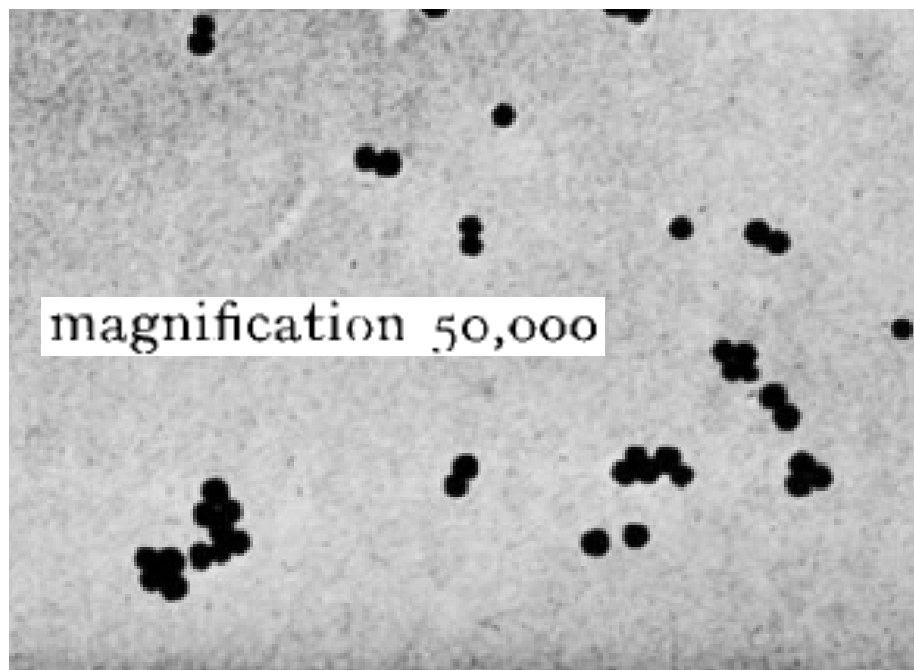


Химия для технологий малых частиц

Индивидуальные задачи для студентов кафедры ФТН:

- записать все химические реакции, протекающие при получении малых частиц;
- указать возможные побочные реакции;
- определить какие реагенты находятся в избытке;
- дать оценки изменения скорости процесса во времени *<как смещаются окислительно-восстановительные или кислотно-основные равновесия? – найти необходимые равновесные потенциалы, рК и т.п.>*;
- рассчитать концентрацию полученного золя или суспензии (в предположении о полном превращении одного или более реагентов).

Золото – «рецепт» М. Фарадея



FARADAY SOL⁴ was prepared in the following way. A saturated solution of white phosphorus in freshly distilled diethyl ether was diluted with three times its volume of diethyl ether. 50 ml. of chlorauric acid solution (50 mg. of Au) was diluted with 45 ml. of distilled water and with 5 ml. of 0.1 N KOH. This solution was treated, using good mechanical stirring, in one case with 2.0 ml. of the phosphorus-ether solution and in the other case with 1.0 ml. of the same solution. The solution turned first brown, then grey, purple and red, finally giving a deep-red product. The sol was then heated to boiling and a

⁴ Faraday, *Phil. Trans.*, 1857, 147, 145

Золото – «рецепт» Дж.Туркевича, самый популярный

CITRIC ACID GOLD SOL.—95 ml. of chlorauric acid solution (containing 5 mg. of Au) were heated to the boiling point and 5 ml. of 1 % citric acid solution was added to the boiling solution with vigorous mechanical stirring. The solution remained clear for about 15 sec. and then suddenly a dark blue-purple sol was formed. There was no further change of colour on prolonged boiling.

Turkevich and Hillier, *Anal. Chem.*, 1949, **21**, 475.

Типичная современная версия этого «рецепта»

6.7 ml solution of HAuCl_4 (10 mg/ml) was diluted with water to a total volume of 100 ml. The solution was heated with vigorous stirring in a reflux setup. To the boiling solution, 1.6 g of tri-sodium citrate was added abruptly. The reduction reaction caused a moderate change in color, from light yellow to gray and finally to deep red. The colloid solution was maintained under boiling and stirring conditions for 15 min and was then cooled slowly to room temperature.

