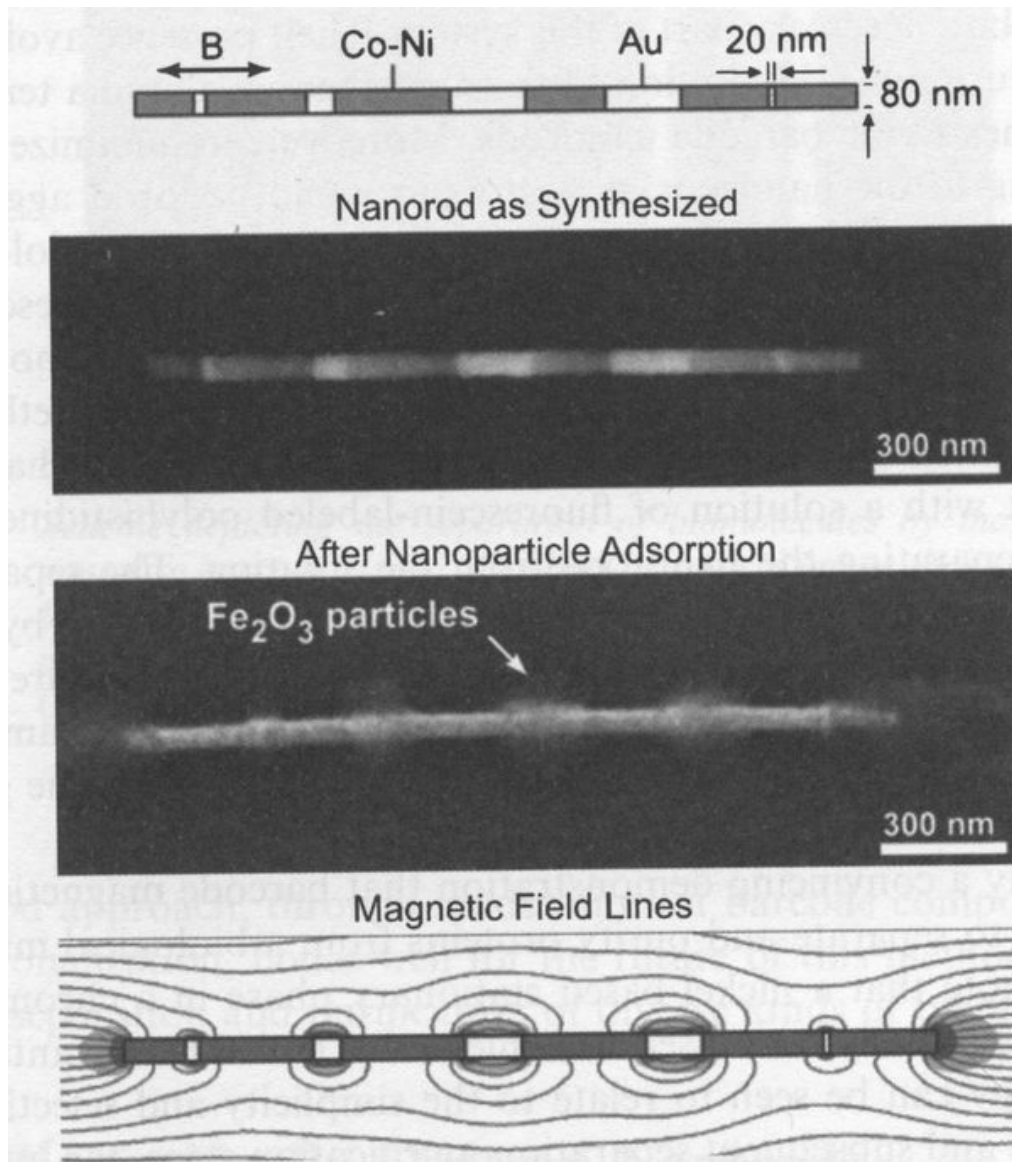


Кривое зеркало из микрозеркал

- resist
- SiO₂
- Si
- Cr
- Au

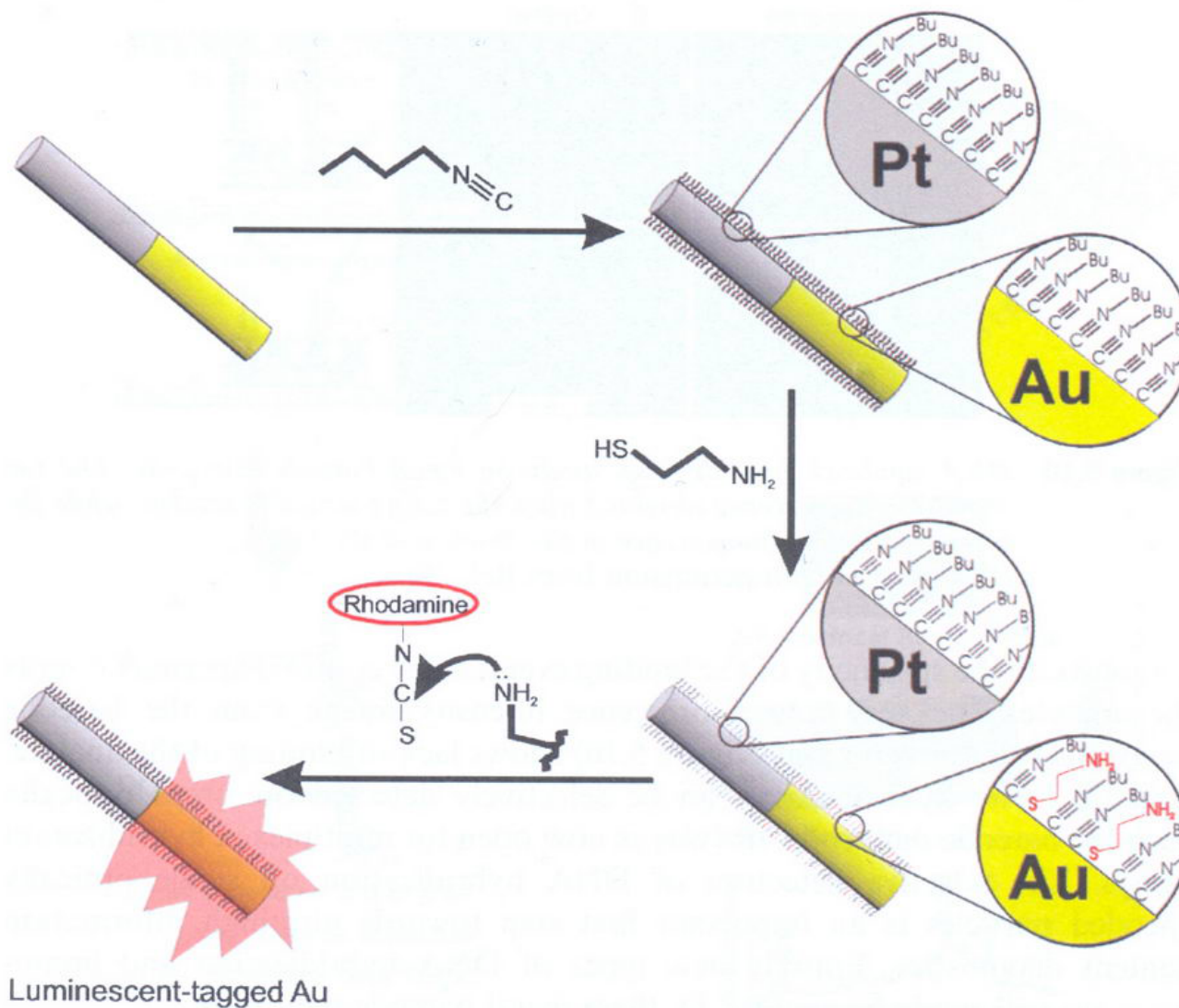


Магнитный «штрих-код»



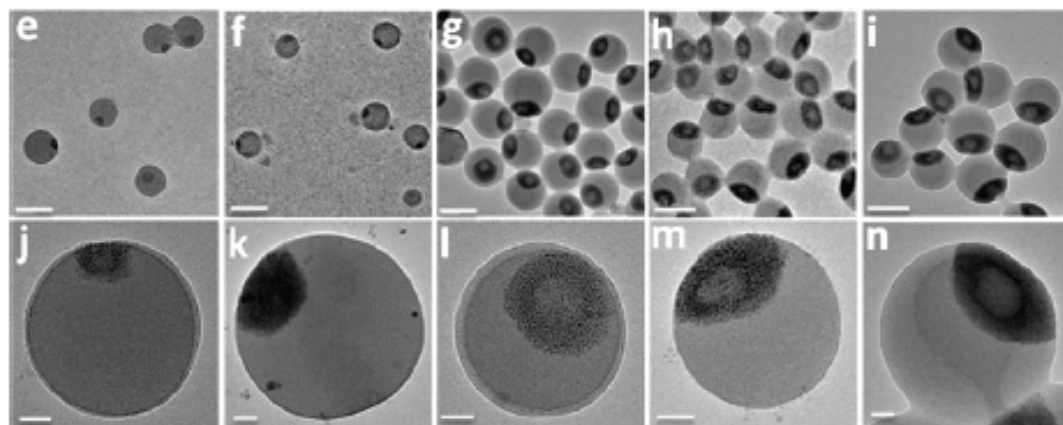
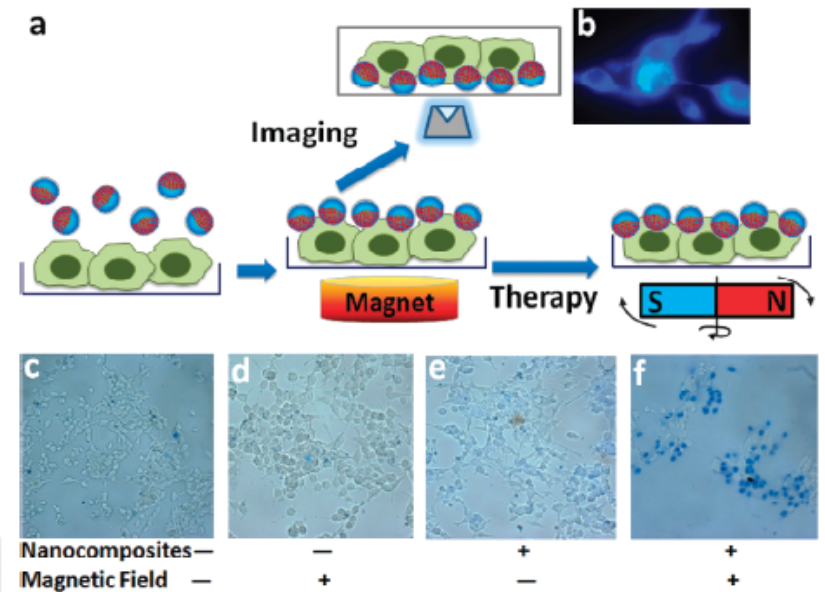
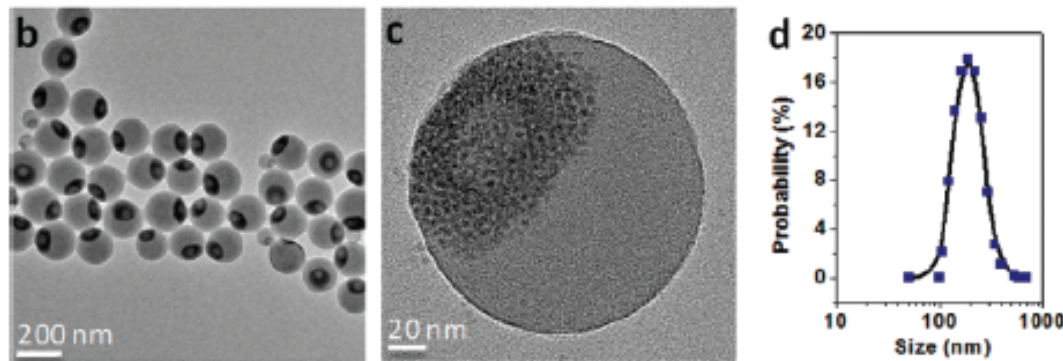
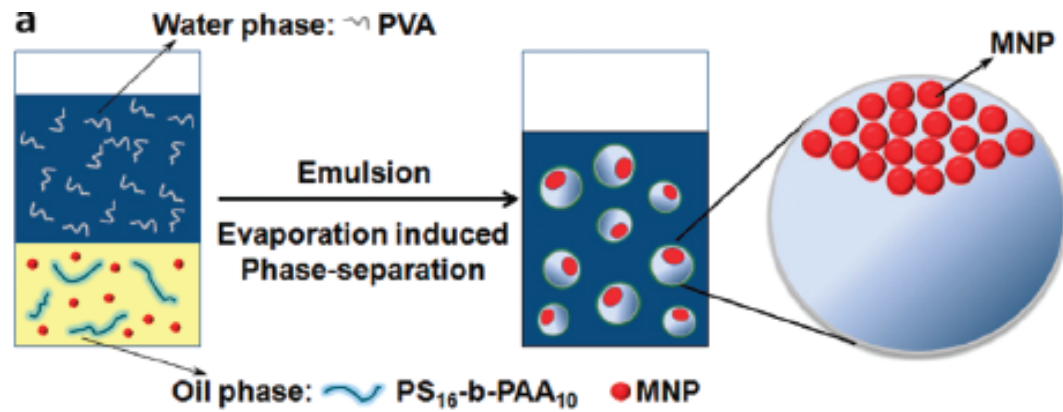
Attraction of magnetic nanoparticles to diamagnetic segments in a magnetic barcoded nanorod.

Модификация нанопроволок



Orthogonal assembly on nanorods. Butylisonitrile is bound to Pt and Au surfaces. Aminoethanethiol displaces isonitriles on gold but not on platinum. Rhodamine isocyanate is reacted with terminal amino groups to fluorescently label gold segments.

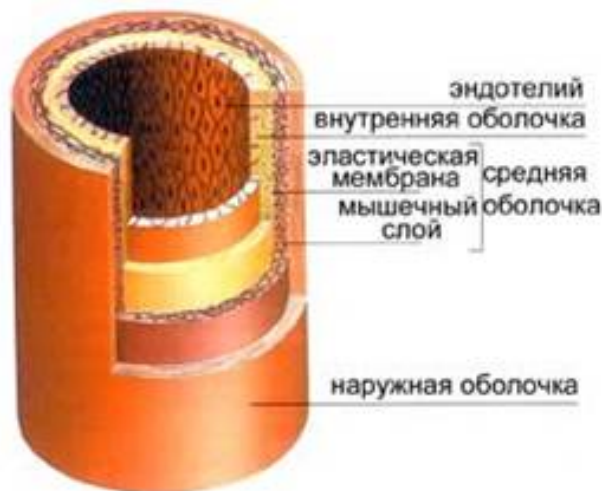
Визуализация и терапия



«Нанобио»



- Малый размер
⇒ могут проникать в капилляры, ткани и клетки
- Развитая поверхность
⇒ «контейнеры» для биологически активных в-в
⇒ частицы неорганических материалов можно сделать нетоксичными
⇒ свойства частиц зависят от состояния поверхности
- Необычные для свойства – магнитные и оптические



Создание новых биосовместимых наноматериалов с нетоксичной защитной оболочкой для медицинской диагностики, программируемой доставки лекарств и лечения онкологических заболеваний.

