Kazakh National University named after Al-Farabi
Faculty of Chemistry and Chemical Technology.

Photocatalysts based on AgCl / Ag nanocomposites.

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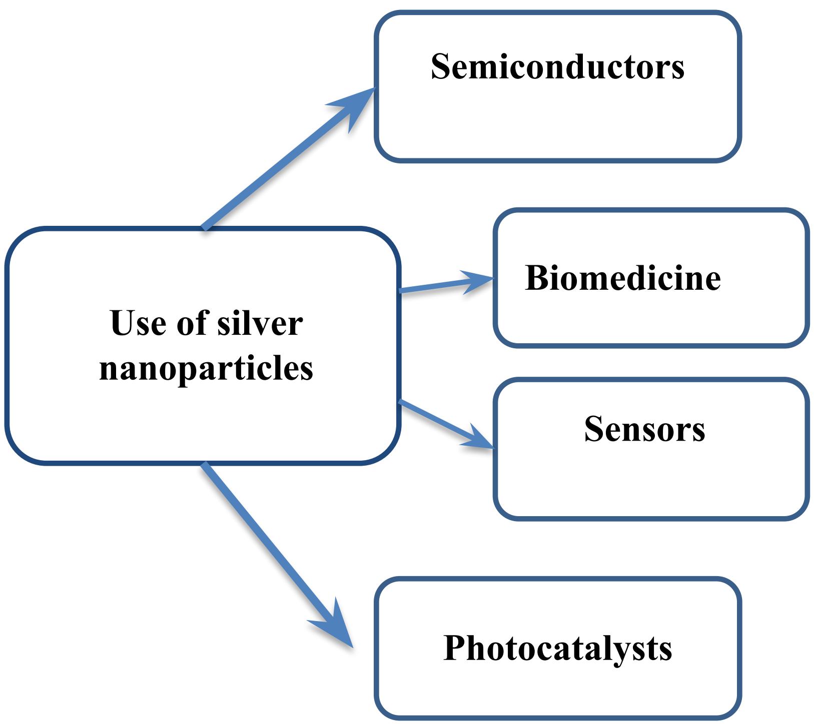
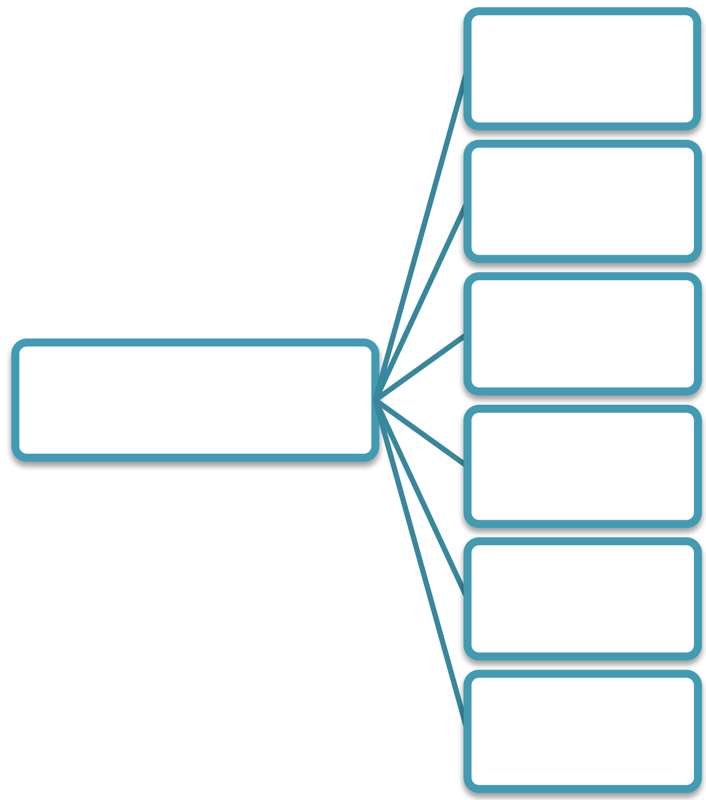
Aim of work: synthesis of nanocompasites of high photocatalytic activity $AgCl/Ag_3PO_4$ through the process of mechanochemical activation and verification of their photocatlytic activity. To achieve this goal, the following tasks will be considered.