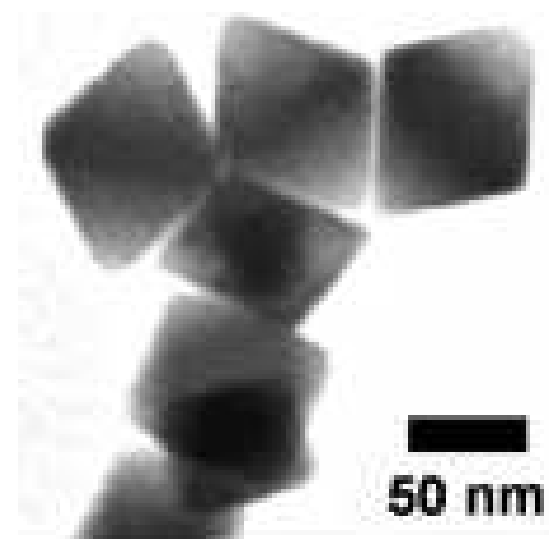
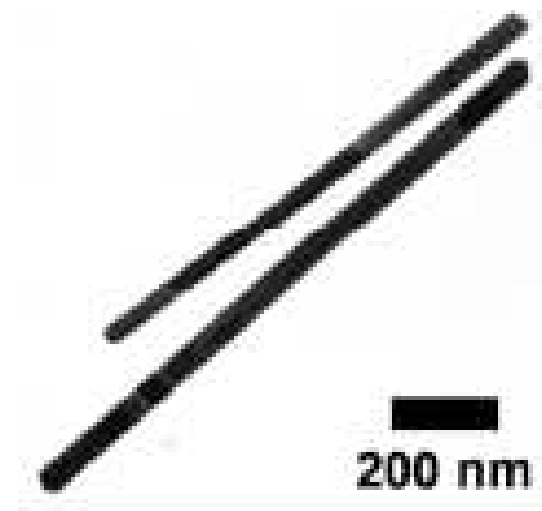
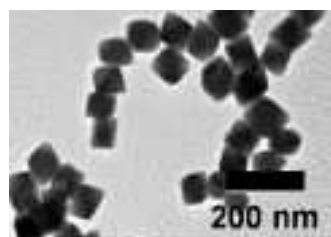


Дополнительный вопрос: чем две эти версии отличаются?

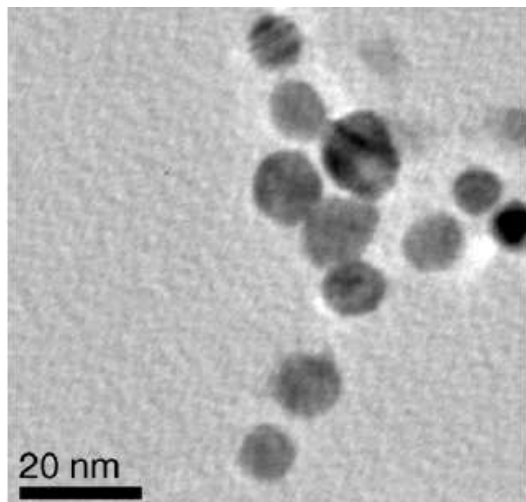
Сверхпроводящий металл (индий) – варьирование формы

In nanoparticles were synthesized by the dropwise addition of a solution of NaBH_4 in tetraethylene glycol (TEG) to a solution of InCl_3 and poly(vinyl pyrrolidone) (PVP, MW = 630000) in isopropyl alcohol (IPA). In a typical synthesis, InCl_3 (10 mg) and PVP (0.10 g) were dissolved in 10 mL of IPA. After purging with Ar, 15 drops ($13 \mu\text{L}/\text{drop}$, $\sim 0.2 \text{ mL}$ total) of a freshly prepared NaBH_4/TEG solution (0.07 g of NaBH_4 in 5 mL of TEG) were added at ambient temperature. After 10 min of stirring, the precipitate was separated by centrifugation and washed several times with ethanol. The isolated product was easily dispersible in water and ethanol. It is important to note that if an IPA solution of NaBH_4 is used, In nanocrystals do not form, presumably because of a faster reaction of NaBH_4 with the alcohol than with In^{3+} . Using TEG as the solvent for NaBH_4 maintains its reactivity long enough to reduce In^{3+} to In^0 after it is added to IPA.

The rate of dropwise addition of the NaBH_4/TEG solution to the InCl_3/IPA solution, and therefore the reduction kinetics, influenced the shape of the In nanocrystals.