Нанобиочастицы

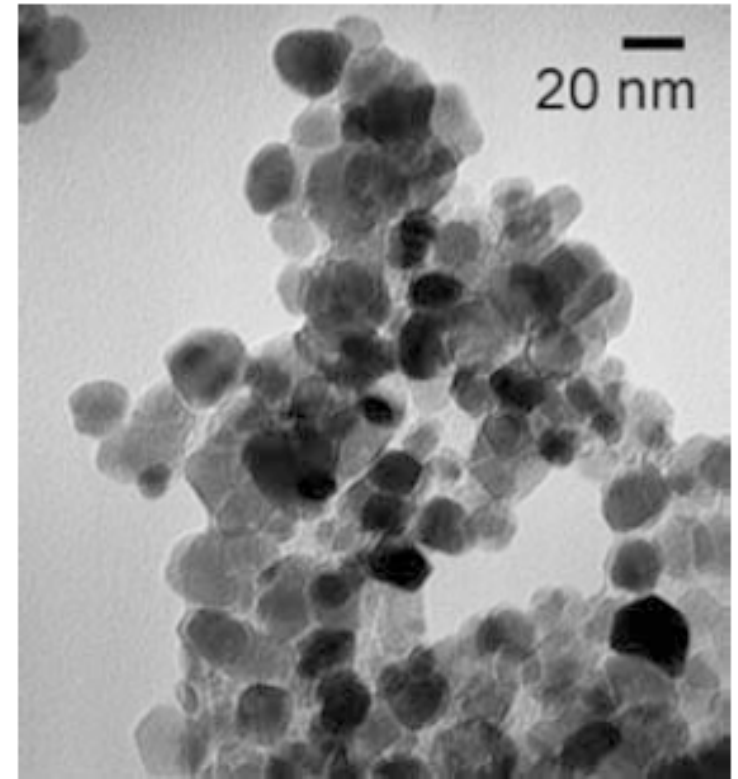
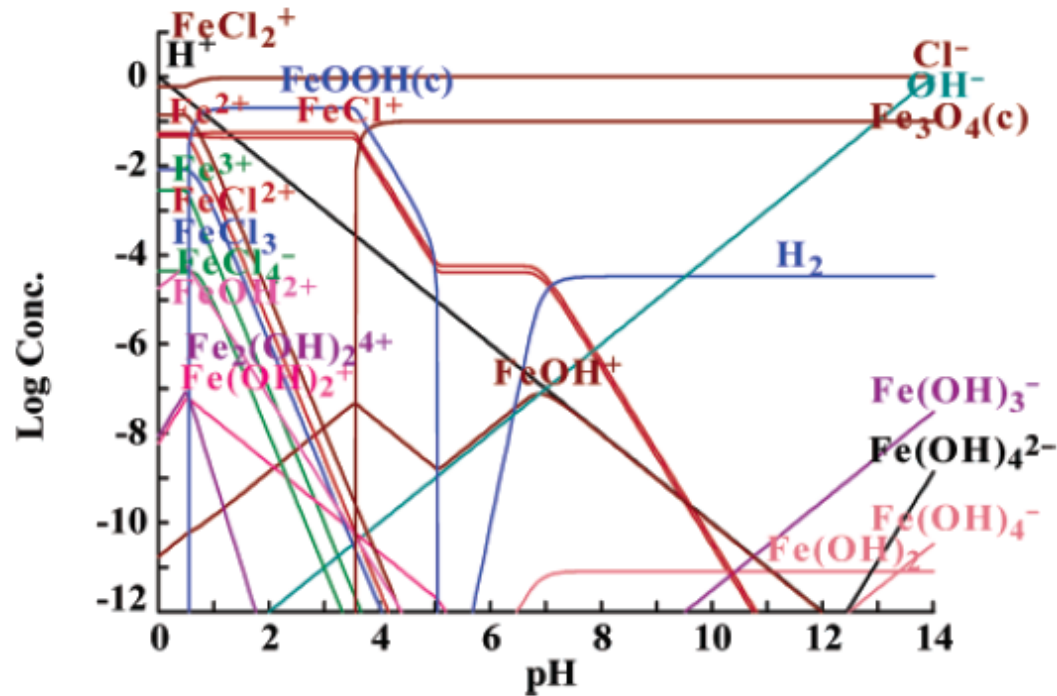
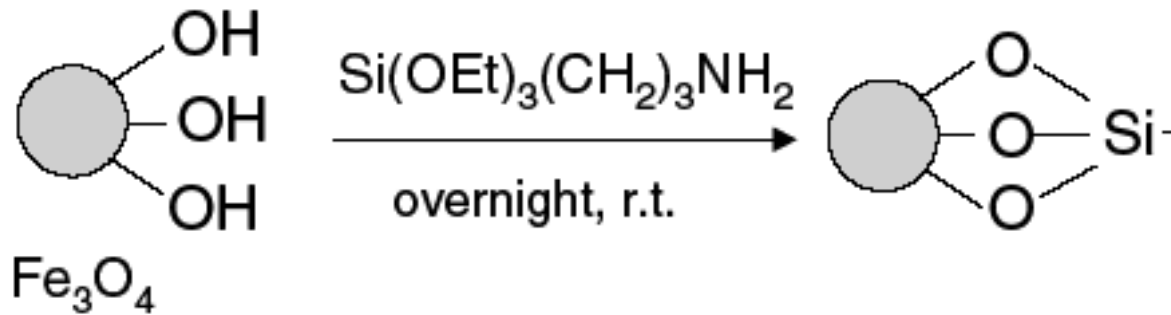
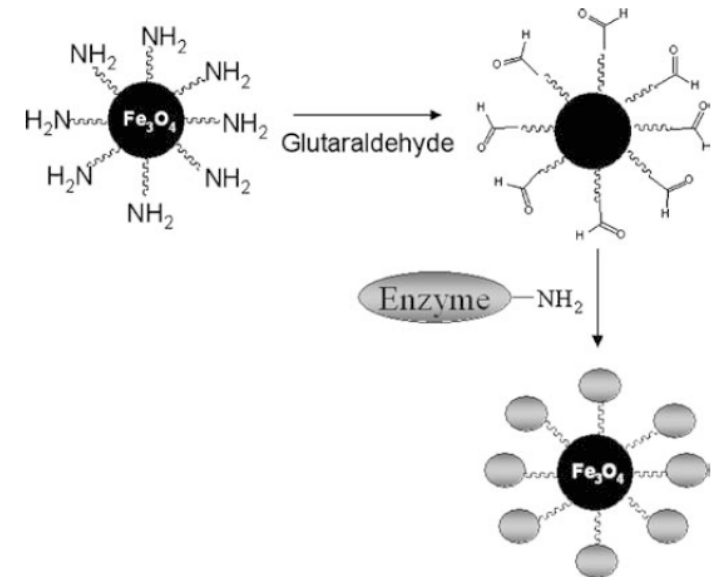
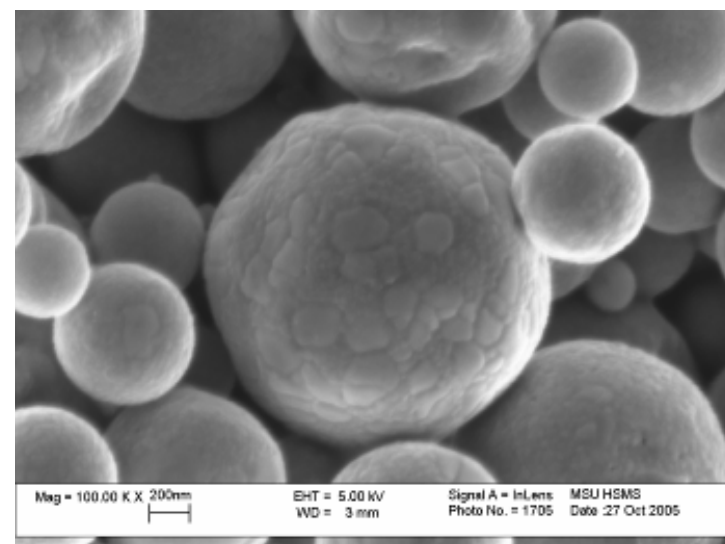
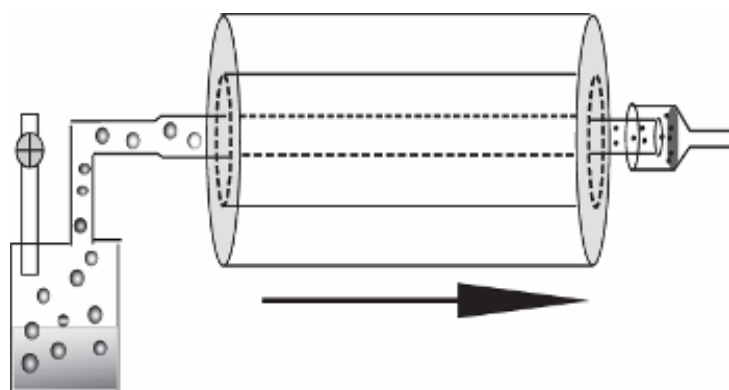


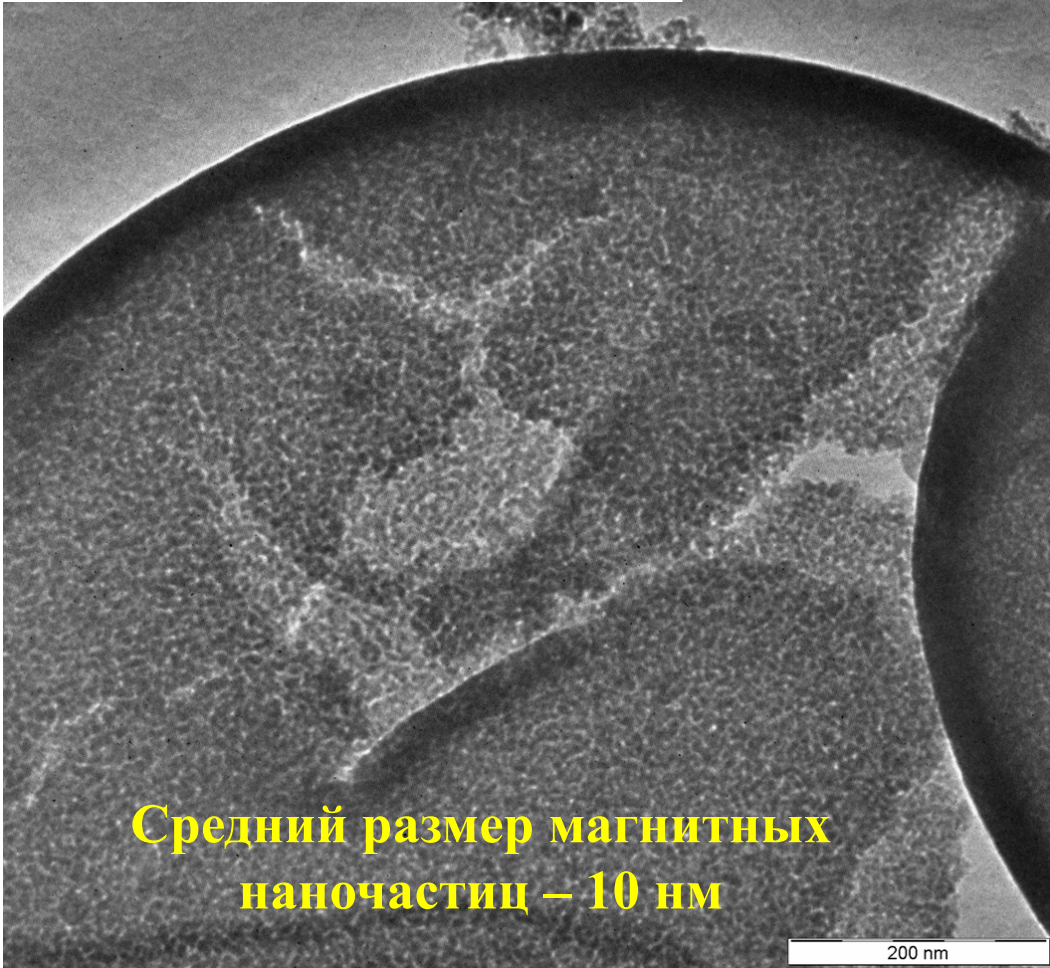
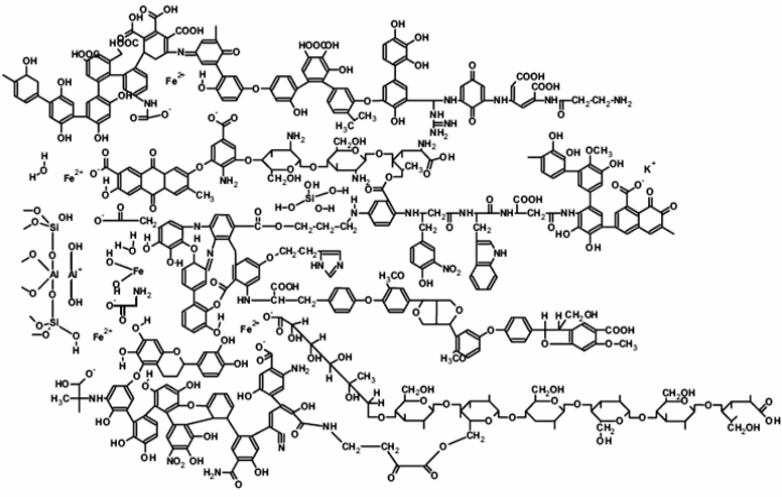
Figure 2. Thermodynamic calculations of the concentrations of all Fe^{2+} and Fe^{3+} species formed at different solution pHs. Initial conditions are $[\text{Fe}^{2+}] = 0.1 \text{ M}$, $[\text{Fe}^{3+}] = 0.2 \text{ M}$, and $[\text{Cl}^-] = 1.0 \text{ M}$.



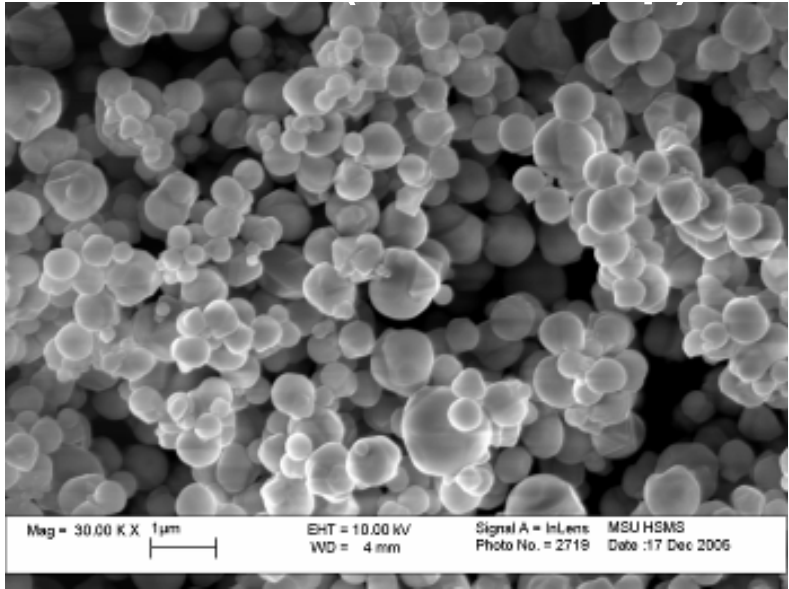
Пиролиз аэрозолей



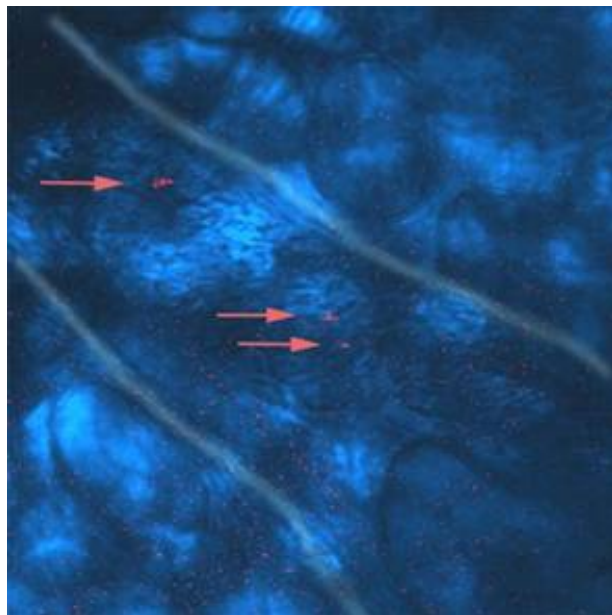
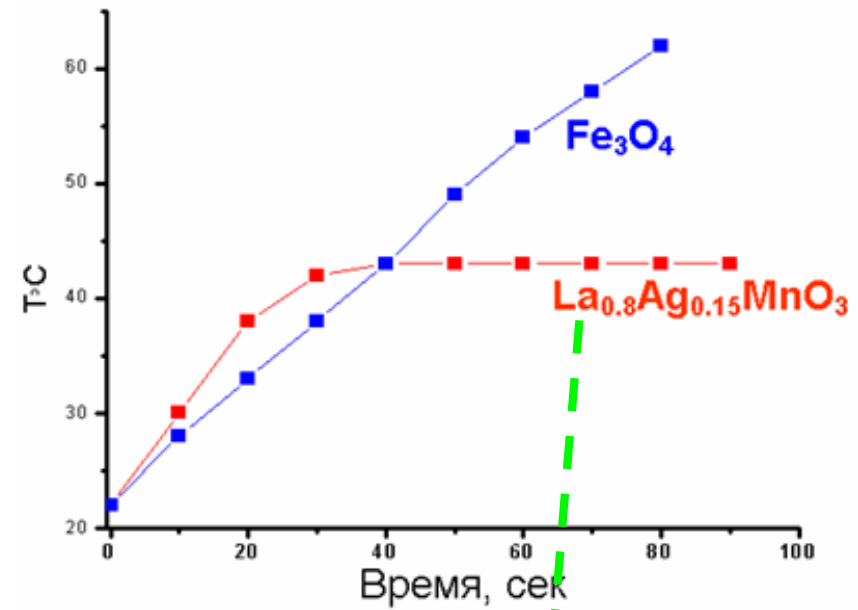
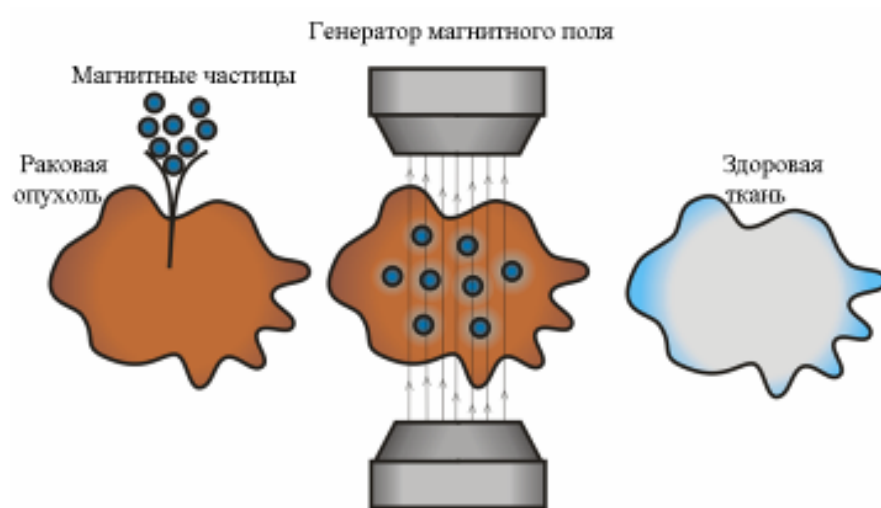
SPION / NaCl