Objectives:

1. To obtain $AgCl/Ag_3PO_4$ nancomoposite by mechanocemical route, to deterimine optimal condition of mechanical acitivation.
2. To determine characterizartion of obtained nanocompositre by XRD, SEM, DSC, SF-56
3. To evaluate their photochemical activity in accordance of metillen blue degrdatrion under simulated solar light (light intensity 15 mW/cm^2)

At present, silver chloride based nanocomposites are widely used in many fields of science as photocatalysts, semiconductor, antibacterial substances. For these reasons, of particular interest is the development of new, effective, simple methods for the synthesis of nanoparticles based on silver chloride and the synthesis of the properties of nanocomposites, especially high catalytically active nanoparticles.





Mechanical activation process

S1(AgCl-75%, Ag3PO4-25%)

1) $AgNO_3 + 5NaNO_3 \xrightarrow{20min\ (MA)} A$
   6mml 30mml
2) $Na_3PO_4 + NaNO_3 \xrightarrow{10min\ (grinding\ in\ agate\ mortar)} B$
   0.5mml 1.5mml
3) $A+B \xrightarrow{10min\ (MA)} AB$
4) $NaCl + NaNO_3 \xrightarrow{10min\ (grinding\ in\ agate\ mortar)} C$
   4.5mml 1.5mml
5) $AB+C \xrightarrow{10min\ (MA)} ABC$

S2 (Ag3PO4-100%)

1) $AgNO_3 + 5NaNO_3 \xrightarrow{20min\ (MA)} A$
   6mml 30mml
2) $Na_3PO_4 + NaNO_3 \xrightarrow{10min\ (grinding\ in\ agate\ mortar)} B$
   2mml 3 mml
3) $A+B \xrightarrow{10min\ (MA)} AB$

S3 (AgCl-100%)

1) $AgNO_3 + 5NaNO_3 \xrightarrow{20min\ (MA)} A$
   6mml 30mml
2) $NaCl + NaNO_3 \xrightarrow{10min\ (grinding\ in\ agate\ mortar)} B$
   6mml 3mml
3) $A + B \xrightarrow{10min\ (MA)} AB$

S4 (AgCl-25%, Ag3PO4-75%)

1) $AgNO_3 + 5NaNO_3 \xrightarrow{20min\ (MA)} A$
   6mml 30mml
2) $Na_3PO_4 + NaNO_3 \xrightarrow{10min\ (grinding\ in\ agate\ mortar)} B$
   3 mml 1.5mml
3) $A+B \xrightarrow{10min\ (MA)} AB$
4) $NaCl + NaNO_3 \xrightarrow{10min\ (grinding\ in\ agate\ mortar)} C$
   0.5mml 1.5mml
5) $AB+C \xrightarrow{10min\ (MA)} ABC$

S5(AgCl-50%, Ag3PO4-50%)

1) $AgNO_3 + 5NaNO_3 \xrightarrow{20min\ (MA)} A$
   6mml 30mml
2) $Na_3PO_4 + NaNO_3 \xrightarrow{10min\ (grinding\ in\ agate\ mortar)} B$
   1.016mml 1.5mml
3) $A+B \xrightarrow{10min\ (MA)} AB$
4) $NaCl + NaNO_3 \xrightarrow{10min\ (grinding\ in\ agate\ mortar)} C$
   2.95mml 1.5mml
5) $AB+C \xrightarrow{10min\ (MA)} ABC$

Planetary ball mill "Activator-2SL"

Options:

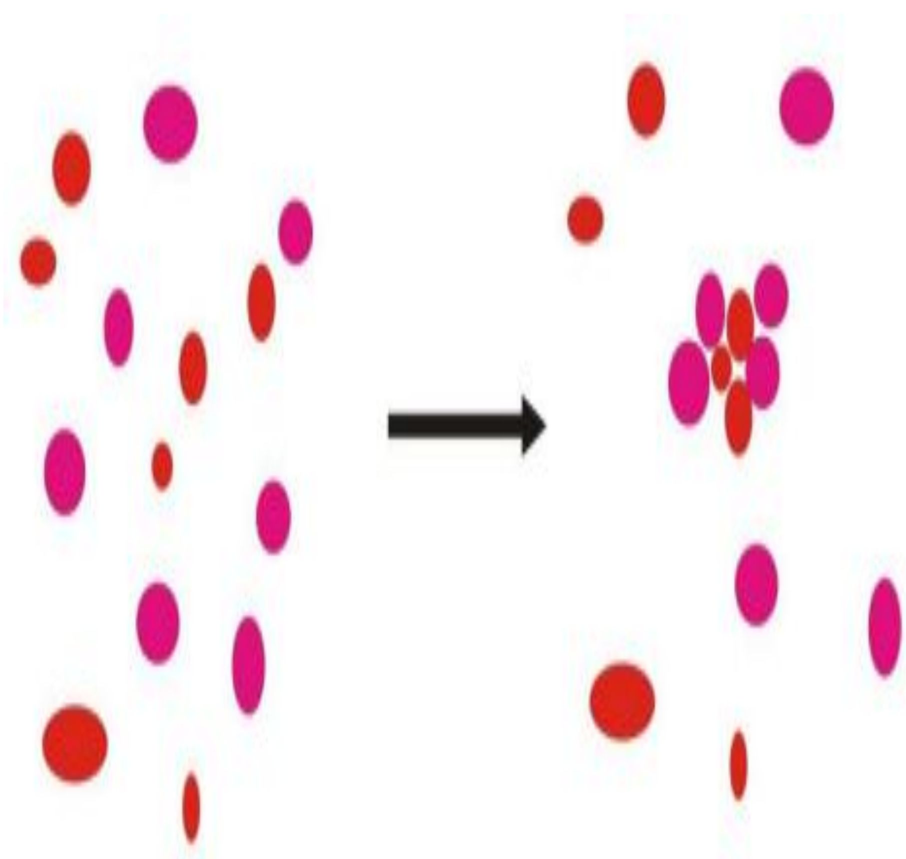
Nitride balls m=1.6g

Rotational speed = 3000 turn / min

Number of balls = 18

Duration of synthesis = 15-20 min.

Problems in obtaining nanoparticles and nanomaterials



Agglomeration is an alternative way to reduce the surface energy of nano particles. Agglomeration also occurs at low temperatures and may be irreversible.

When producing nanomaterials, the methods used should solve the following problems:

1. Nanoparticles and nanomaterials are characterized by a large size of the interface area. Therefore, during the synthesis it is necessary to ensure the stability of the system with a giant surface energy.

2. Often one of the tasks to be solved is to obtain a material with the required size of crystals, a narrow particle size distribution, necessary morphology, chemical composition and microstructure [20].

3. The resulting material, if special measures are not taken, is unstable with respect to the processes leading eventually to the enlargement of particles or crystals.

According to the calculations of the mass of the initial components are given in this table