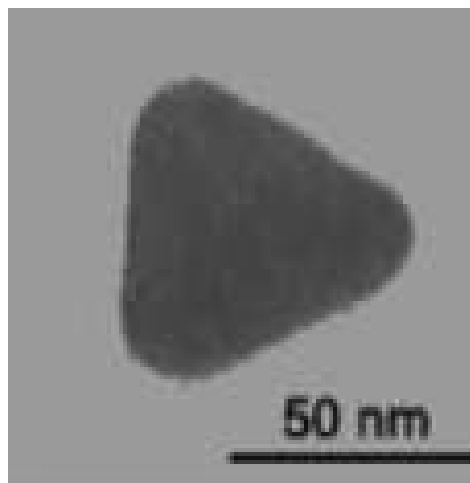
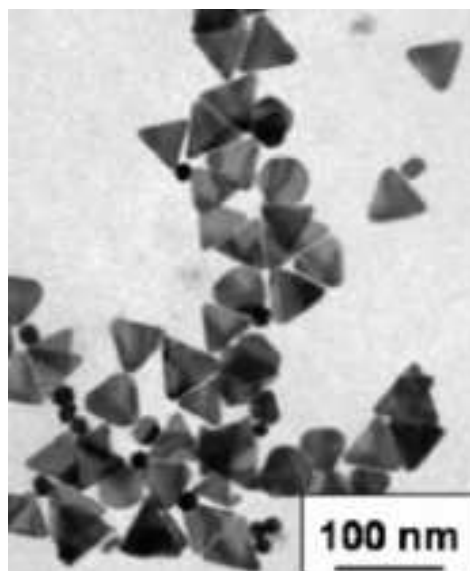
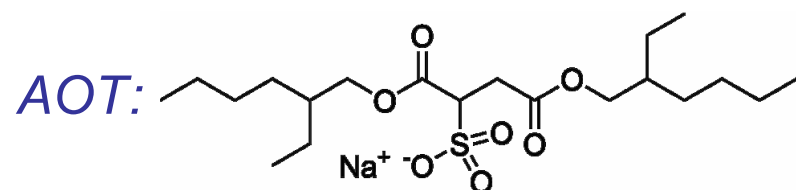
Серебро для оптических методов и устройств



A 10-mL volume of 1.0 mM silver nitrate was added dropwise (about 1 drop/second) to 30 mL of 2.0 mM sodium borohydride solution that had been chilled in an ice-bath. The reaction mixture was stirred vigorously on a magnetic stir plate. The solution turned light yellow after the addition of 2 mL of silver nitrate and a brighter yellow (Figure 1A) when all of the silver nitrate had been added. The entire addition took about three minutes, after which the stirring was stopped and the stir bar removed.

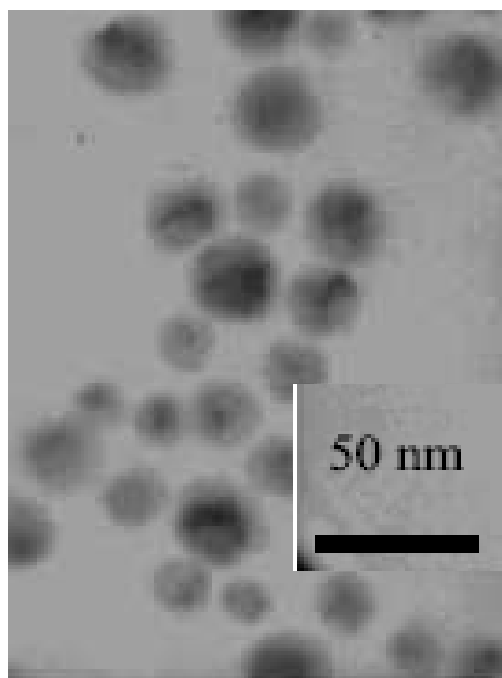


Серебро для оптических методов и устройств – - варьирование формы



2.2. Synthesis of Silver Nanoplates. The synthesis of silver nanoplates mainly followed the procedures described in our recent study.¹⁶ It was conducted at room temperature ($\sim 25^\circ\text{C}$). In a typical procedure, three steps were involved. First, 5.0 mL of aqueous AgNO_3 (0.01 M) and 5.0 mL of NaAOT (0.02 M) solution were added to a 250-mL conical flask, then Milli-Q water was added to the flask, and the final volume of the mixture was fixed to 200 mL, which was followed by stirring for around 10 min. Second, 0.67 mL of citrate acid (0.10 M) and 0.56 mL of L-ascorbic acid (0.10 M) freshly made aqueous solution were quickly added to the mixed solution containing Ag^+ ions and AOT, followed by vigorously stirring for ~ 1 min. Finally, 10.0 μL of ice-bathed aqueous NaBH_4 solution (0.01 M) was quickly added to the above mixed solution and was stirred for about 30 s. Gradually, the color of the solution changed from light yellow to purple, pink, green, and dark blue over about 10 min, in which the as-prepared silver nanoplates formed.