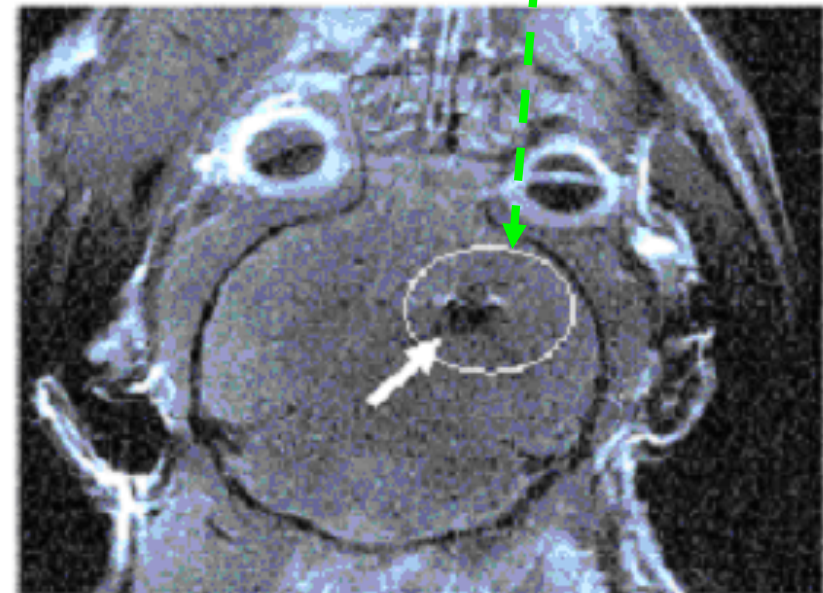
Средний размер магнитных наночастиц – 10 нм



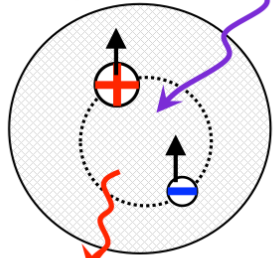
Локальная гипертермия



43-45°C:



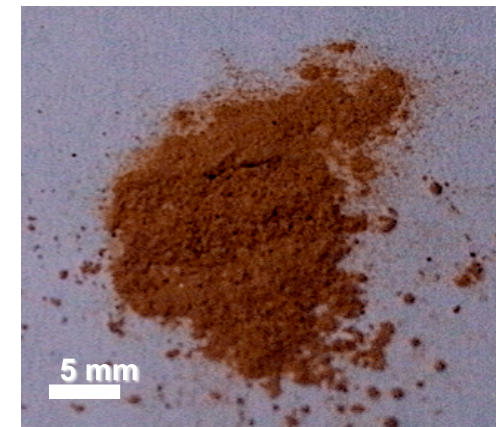
Нанокристалл
кремния



Синглетный
кислород

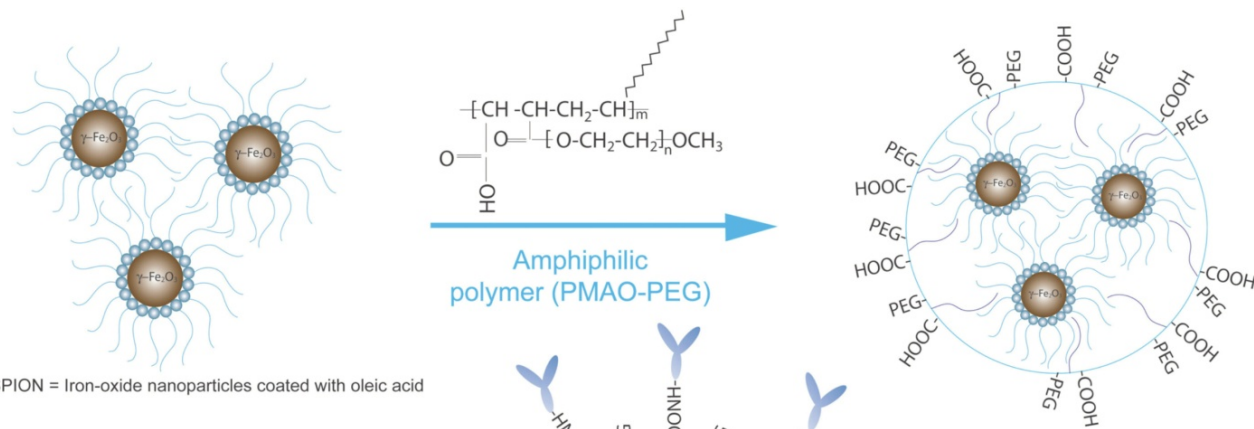
«Нанокремний»

D. Kovalev, V. Timoshenko et al., Phys. Rev. Lett. 89 (2002)

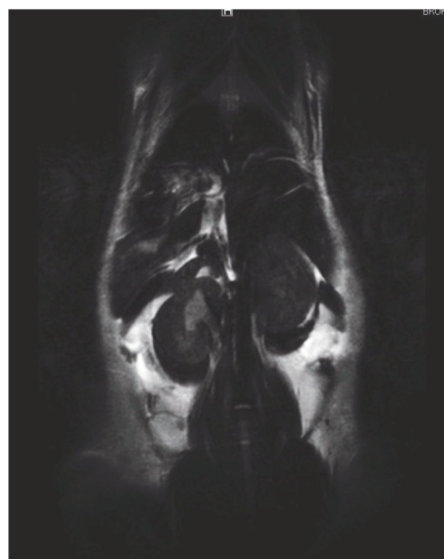
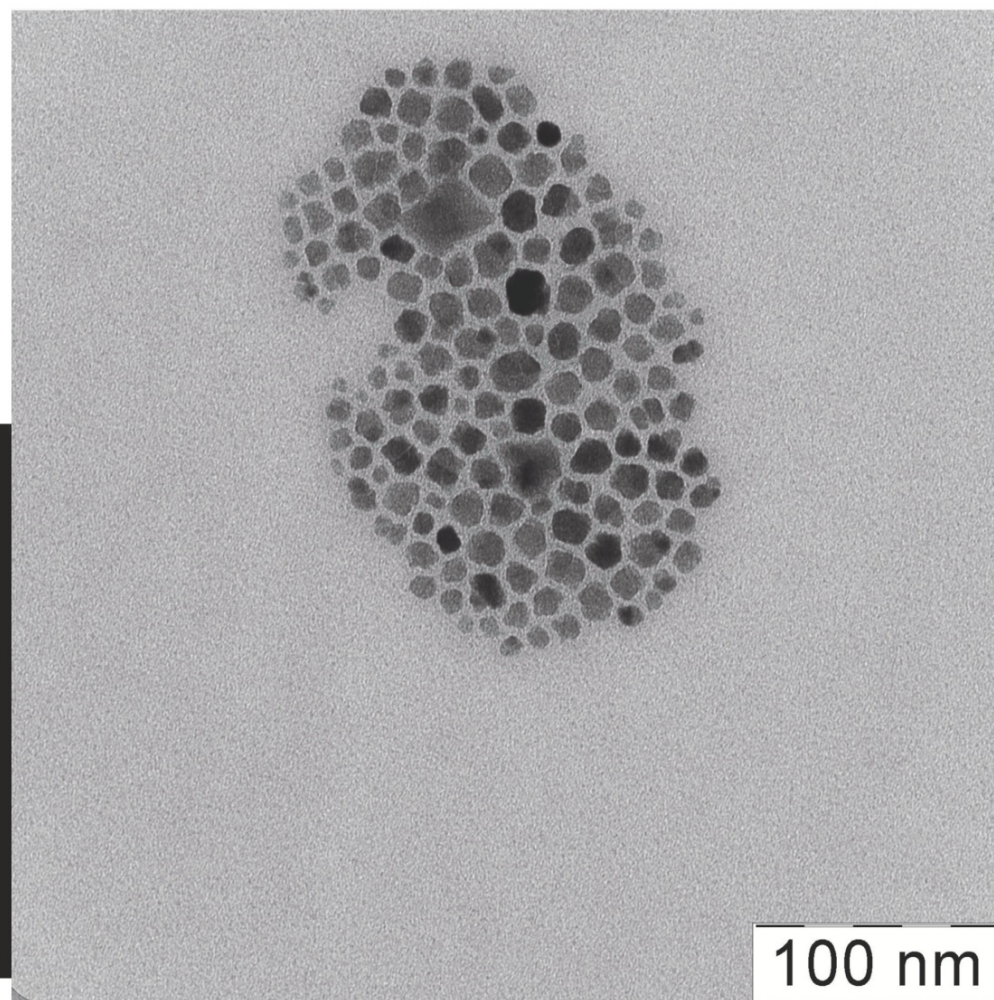
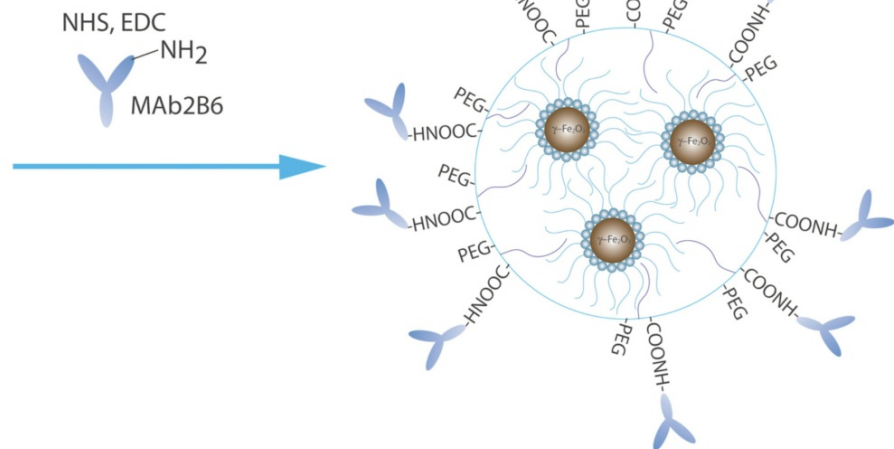


№ опыта	Время от введения препарата до облучения (час)	Время от облучения до забоя животного (час)	% распада (уменьшения) опухоли	Проникн. частиц в клетки: 0 – нет; 1 – да
1	0,5	24	30	0
2	0,5	4,5	50	0
3	0,75	24	55	0,5
4	0,4	72	60	0,5
5	4	48	70	1

- 1) Препарат может проникать в клетки, но не приводит к заметному некрозу в темновых условиях.
- 2) Активность препарата коррелирует со степенью его проникновения в клетки и наличием освещения, что указывает на протекание внутриклеточных фотохимических реакций.



SPION = Iron-oxide nanoparticles coated with oleic acid



Surface-Enhanced Raman Scattering

Поверхностно-усиленное комбинационное рассеяние (спектроскопия комбинационного рассеяния)



Леонид Исаакович
Мандельштам



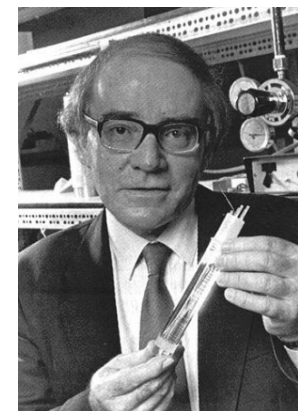
Григорий Самуилович
Ландсберг



Sir Chandrasekhara
Venkata Raman



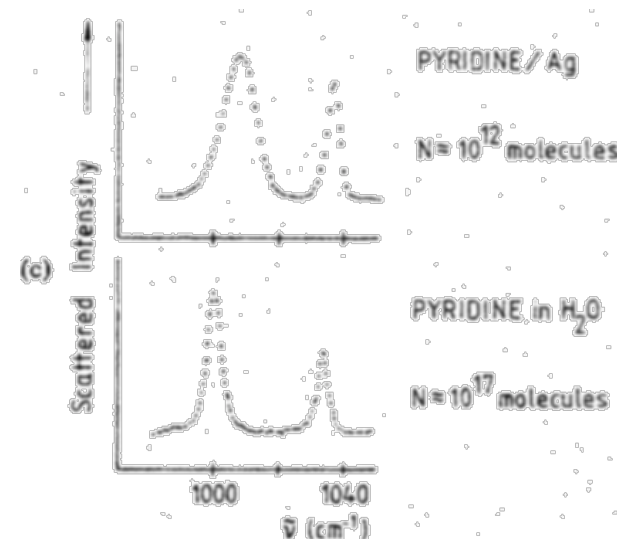
Kariamanikkam
Srinivasa Krishnan



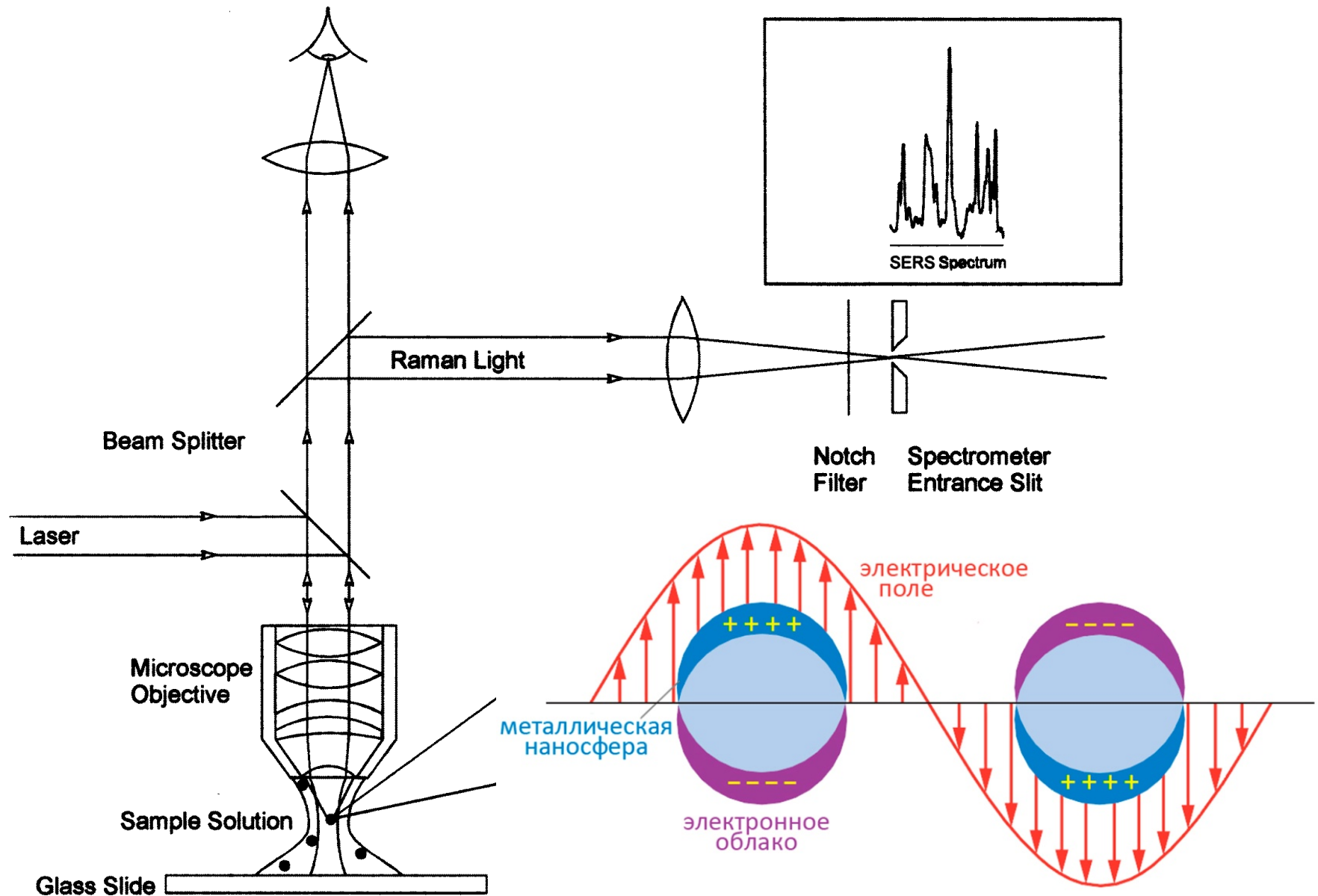
Martin
Fleischmann

1928 г. – открытие явления комбинационного рассеяния света Л.И.Мандельштамом и Г.С.Ландсбергом (Россия) для кристаллов и независимо от них Ч.В.Раманом и К.С.Кришнаном (Индия) для жидкостей.