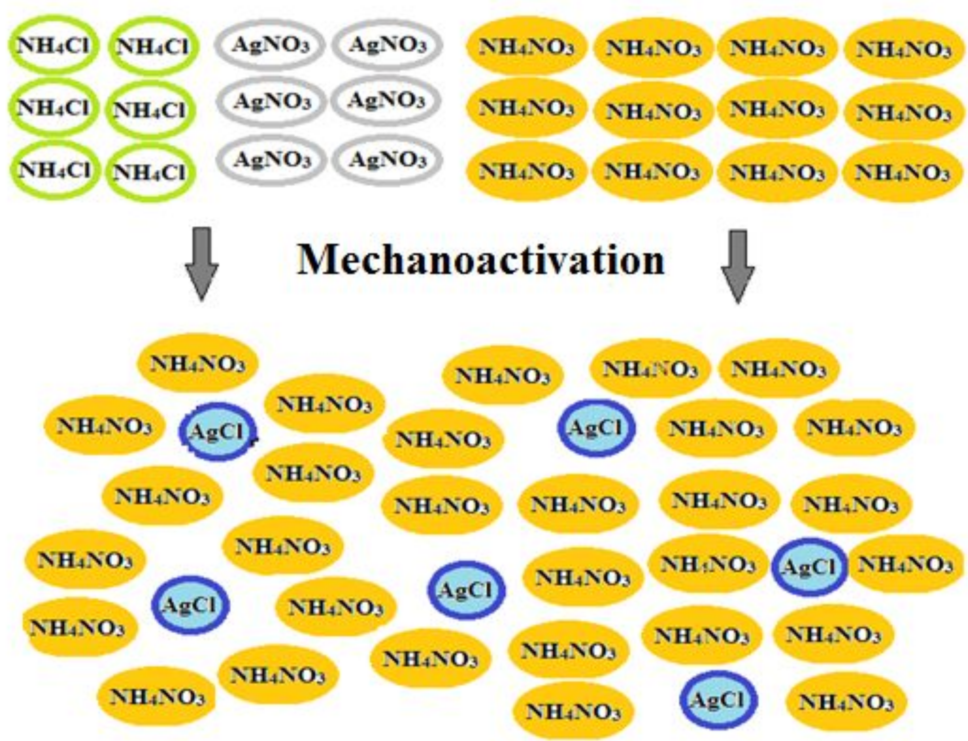
Photocatalyst	Method	Thinks	Compound	Mass,mg
S-1	MA	A	AgNO3	1019.22
			NaNO3	2550
	Agate mortar	B	Na3PO4	82
			NaNO3	127.5
	MA	A+B	A	3569.22
			B	209.5
	Agate mortar	C	NaCl	263.25
			NaNO3	127.5
	MA	AB+C	AB	3778.72
			C	390.75
S-2	MA	A	AgNO3	1019.22
			NaNO3	2550
	Agate mortar	B	Na3PO4	328
			NaNO3	255
	MA	A+B	A	3569.22
			B	583
S-3	MA	A	AgNO3	1019.22
			NaNO3	2550
	Agate mortar	B	NaCl	351
			NaNO3	255
	MA	A+B	A	3569.22
			B	606
S-4	MA	A	AgNO3	1019.22
			NaNO3	2550
	Agate mortar	B	Na3PO4	248
			NaNO3	127.5
	MA	A+B	A	3569.22
			B	375.5
	Agate mortar	C	NaCl	86
			NaNO3	127.5
	MA	AB+C	AB	3944.72
			C	213.5

Kind of silver chloride powders.

According to the calculations of the mass of the initial components are given in this table

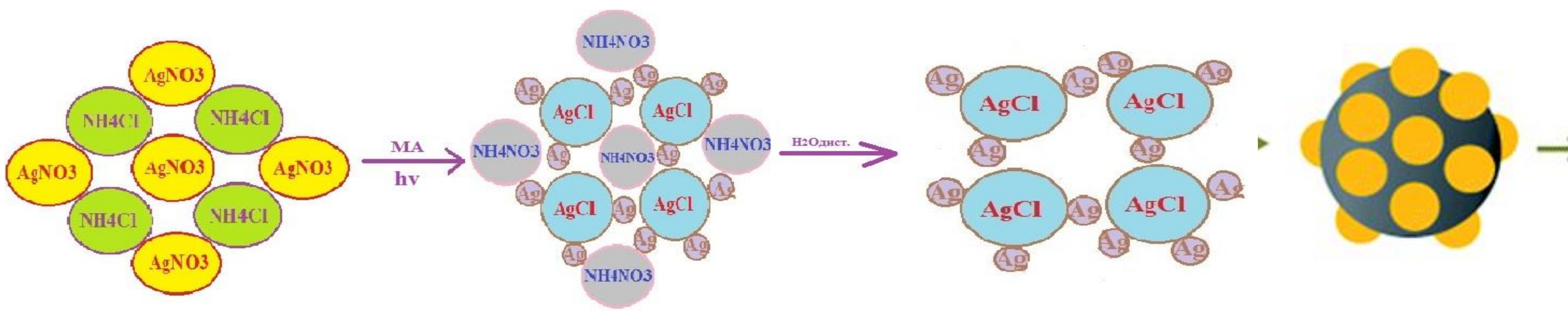
Photocatalyst	Method	Thinks	Compound	Mass,mg
S-5	MA	A	AgNO3	1019.22
			NaNO3	2550
	Agate mortar	B	Na3PO4	167
			NaNO3	127.5
	MA	A+B	A	3569.22
			B	294.5
	Agate mortar	C	NaCl	173
			NaNO3	127.5
	MA	AB+C	AB	3863.72
			C	300.5