Серебро для оптических методов и устройств – - оболочка на золотом ядре



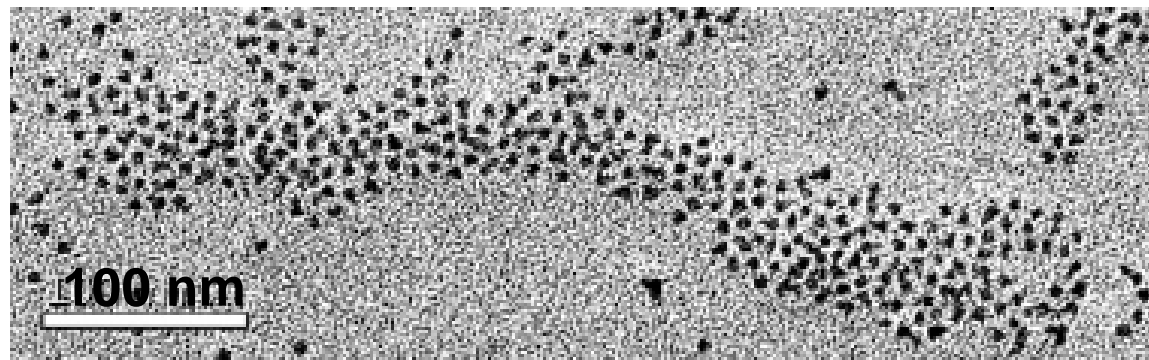
A 100 ml solution containing 0.01 g $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was heated to boiling, and then 3 ml of a 1% sodium citrate solution was added to the boiling solution. The solution was further boiled for 40 min and then left to cool to room temperature. From transmission electron microscopy (TEM) measurements, the average particle diameter obtained was 12 nm, with a standard deviation of 2 nm. The preparation of core-shell Au–Ag composite nanoparticles was as follows. Five sets of solutions (A, B, C, D, E) containing 0.5 ml of 10 mM AgNO_3 , 1 ml of 100 mM ascorbic acid, and 20 ml of 50 mM CTAB were prepared. Afterwards, different amounts (2, 1, 0.5, 0.2, 0.1 ml) of the 12 nm seed solution were added, respectively, and then 0.1 ml 1M NaOH was added drop-by-drop to the above solutions while stirring. Within 1–10 min, a color change occurred varying from red to brown depending on the seed concentration, suggesting the formation of composite nanoparticles.

Квантовые точки (теллурид кадмия)