1974 г. – работа по исследованию пиридина, адсорбированного на серебряном электроде.



Surface-Enhanced Raman Scattering/Spectroscopy



Event/discovery



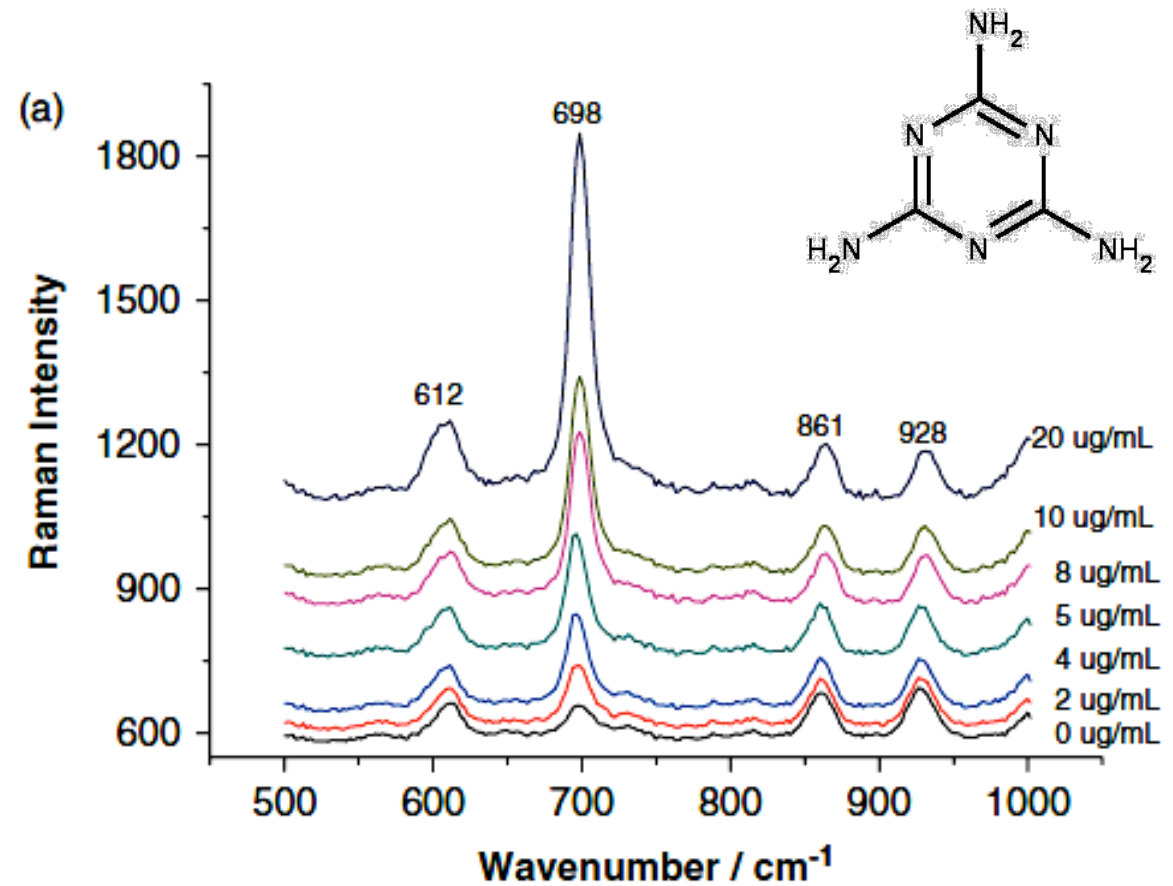
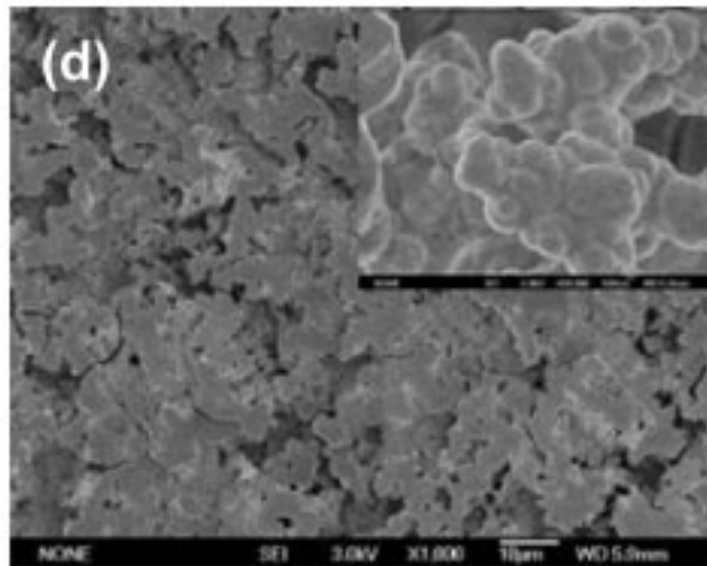
- 2018 ExoMars Rover, taking Raman spectroscopy to Mars
2010 Video-rate *in vivo* SRS Raman imaging by Sunny Xie
2010 SESORS reported by Graham, Faulds, Stone and Matousek
2009 Boyle and Smith awarded Nobel Prize in Physics for CCD
2005 SORS invented by Pavel Matousek
2000 TERS developed by Volker Deckert
1997 Single molecule SERS reported by Katrin Kneipp
1990s Significant increase in commercial instrumentation
1983 Enhancement of 10^{14} reported by Richard van Duyne
1982 Use of Ag and Au colloids for SERS by Lee and Meisel
1980s CCD detectors used for Raman
1980s Fibre optics coupled with Raman
1974 Fleischman and colleagues observe surface enhanced Raman scattering (SERS)
1970s Raman coupled with microscopy
1969 Invention of charge-coupled device (Willard Boyle and George Smith)
1964 Townes, Basov and Prochorov awarded Nobel Prize in Physics for invention of the laser
1960s Stimulated Raman and coherent anti-Stokes Raman (CARS) invented
1960s Lasers used as light source for Raman spectrometers
1957-59 Light amplification by stimulated emission of radiation constructed
1953 First commercial Raman spectrometer
1950 Observation of resonance Raman (RR) spectra
1940s Invention of Raman grating spectrometer
1930s Invention of the monochromator
1930 Sir Chandrasekhara Venkata Raman awarded Nobel Prize in Physics
1928 C.V. Raman and K.S. Krishnan: discovery of Raman effect experiments on 28 Feb
1928 Landsberg and Mandelstam: independent observation of inelastic light scattering
1927 Compton awarded Nobel Prize in Physics
1923 Arthur Compton (effect): discovered inelastic X-rays & γ -rays scattering in matter
1923 Adolf Smekal's prediction of the Raman effect
1922 CV Raman's monograph published on the Molecular Diffraction of Light
1921 CV Raman's experiments on the colour of the sea, showing that the colour was due to molecular diffraction
1917 Albert Einstein first theorizes about stimulated emission (On the Quantum Theory of Radiation)
1871-1899 Lord Rayleigh (John Strutt) further refines his theory of scattering in a series of papers
1871 Rayleigh scattering first described

Year

Fig. 1 A timeline of events and discoveries in the history of Raman spectroscopy, Nobel Prizes marked in red (photo of Sir C.V. Raman in the sculpture park of Nehru Science Centre, Mumbai, India, by Prof. Paul O'Brien FRS, School of Chemistry, University of Manchester).

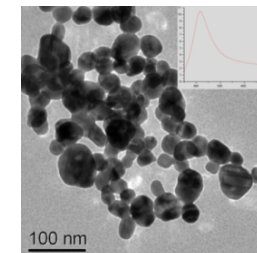
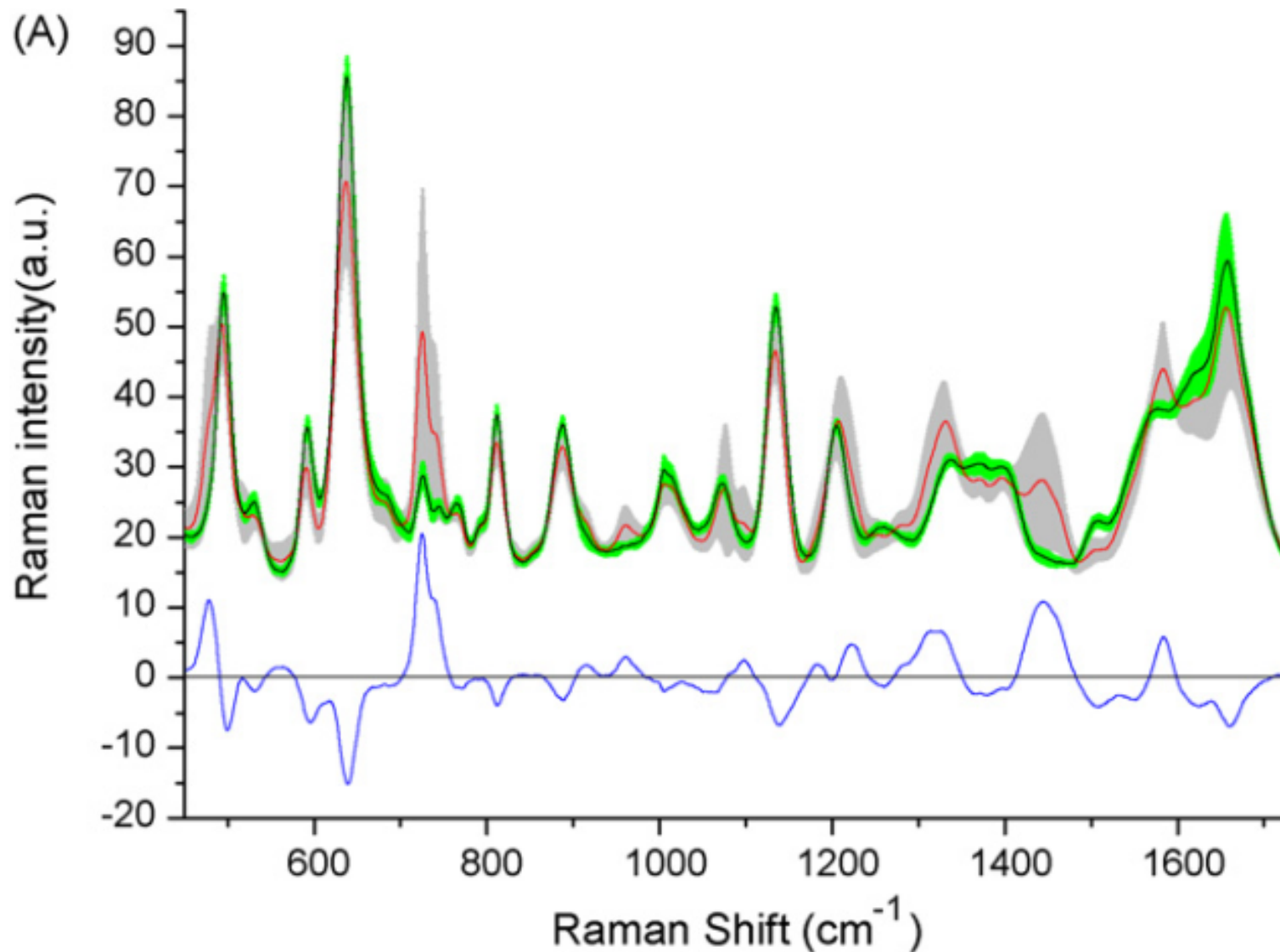
Детектирование меламина в молоке

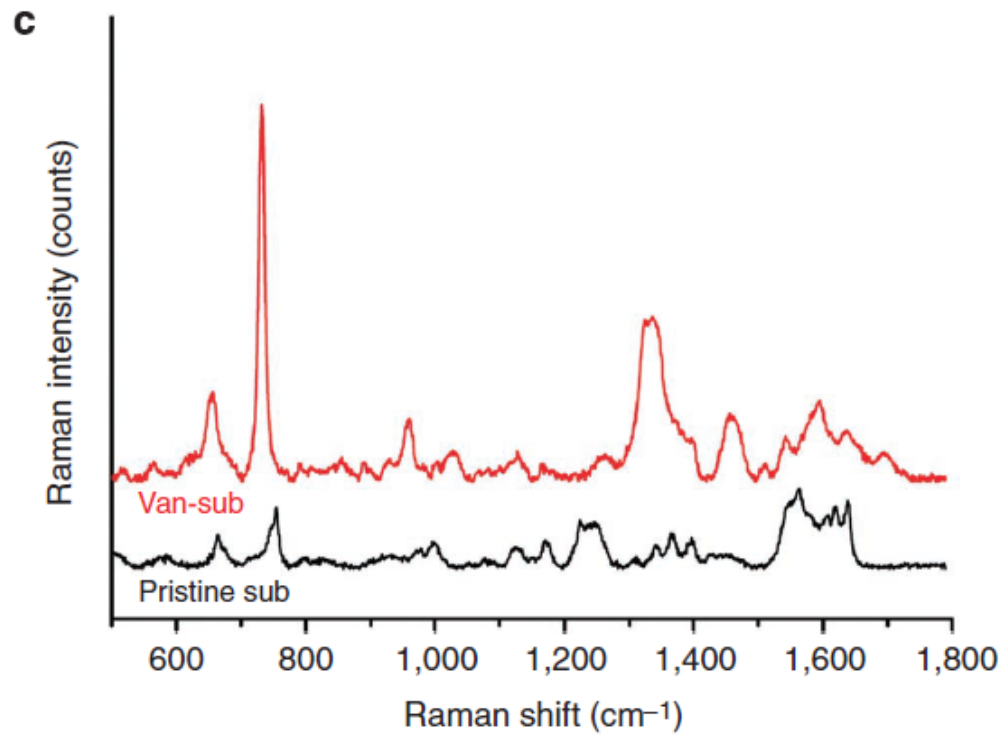
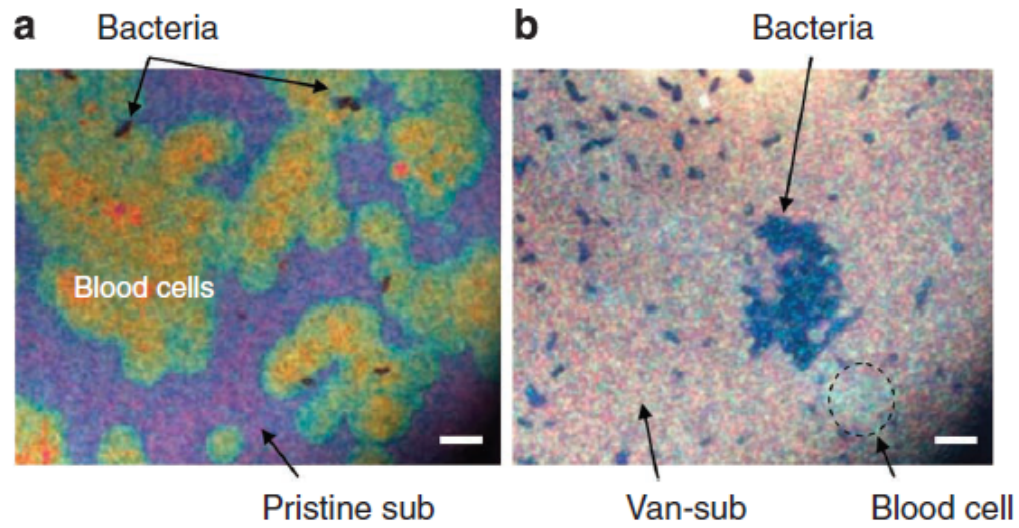
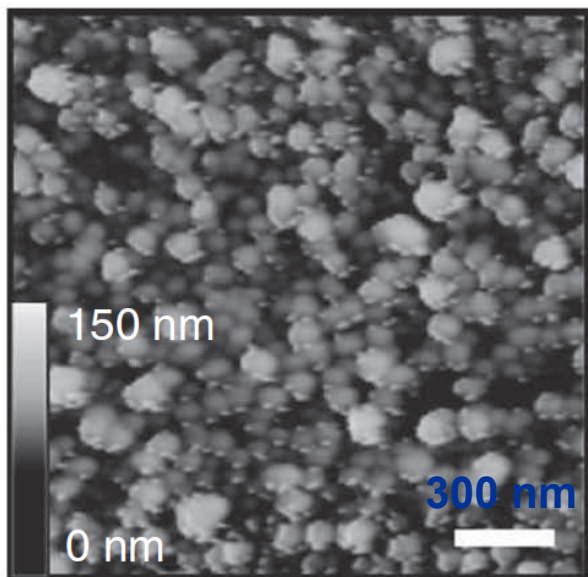
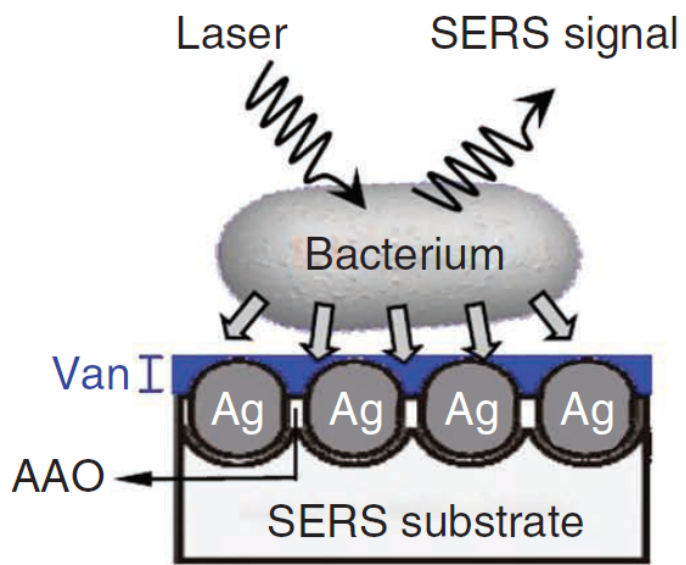
AgNO_3 , цитрат натрия ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) [нагревание до 100°C] {Lee, Meisel, 1982}