Reaction mechanism of mechanochemical activation

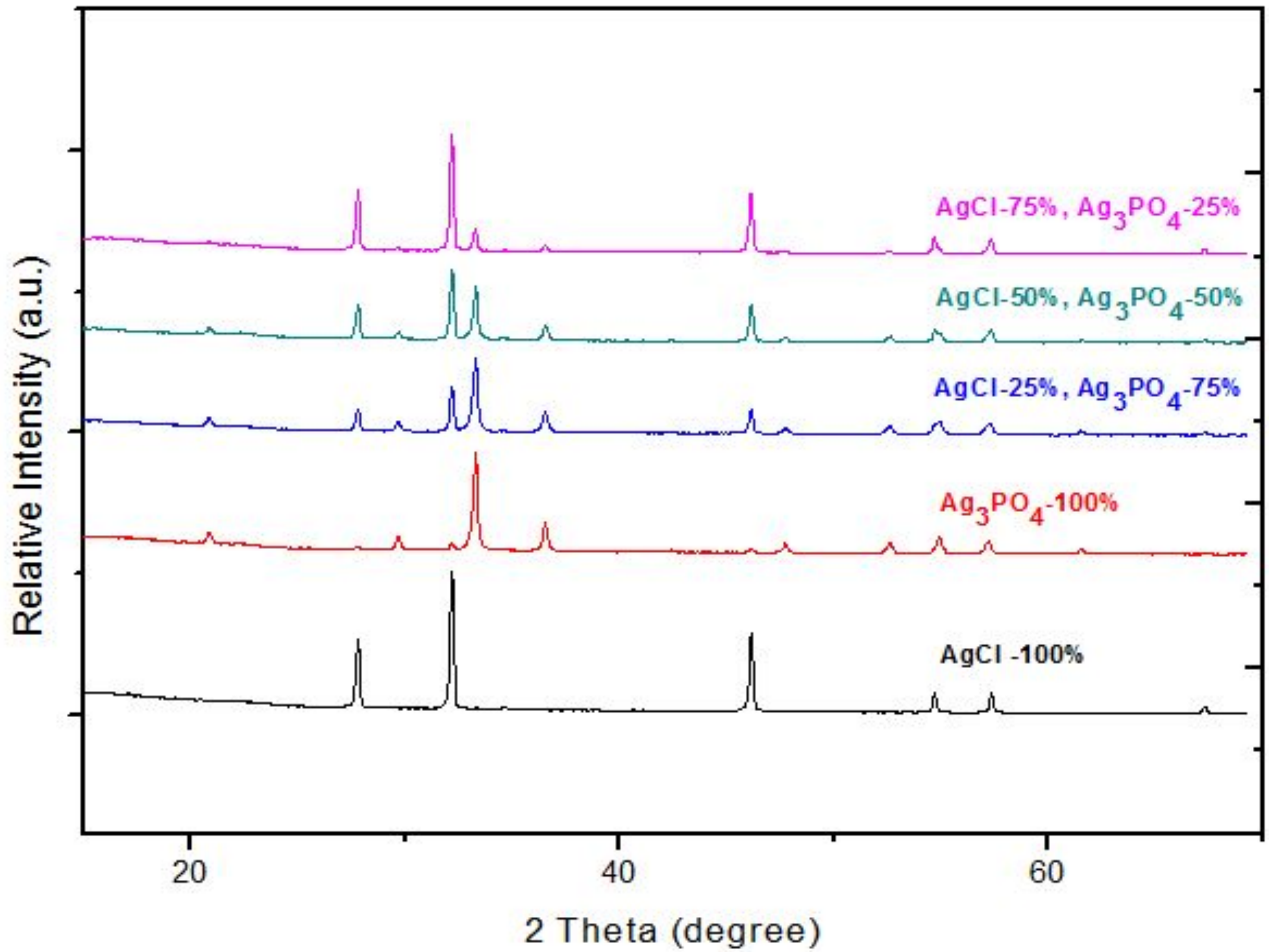


The mechanism of the reaction of dilution McCormick end product.

This scheme is mainly suitable for all halides. Here, $NaNO_3$ was used as a diluent. It can be seen that as a result of the reaction, Ag / AgCl is formed. Diluents are added to the reaction in order to avoid the occurrence of an agglomeration process.