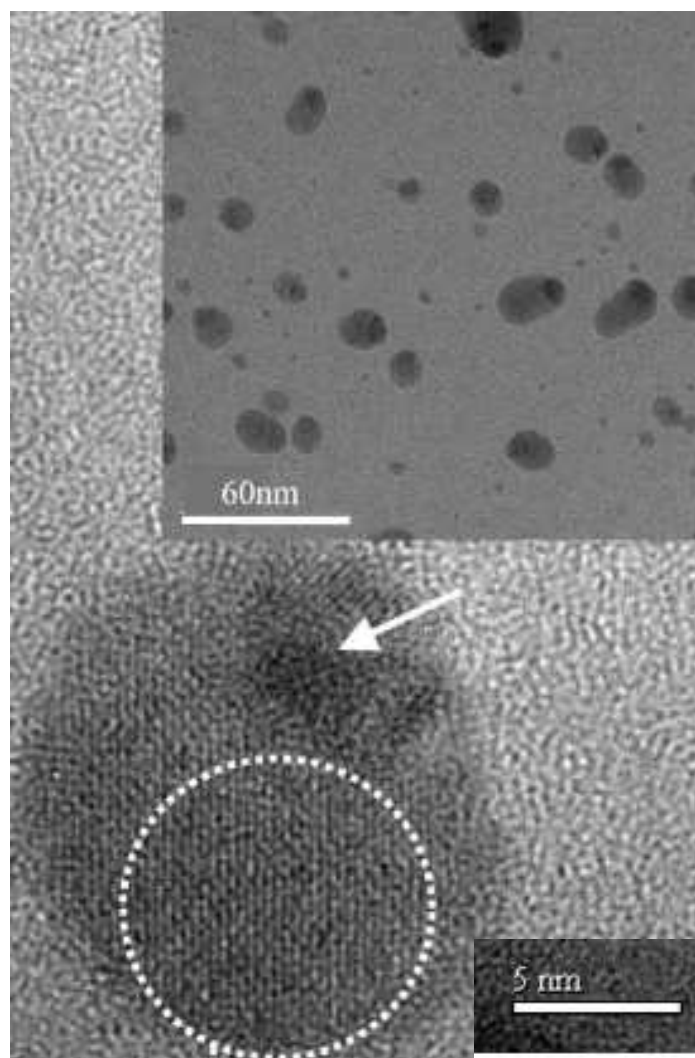
TGA = тиогликолевая кислота

0.095 g

of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ was dissolved in 5 mL of Mill-Q water and 0.092 g of TGA was added. Then the solution was adjusted to pH 11 with 1 M NaOH and deaerated with N_2 for 30 min. Next, oxygen-free NaHTe solution, which was freshly prepared from tellurium powder and NaBH_4 in water, was injected into the above solution under vigorous stirring. The solution was then heated at 95°C and further refluxed for 2 h.



Квантовые точки (сульфид кадмия), модифицированные серебром



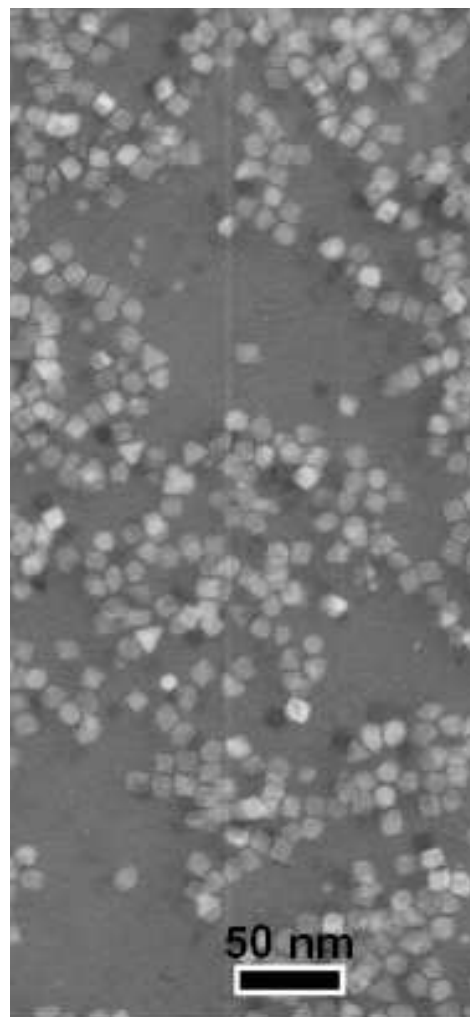
$\text{Cd}(\text{ClO}_4)_2$ solution (0.1 mol dm^{-3}) was added drop-wise to HMP solution in a 500 ml flat bottom flask to obtain a reaction mixture having $3 \times 10^{-4} \text{ mol dm}^{-3}$ of each of these reactants. The pH was adjusted to nine and argon gas was flushed for about 15 min. Stoichiometric amount of SH^- was injected under vigorous stirring. The solution was finally flushed with N_2 for about 5 min.

the polyvinyl sulfate polymer was added to CdS solution to avoid the coalescence of the particles. Excess of ionic compounds was removed from the sol before PVS addition by treatment with Amberlite; second, $2 \times 10^{-4} \text{ M}$ formaldehyde was added to 50 ml of CdS solution ($\text{pH} = 7.5$). The solution was in a round flask under nitrogen. Several milliliters of deaerated silver nitrate solution (5×10^{-5} and 10^{-3} M) was slowly injected under strong striring. During the injection, the spectral change took place immediately.