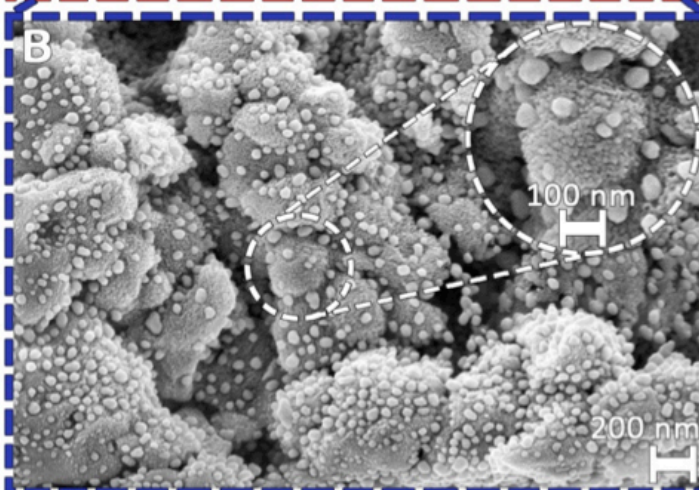
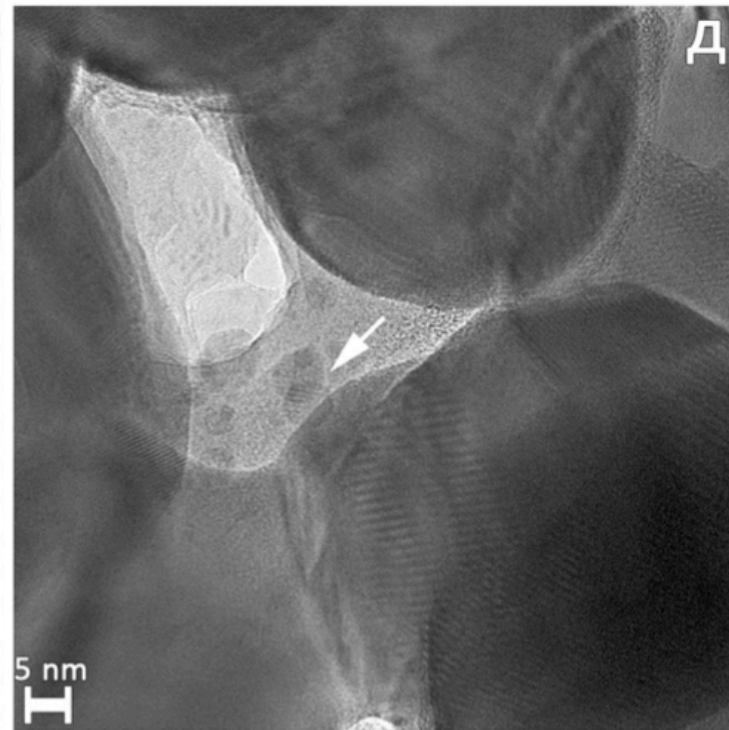
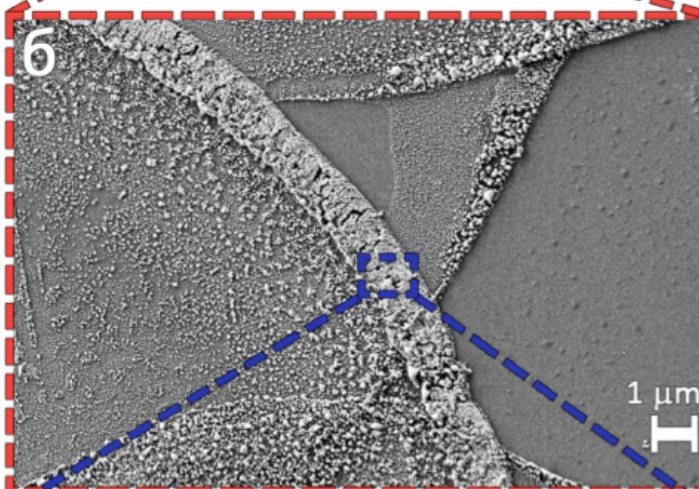
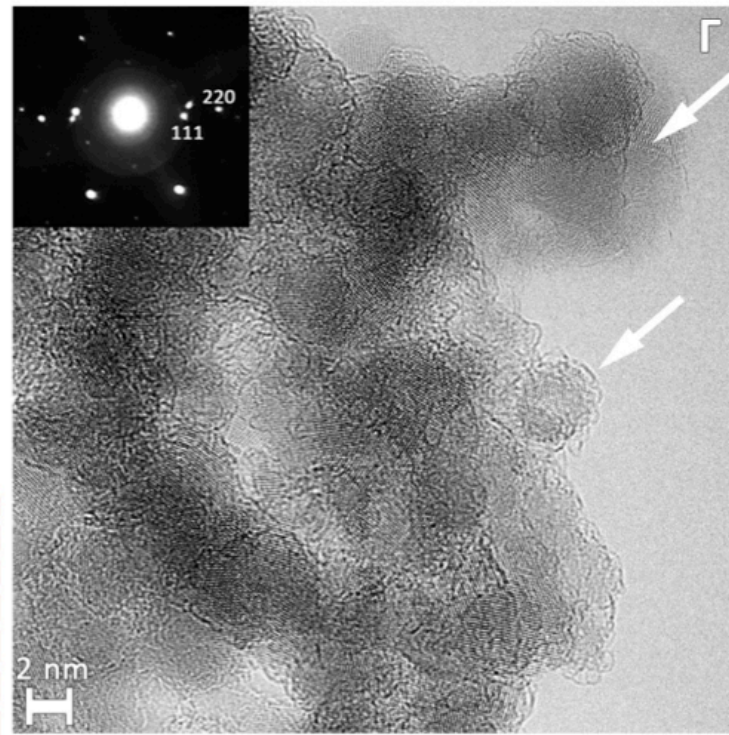
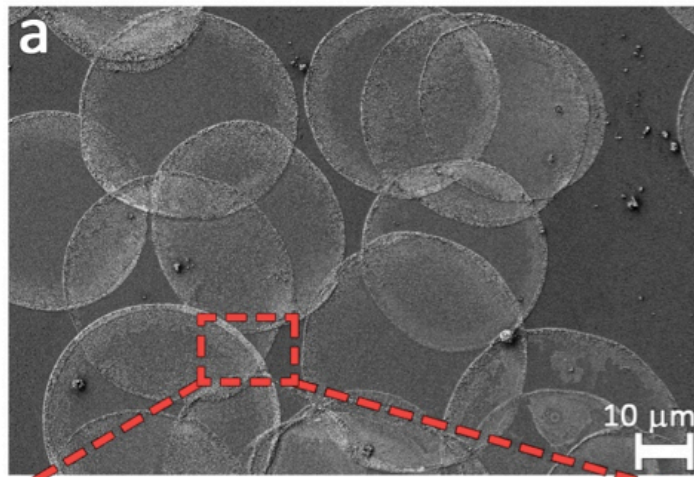


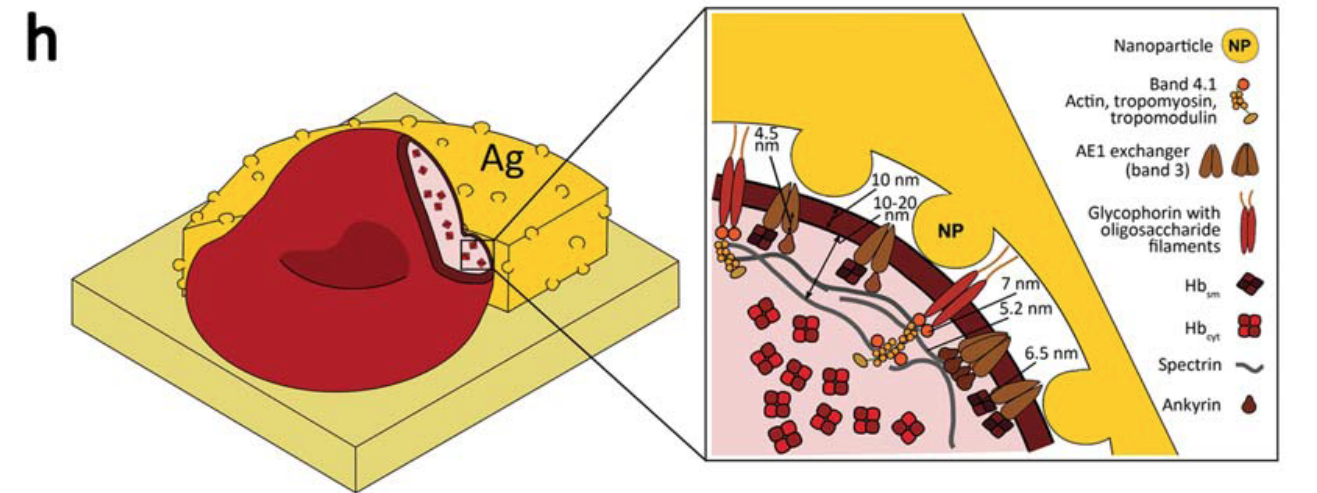
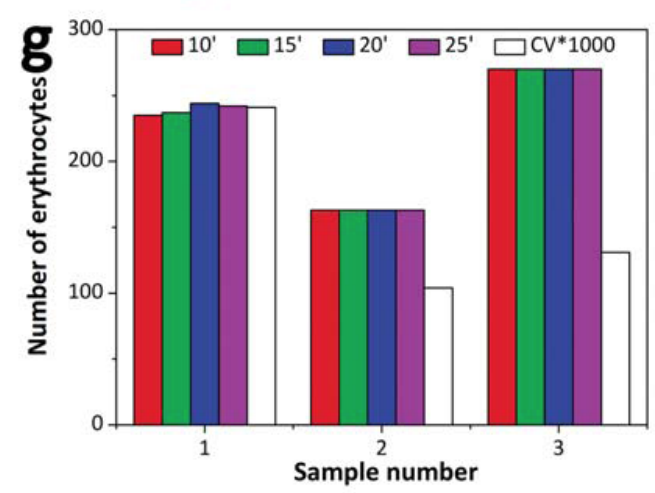
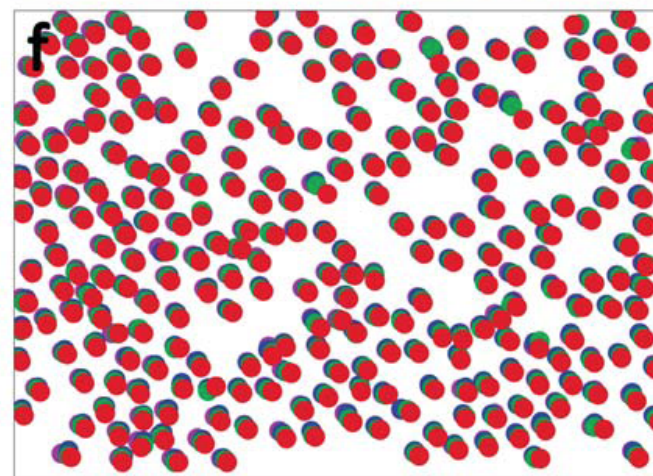
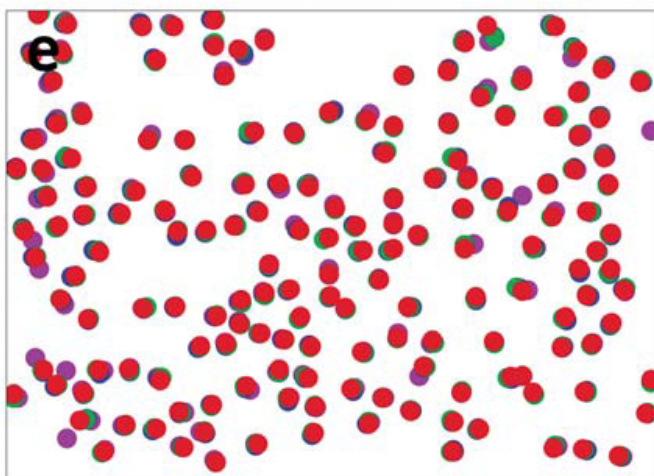
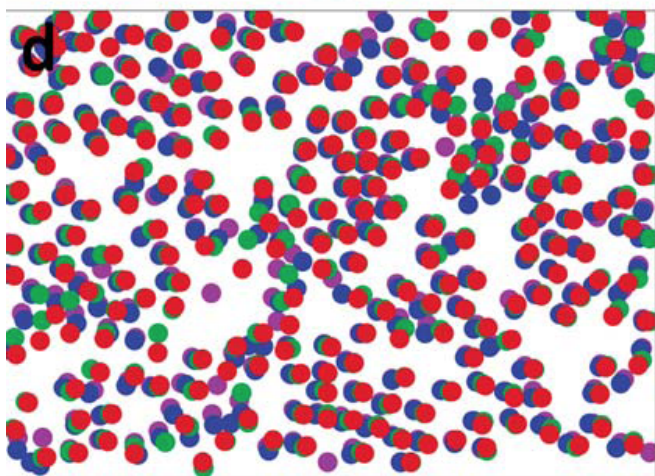
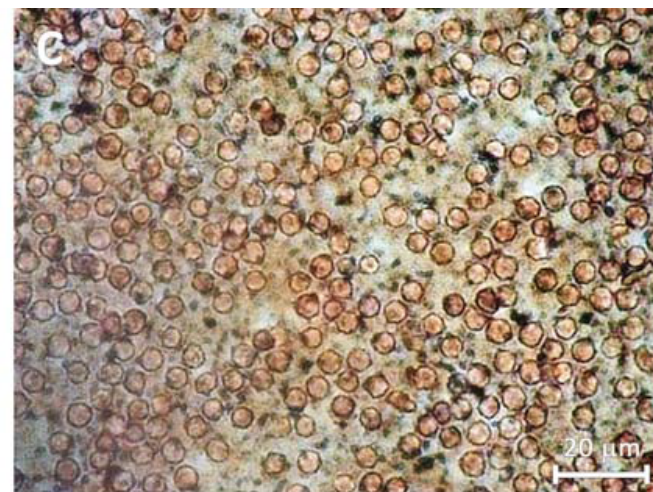
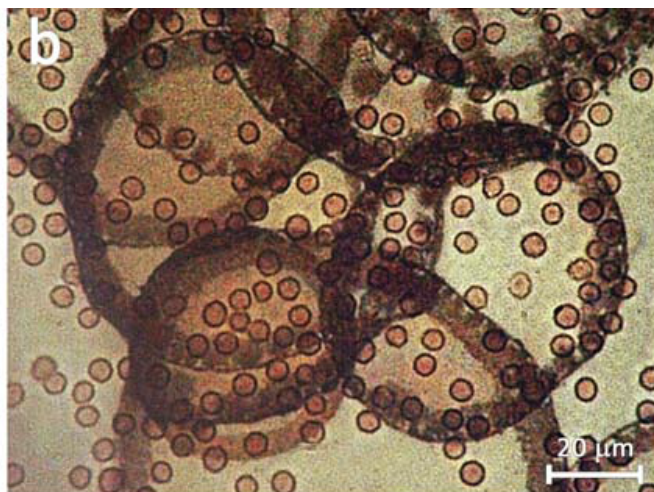
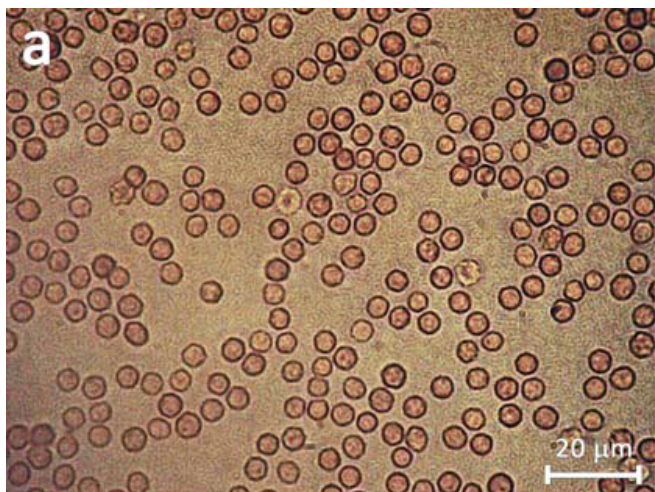
Диагностика онкологических заболеваний