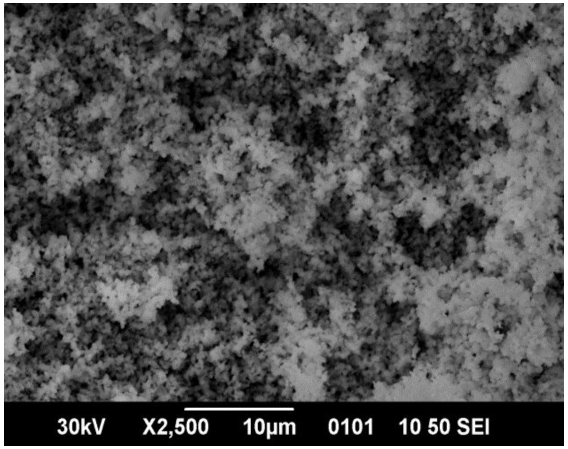


X-ray phase analysis results

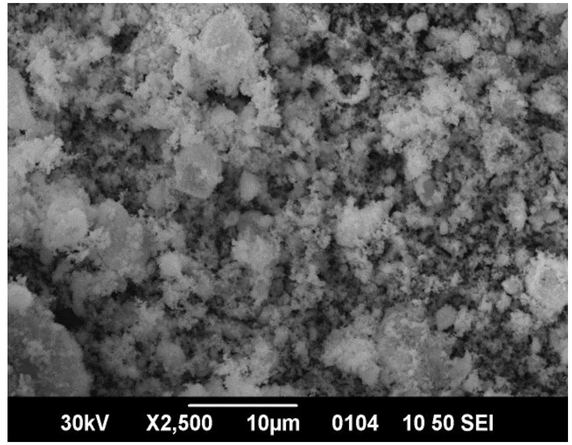


It is clearly visible here that all photocatalysts were purely synthesized. The figure shows one hundred percent silver chloride and silver phosphate. And then their composites are 75%, 50%, 25%. All the peaks of things coincide and the synthesized substance is pure. If you look closely, you can see that with a decrease in the ratios of substances 75%, 50%, 25%, their intensity in the graph will fall.

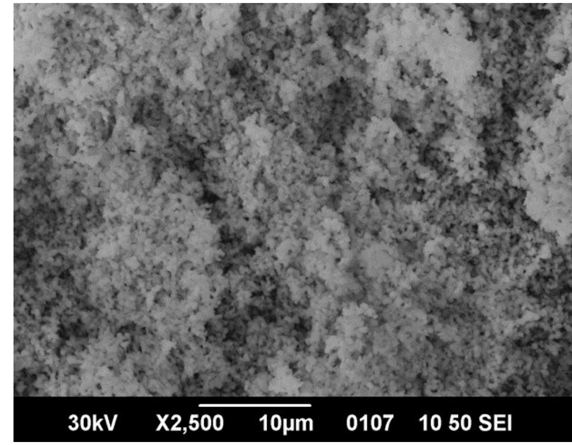
Composites imaging scanning electron microscope



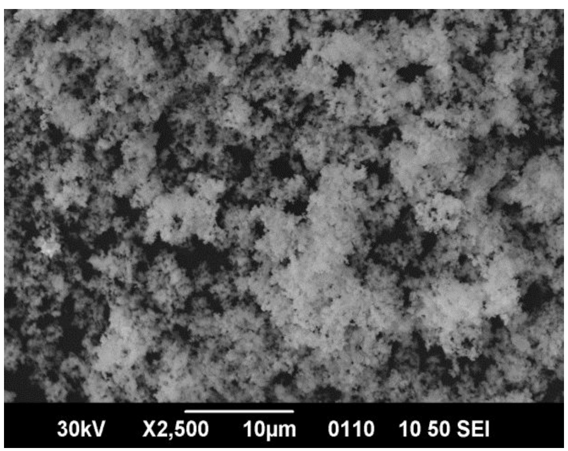
AgCl /Ag3PO4 (75:25) images on a (SEM).



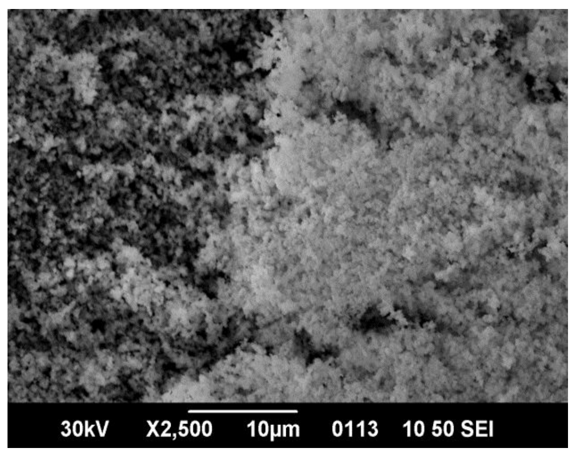
Ag_3PO_4 (100) images on a (SEM)



AgCl (100) images on a (SEM).