Платина для изготовления катализаторов

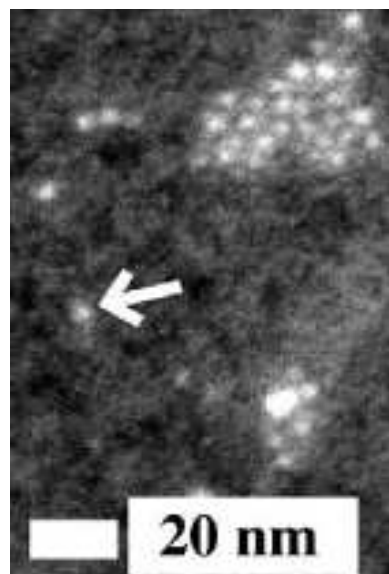
EG = этиленгликоль

PVP = поливинилпирролидон

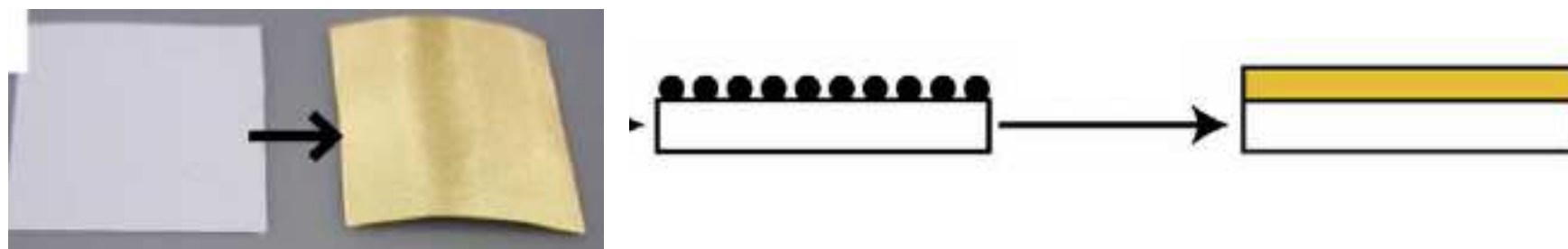


4 mL of EG and 0.5 mL of 0.04 M AgNO_3 , 2 mL of 0.0625 M H_2PtCl_6 , and 4 mL of 0.375 M PVP were used. Then, every 30 μL of 0.0625 M H_2PtCl_6 in 2 mL of the total volume was added into the reaction flask with a reflux condenser. After 30 s, 60 μL of PVP of 0.375 M was added into the flask in many times so that a volume of the solution of 0.375 M PVP was more two times than a volume of the solution of 0.0625 M H_2PtCl_6 until 2 mL of H_2PtCl_6 and 4 mL of 0.375 M PVP were completely used. The next additions of H_2PtCl_6 and PVP were repeated as the first addition and done until the contents of 4 mL of 0.375 M PVP and 2 mL of 0.0625 M H_2PtCl_6 were completely used. The resultant mixture was heated and continuously refluxed at 160 °C for the chemical reduction. After that, the color of the resultant solution became dark-brown during a preparation procedure changing from 15 to 35 min.