AgNO_3 , гидрохлорид гидроксилamina ($\text{NH}_2\text{OH}\cdot\text{HCl}$), NaOH {*Leopold, Lendl, 2003*}









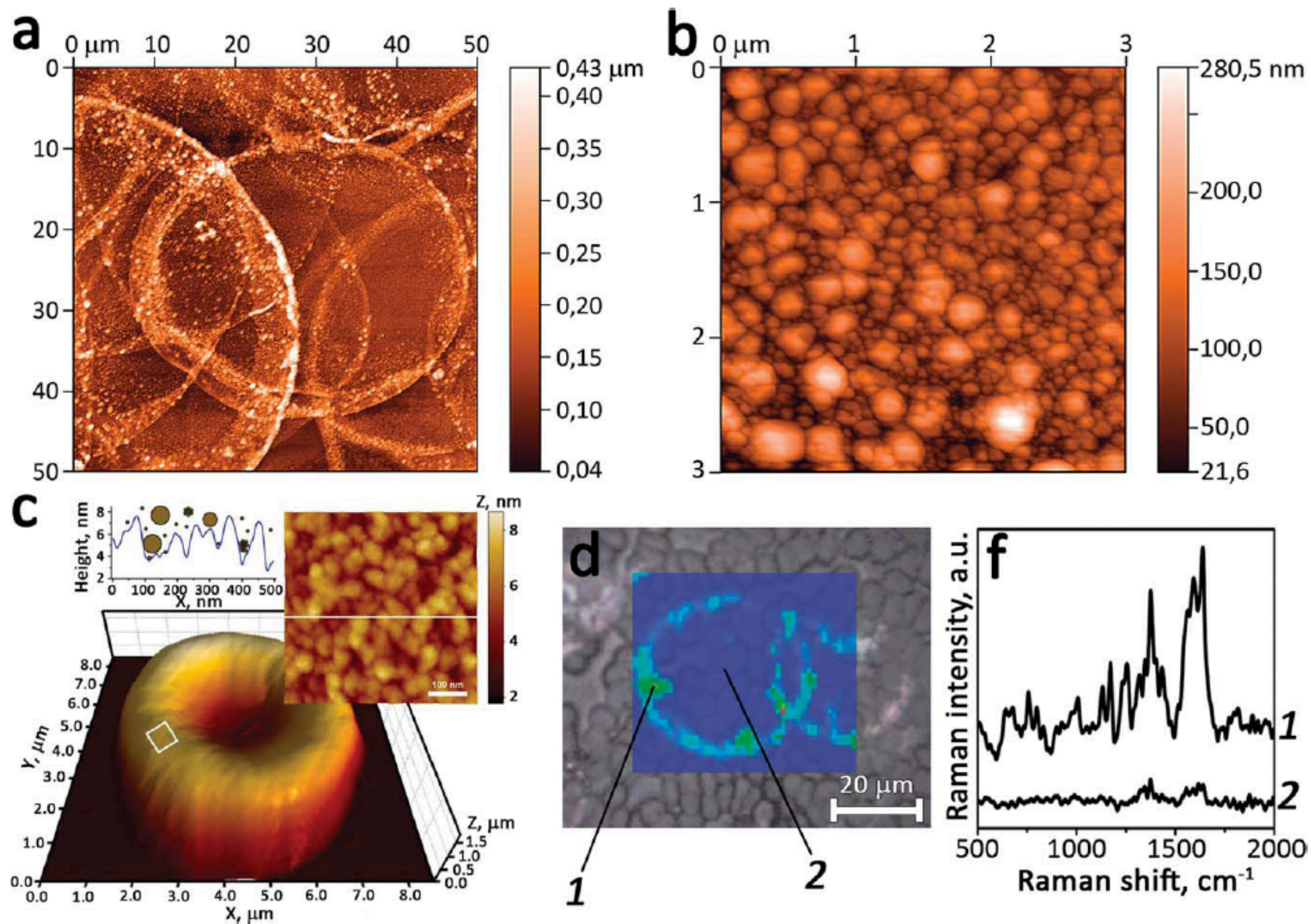
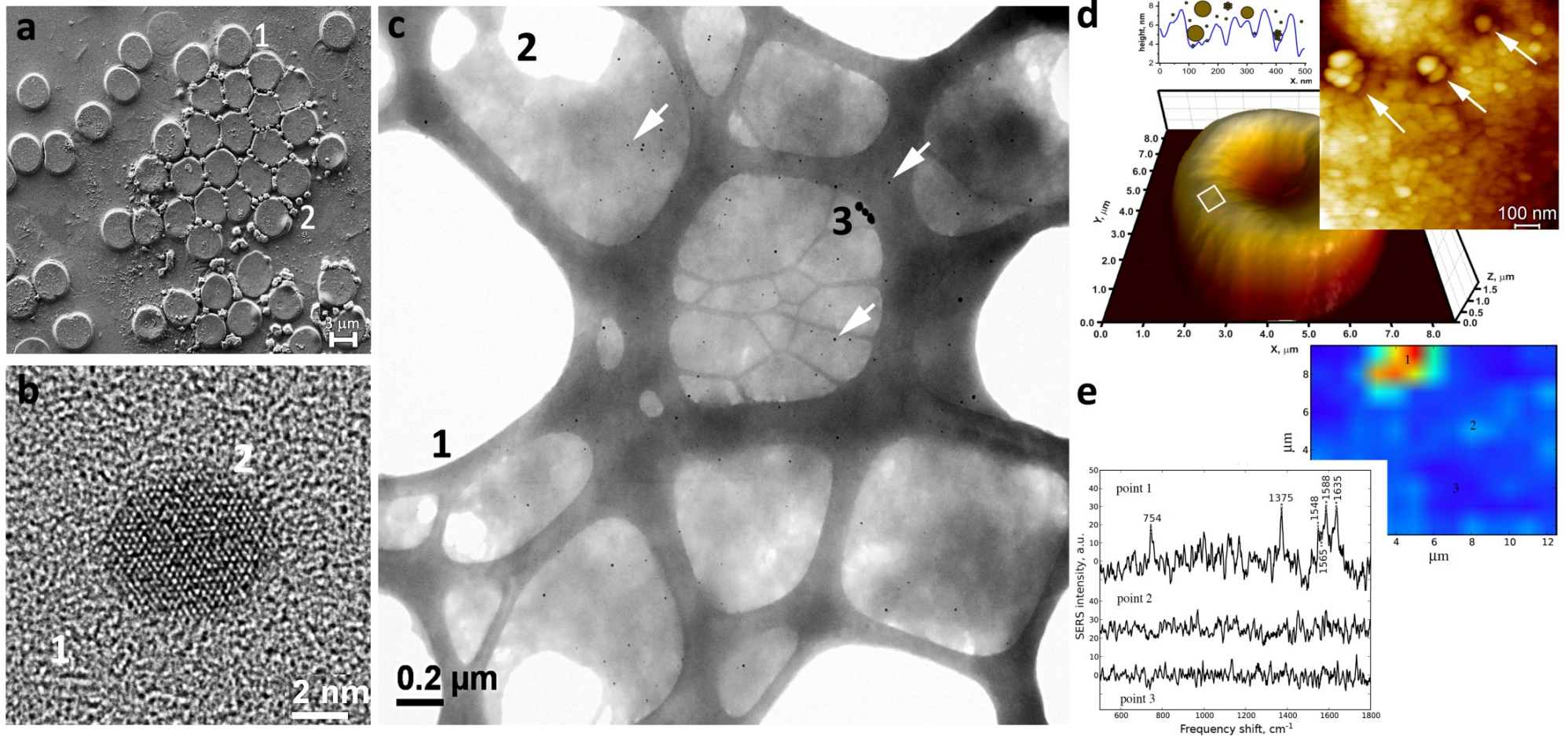
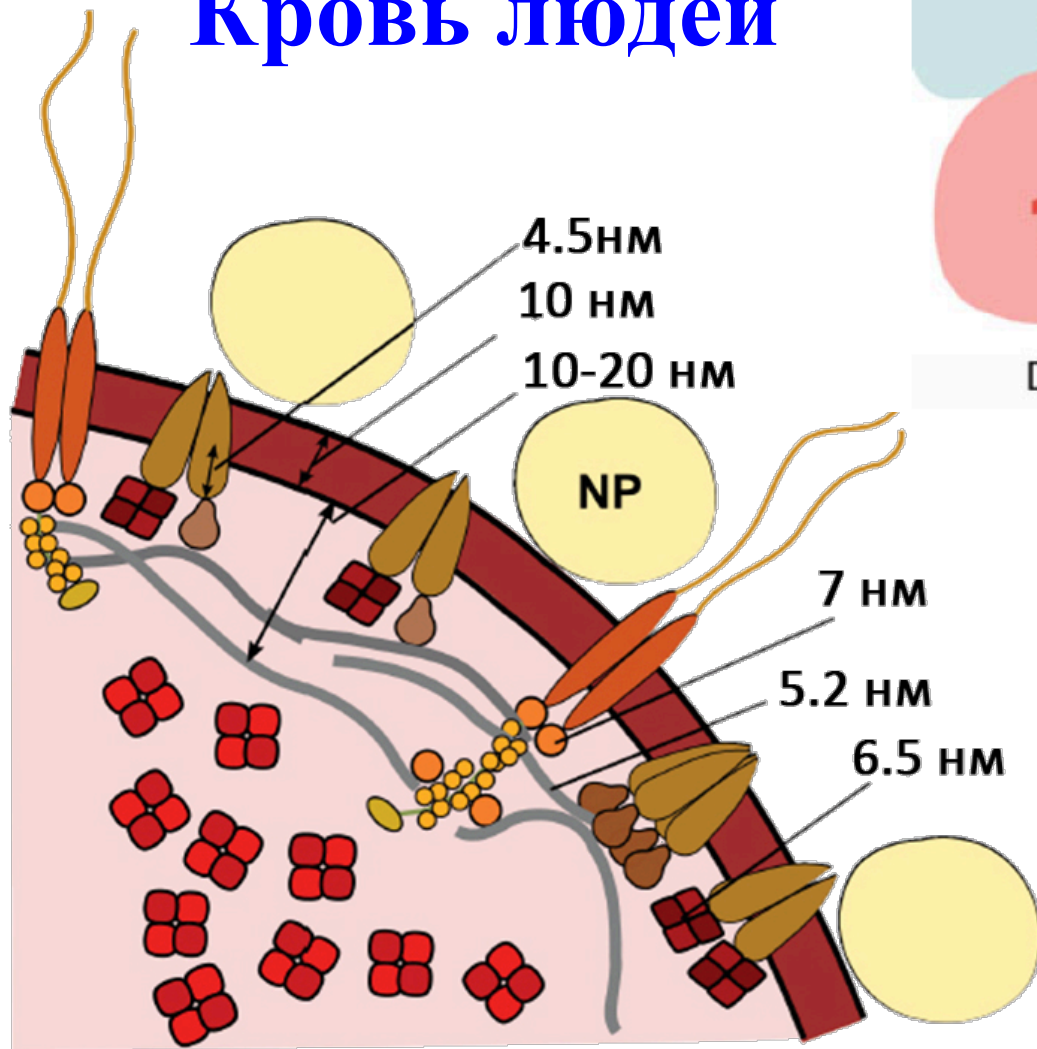


Fig. 10 The lock and key concept of successful SERS of living erythrocytes on USR substrates. (a) AFM image showing typical sizes of silver crater walls concentrating plasmonic silver; (b) AFM image of silver wall surfaces with elements suitable in their sizes ("key") for penetrating in erythrocyte membrane invaginations ("lock"); (c) AFM image of a single erythrocyte showing nanoscale details of its external surface; the profile graph is given for the white rectangular area, the spheres show hypothetically silver wall elements attempting to enter invaginations; (d) SERS mapping of erythrocytes on the USR substrate and typical SERS spectra measured from different points: on a crater wall and on a flat surface.

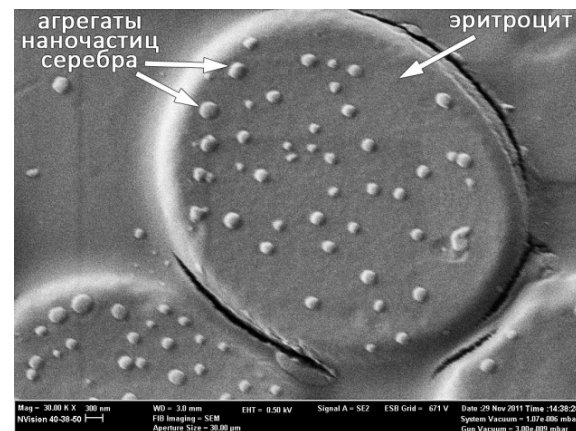
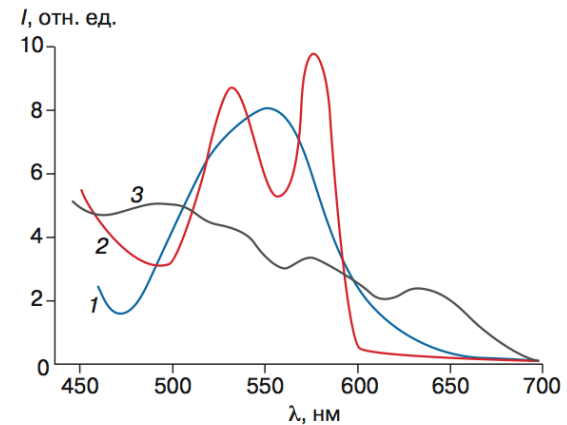
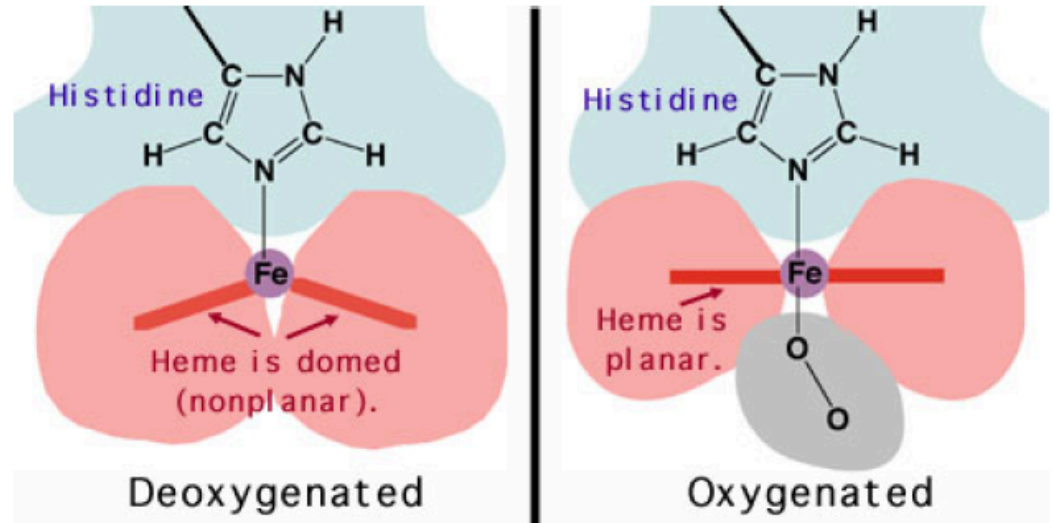
Серебро и клеточная мембрана

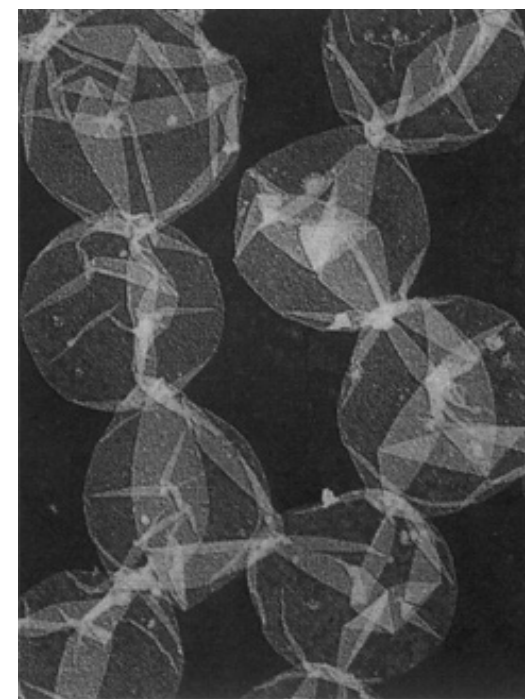
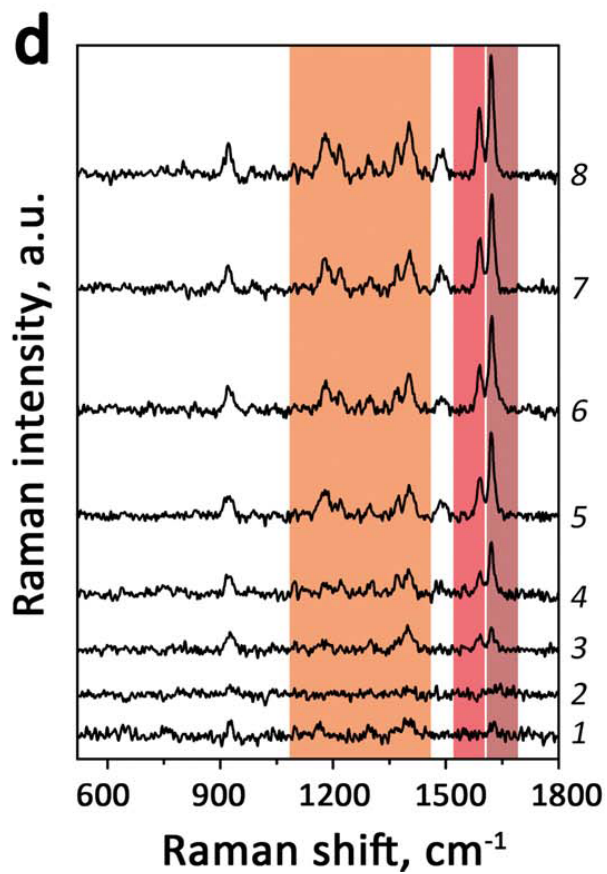
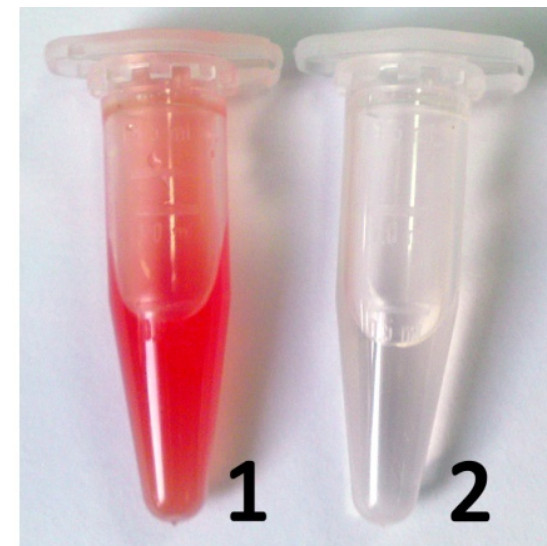
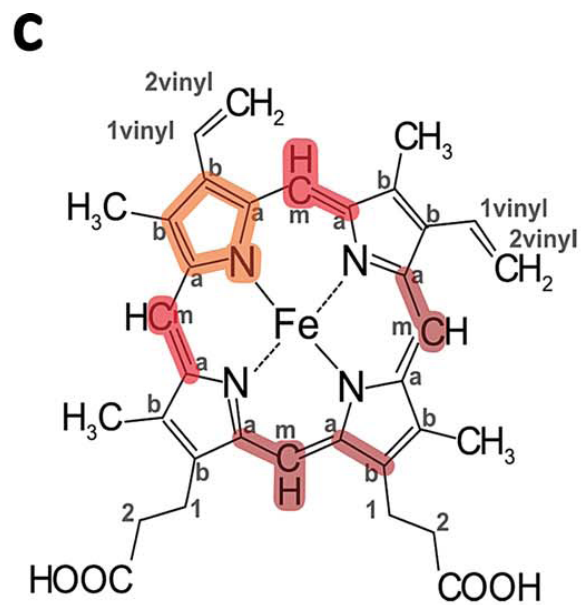
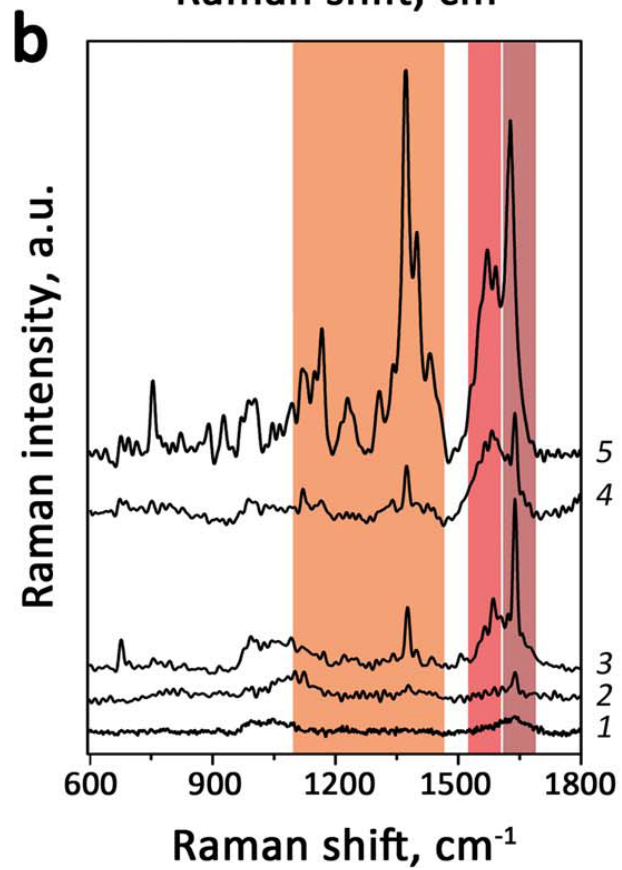
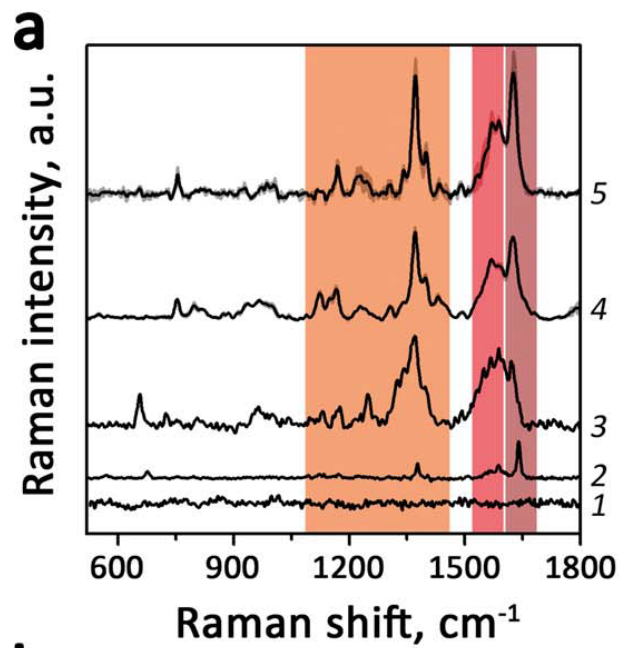


Кровь людей

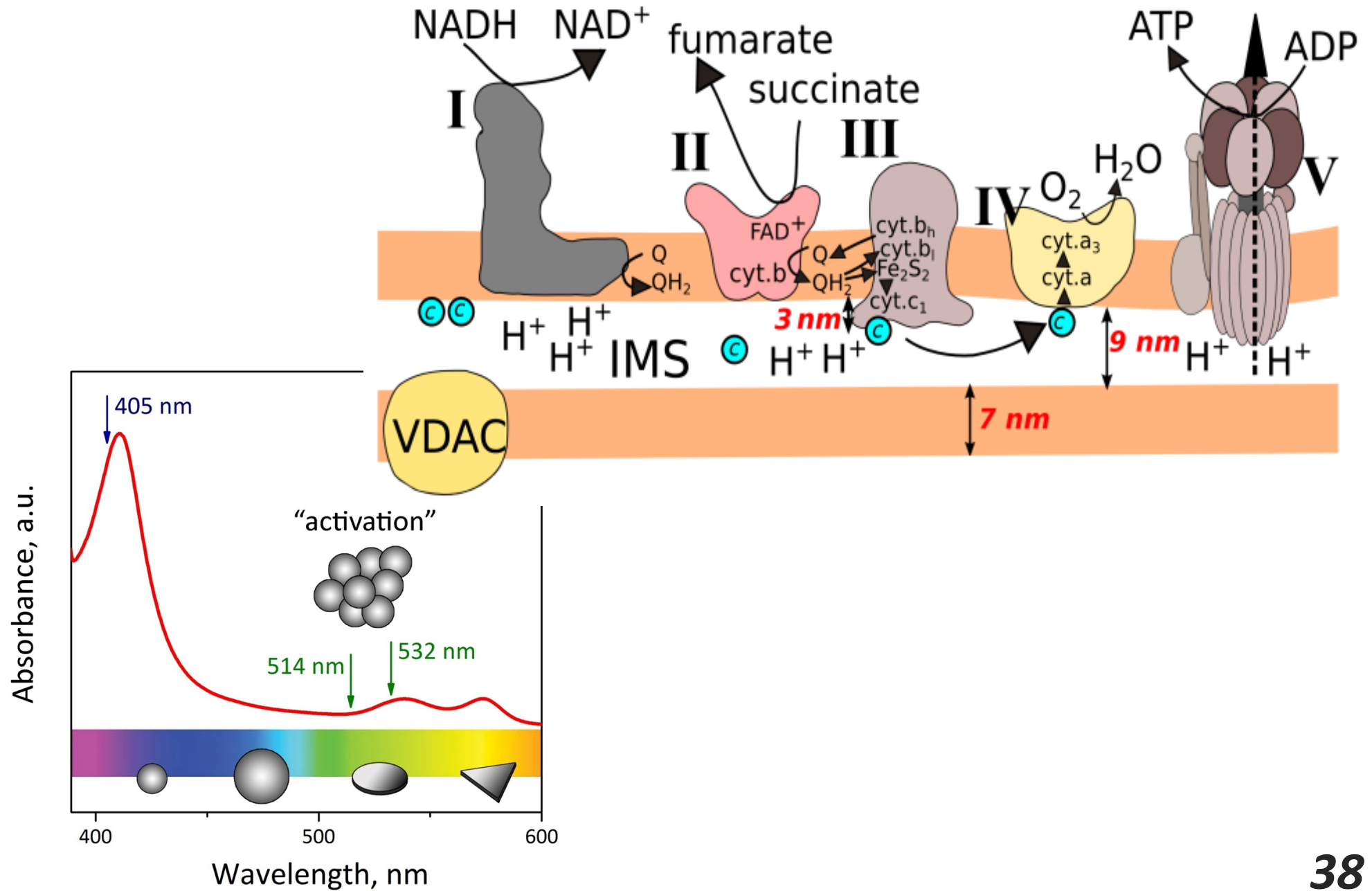


- NP Наночастица
- Гб_{мс} Гб_{цит} АЕ1 обменник (белок полосы 3)
- Анкирин
- Гликофорин
- Спектрин
- Белок полосы 4.1
- Актин, тропомиозин, тропомодулин

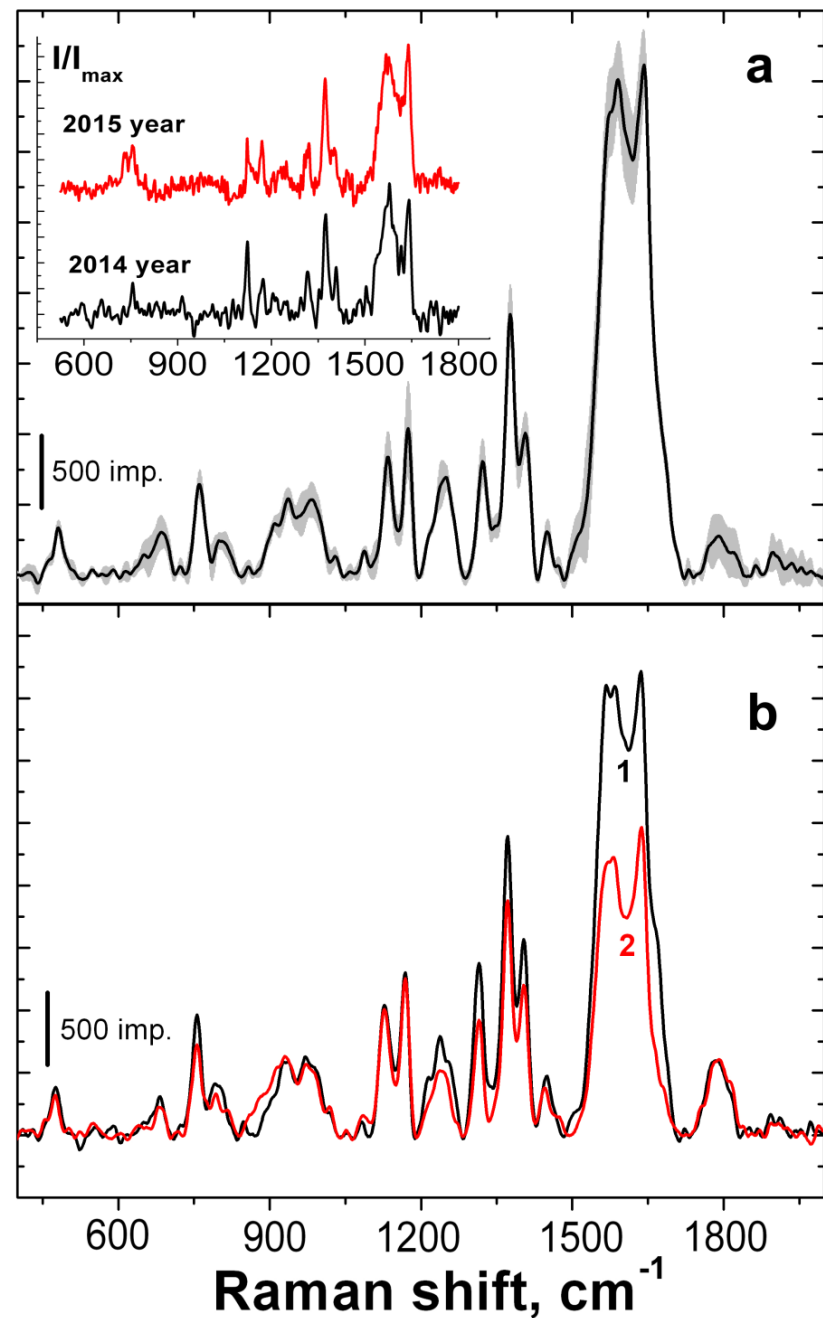
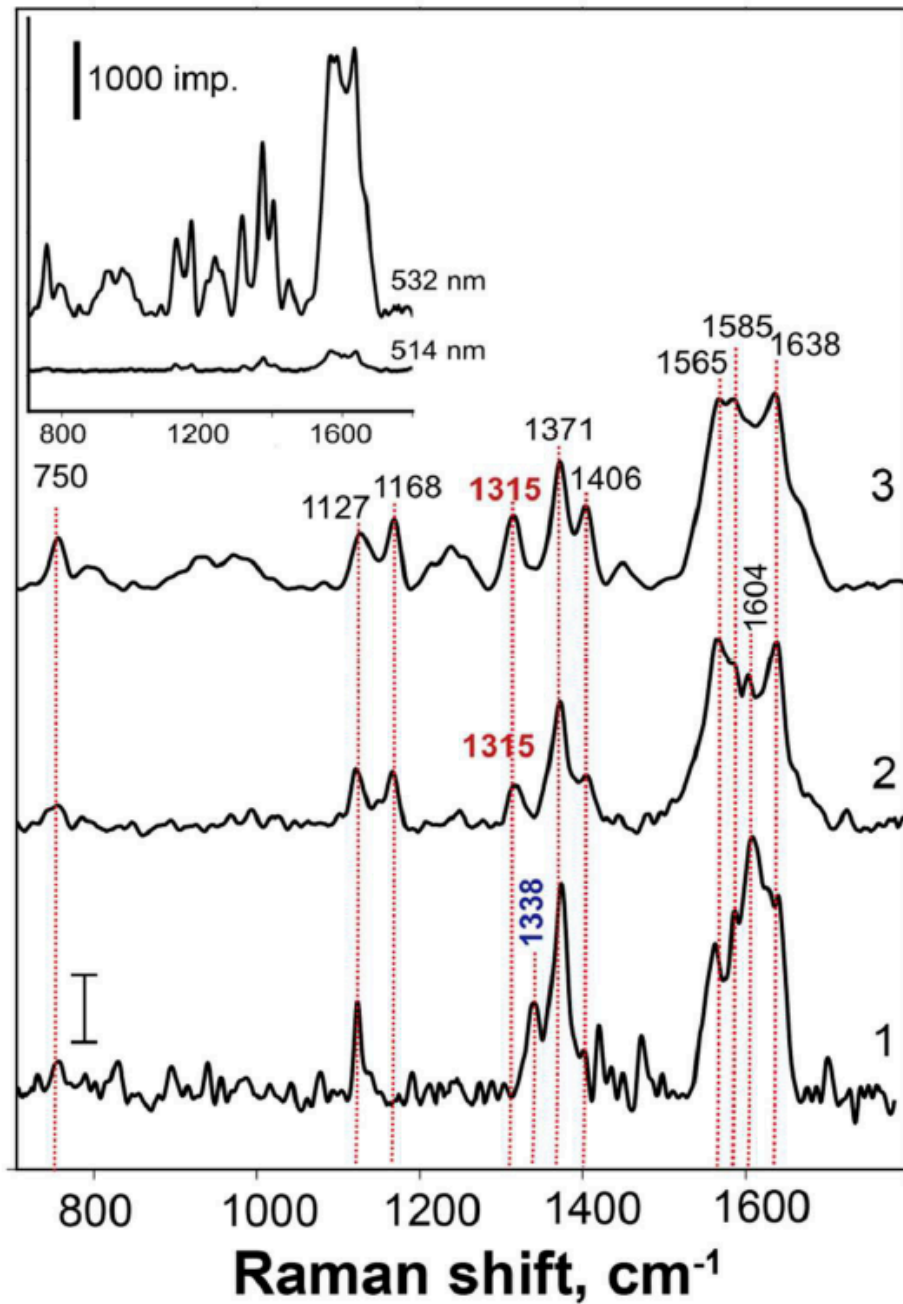