Платина, палладий, золото как «затравки» для металлизации полимеров

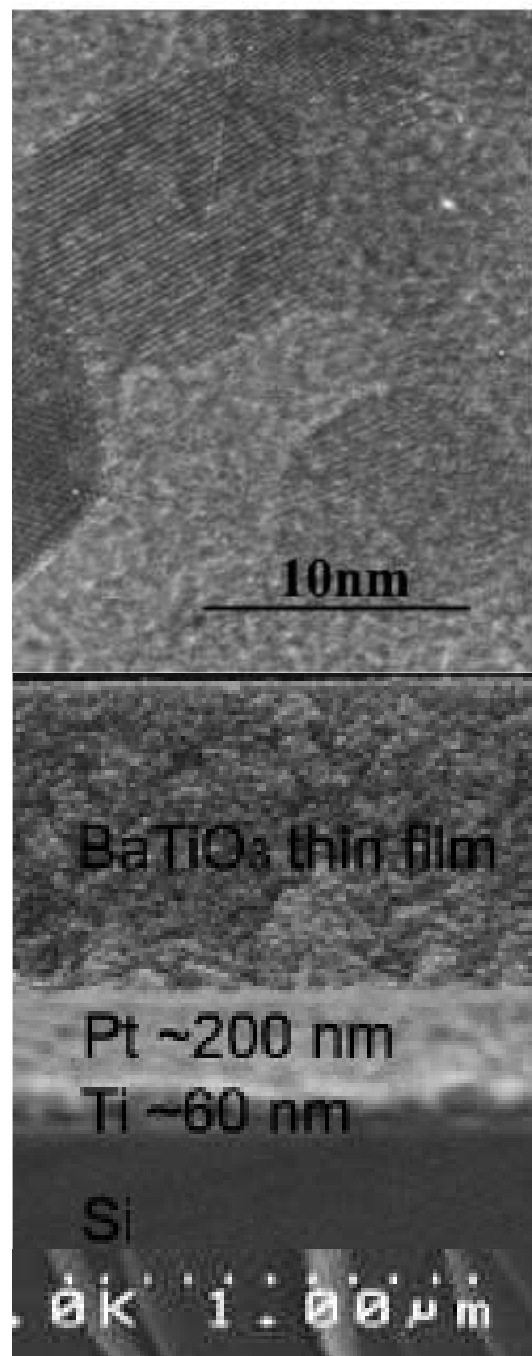


Pt, Au and Pd colloids were synthesized by the reduction of a metal salt by NaBH_4 in the presence of polyvinylpyrrolidone (PVP) at room temperature for one day, which gave a stable aqueous suspension containing 100 ppm metal nanoparticle [32]. A 0.05 mmol of noble metal salt ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, or PdCl_2) was dissolved in 91.5 ml water. In the case of PdCl_2 , NaCl (0.25 mmol) was added to dissolve it. For the preparation of the Pt and Au colloids, an aqueous solution (5 ml) of 10 mg of PVP was added to the solution, and then, an aqueous solution (1 ml) of NaBH_4 (0.2 mmol) was poured into the mixture with vigorous stirring. For the Pd colloid preparation, the amount of PVP was reduced to 1 mg to enhance the catalytic activity. After stirring for 1 min, the solution was left to be stand at room temperature for one day, giving the solution dark-brown coloration.



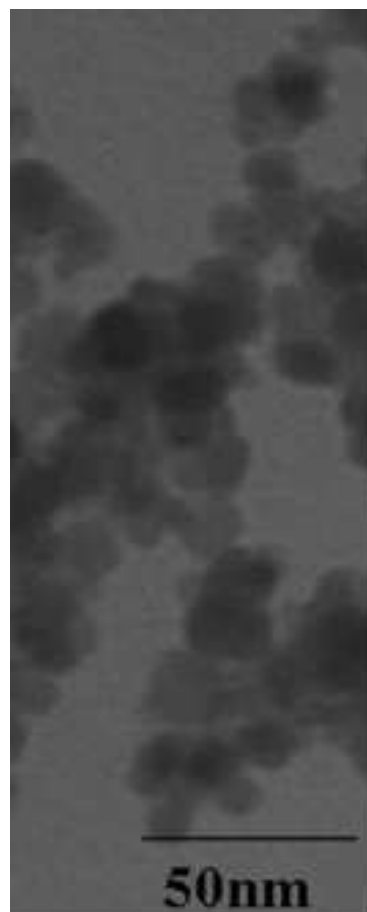
Титанат бария (ВТО) – для электрофоретического нанесения сегнетоэлектрических пленок

At first, high purity barium diethoxide ($\text{Ba}(\text{OC}_2\text{H}_5)_2$, >99%) was dissolved in a mixed solvent of methanol (CH_3OH , >99%) and 2-methoxyethanol ($\text{CH}_3\text{OC}_2\text{H}_4\text{OH}$, EGMME, >99.8%) with a volume ratio of 3:2 and stirred for 24 h. Then, titanium tetra-iso-propoxide ($\text{Ti}(\text{O}i\text{C}_3\text{H}_7)_4$, >99%) was added to form BTO precursor solution and again stirred for 24 h. The concentration of the precursor solution was 1.0 mol/l. The obtained precursor solution was then hydrolyzed by adding a mixed solution of distilled water and EGMME with a volume ratio of 1:1. The molar ratio of H_2O and BTO was 10:1. All above processes were performed in a dry N_2 atmosphere. After stirring for 10 min, the hydrolyzed solution was sealed in an autoclave and aged in a 90°C oven for 1 h. After extraction, the residual liquid, the BTO gel was dispersed into EGMME by ultrasonication for several hours. Then acetylacetone (Acac, $\text{CH}_3\text{COCH}_2\text{COCH}_3$, >99%) was added and again ultrasonicated to form BTO suspension.

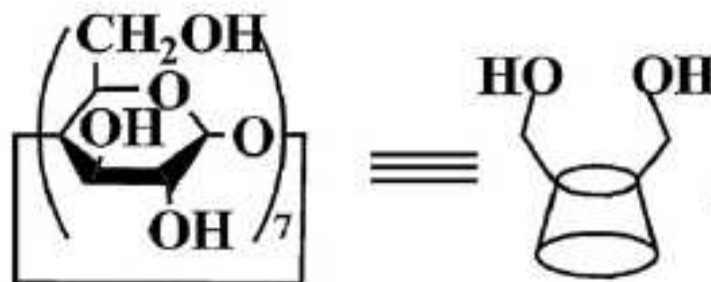


Fe₃O₄ – магнитные зонды для сенсорных и биологических задач

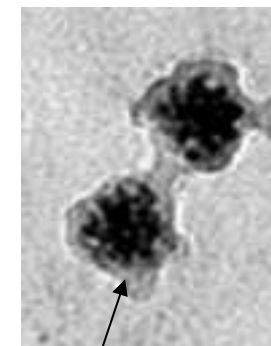
Magnetic nanoparticles were synthesized based on the chemical coprecipitation method [27]. Calculated amounts of FeCl₂·4H₂O and FeCl₃·6H₂O (molar ratio 1:1) in grams were dissolved in 200 mL doubly distilled water with a three necked flask. Chemical precipitation was achieved at 25 °C under vigorous stirring by adding NH₄OH solution (25%). During the reaction process, the pH was maintained at about 10. The precipitates were heated at 80 °C for 30 min, then washed several times with water and ethanol until the solution was near neutral, finally dried in a vacuum oven at 70 °C, and stored in glass vials.



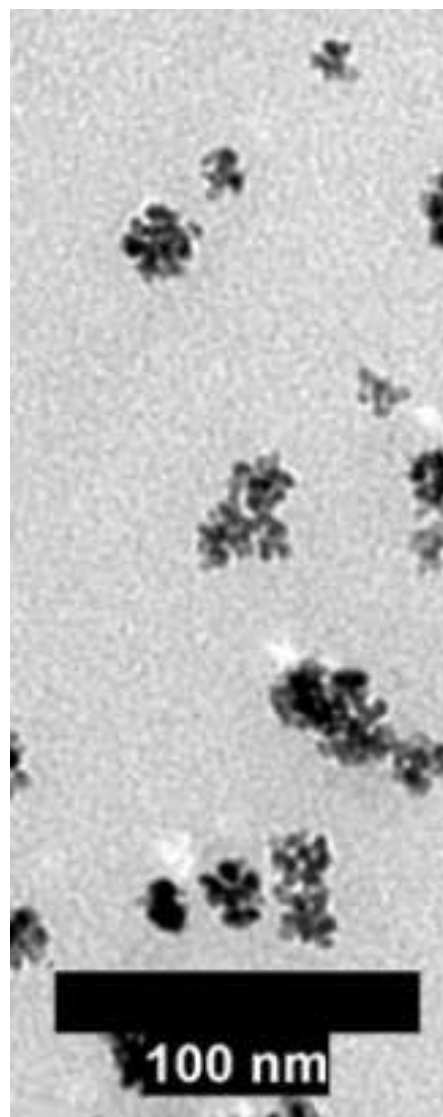
Кто разберется с этой задачей – сможет узнать продолжение: Как стабилизируют такие частцы молекулами-«стаканчиками» (циклодекстринами), вот такими:



Палладий для электронно-микроскопической визуализации биологических макромолекул



Human fibrinogen



Solutions of freshly prepared 1% K_2PdCl_4 (Sigma-Aldrich, St. Louis, MO) and 10% L-ascorbic acid, aged approximately two weeks, were chilled in an ice-water bath. Sols consisting of umbonate cPd particles were prepared by the addition of 4.1 mL of the K_2PdCl_4 solution to 495.9 mL of the L-ascorbic acid solution with rapid agitation. The final Pd^{+2} concentration was approximately $250 \mu M$. Formation of the sol was indicated by the development of a yellow tint within a few minutes, gradually intensifying to golden brown. Preparations were then kept overnight in ice water to ensure that the reactions had come to completion.