Митохондрии



Старение и воспроизводимость



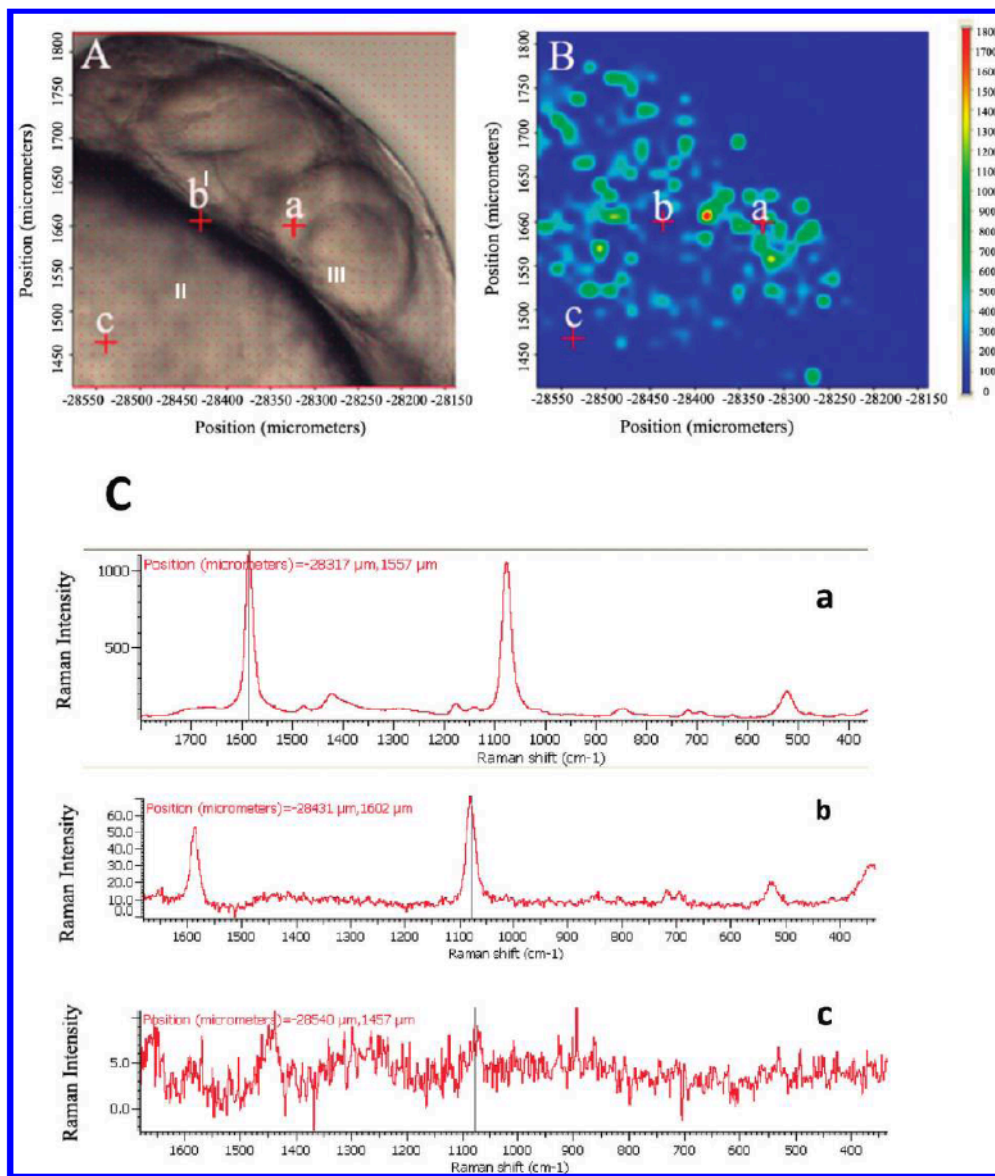


Figure 6. Raman mapping of the dorsal region of zebrafish embryo (14–16 hpf) injected with SERS NPs. (A) Optical image of the dorsal region of the zebrafish embryo and the markers highlight representative areas: (I) forebrain, (II) hatching gland, (III) eye. (B) SERS intensity map of the C–C vibration band from SERS NPs at 1078 cm⁻¹. (C) SERS spectra coll as shown in panels A and B.

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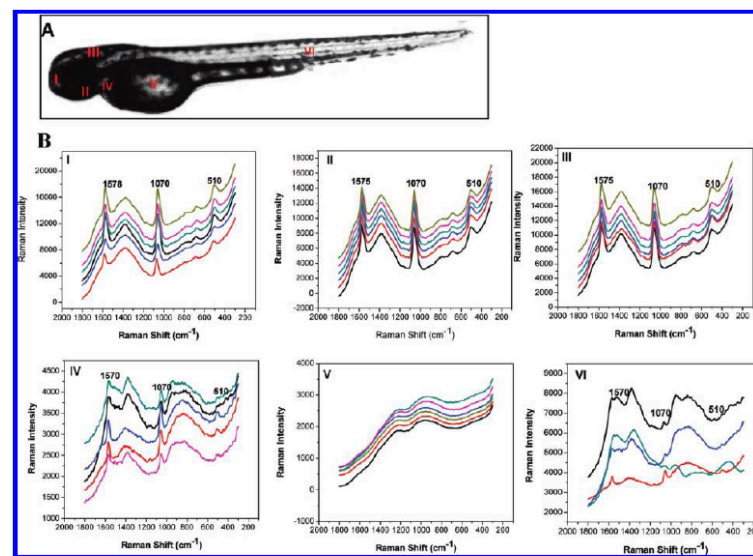


Figure 9. Characterization of SERS NPs embedded inside a fully developed (48 hpf) zebrafish using SERS measurement. (A) Optical image of a normally developed zebrafish. The red markers highlight representative areas: (I) forebrain, (II) pharyngeal skeleton, (III) hind-brain, (IV) heart, (V) yolk, and (VI) somite. (B) SERS spectra obtained from those tissue sections outlined in panel A.

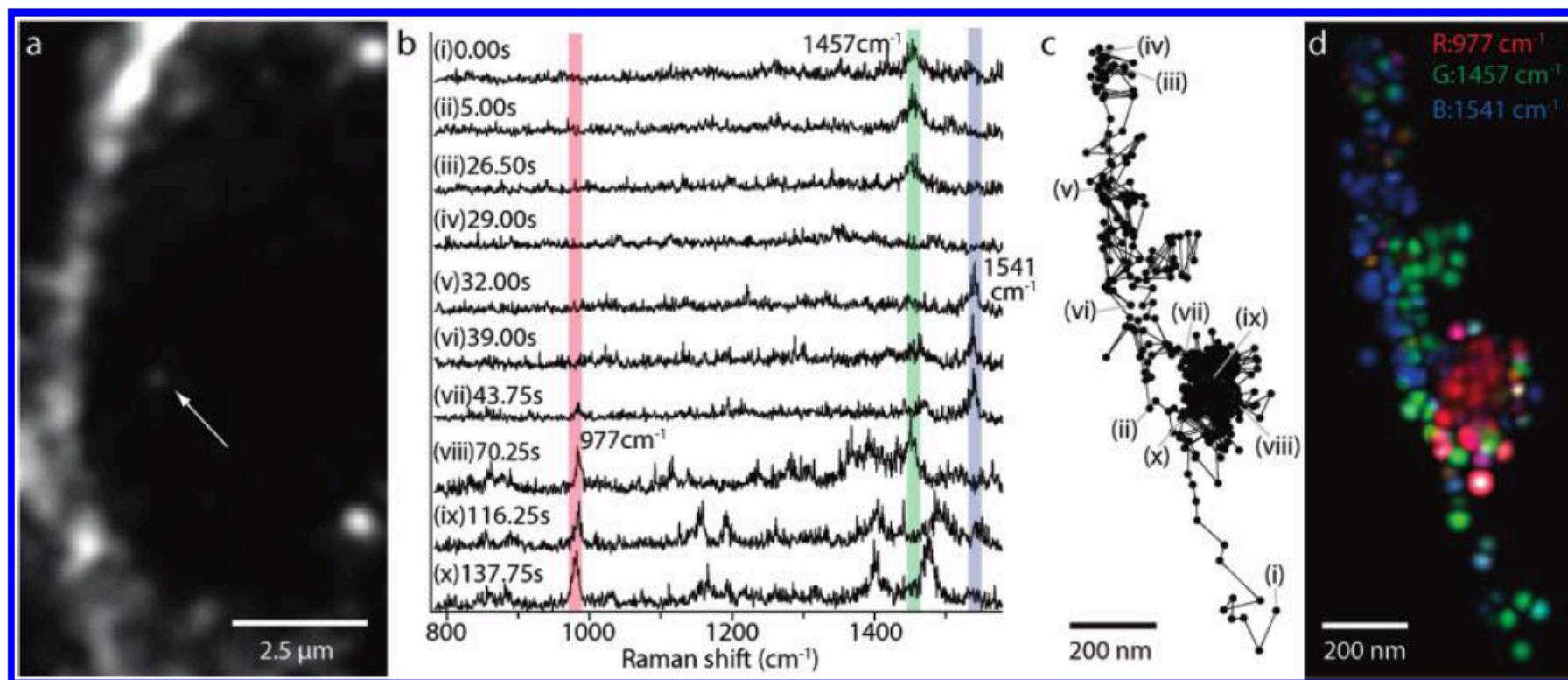
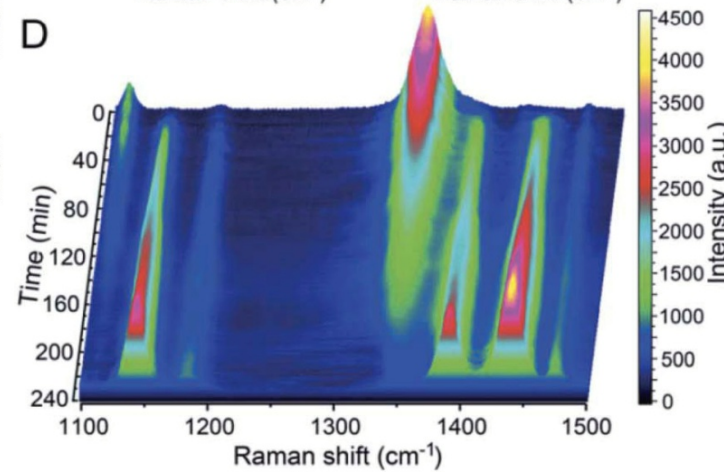
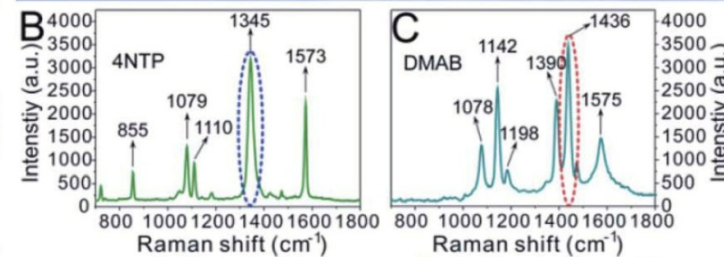
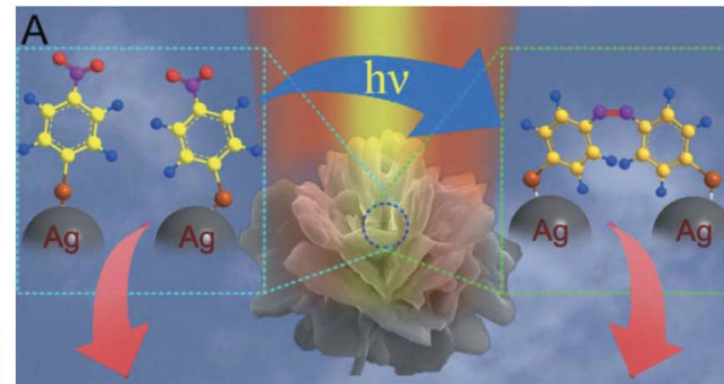
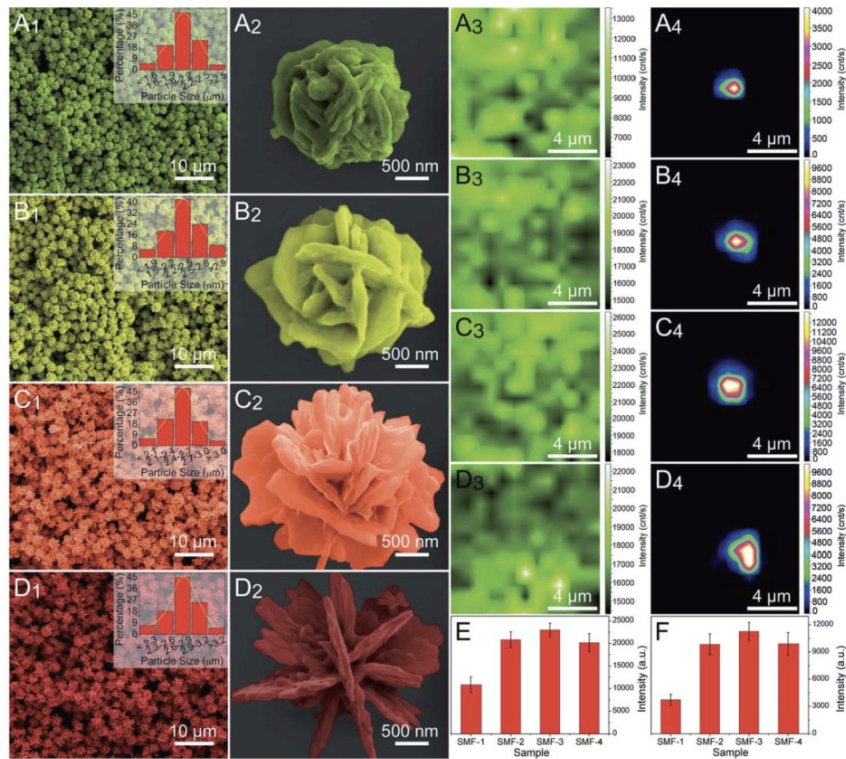


Figure 1. SERS analysis of the cellular pathway with an endocytosed gold nanoparticle. (a) An image of a J774A.1 macrophage cell taken by dark-field microscope. The white arrow indicates a gold nanoparticle seen as a small white spot. The gold nanoparticle is taken up by endocytosis of the cell. (b) SERS spectra, obtained from the nanoparticle indicated in panel a. Characteristic Raman peaks were observed at 977 cm^{-1} (assigned to the vibration mode of phosphate), 1457 cm^{-1} (vibration mode of CH_2 and CH_3), and 1541 cm^{-1} (vibration mode of Amide II). These three Raman peaks are overlaid with bars in red, green and blue. (c) Trajectory of the nanoparticle, marked by a white arrow in panel a, obtained from the dark-field images. (d) An RGB color map of the molecular distribution displayed on the nanoparticle trajectory. Green spots show the Raman intensity distribution of 1457 cm^{-1} , blue spots 1541 cm^{-1} , and red spots 977 cm^{-1} . The green and blue color is highlighted during the linear paths, while the red color appears during the confined zone random walk. The spatial resolution is determined as $\sim 65\text{ nm}$, resulting from the particle diameter $\sim 50\text{ nm}$ and measurement accuracy $\sim 15\text{ nm}$.

Фотоиндуцированный катализ и in situ SERS



X. Tang et al. Nanoscale, 2014

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