AgCl /Ag3PO4 (25:75) images on a (SEM).

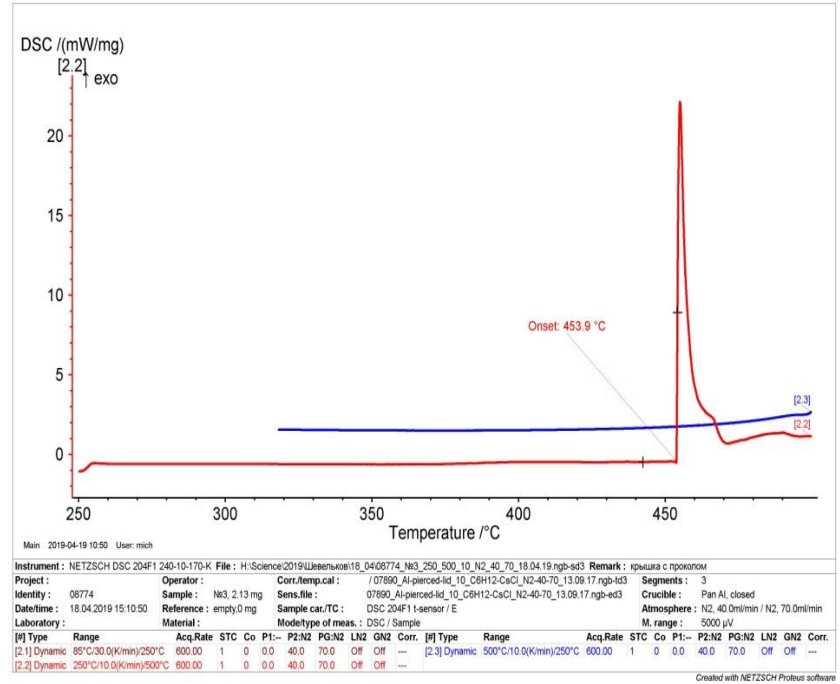


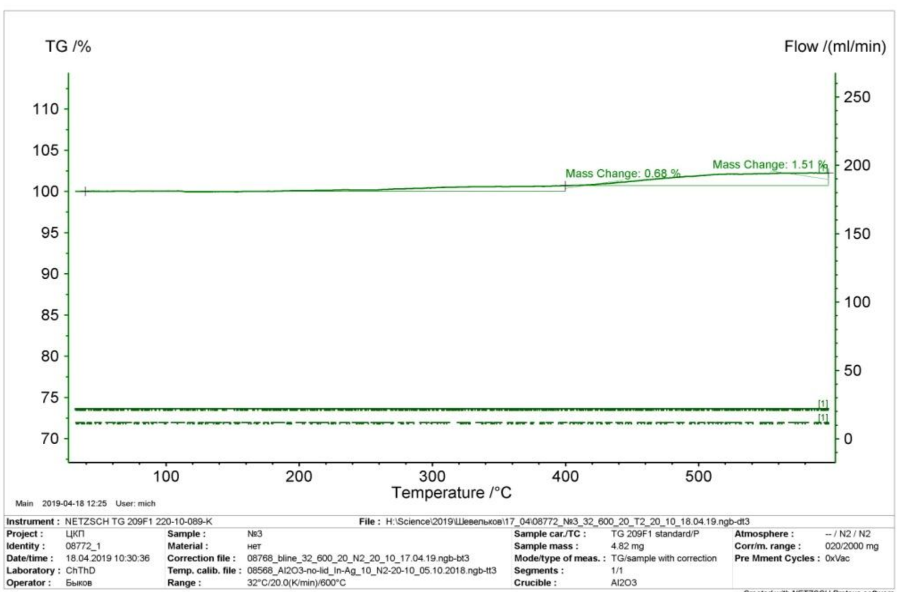
AgCl /Ag3PO4 (50:50) images on a (SEM).

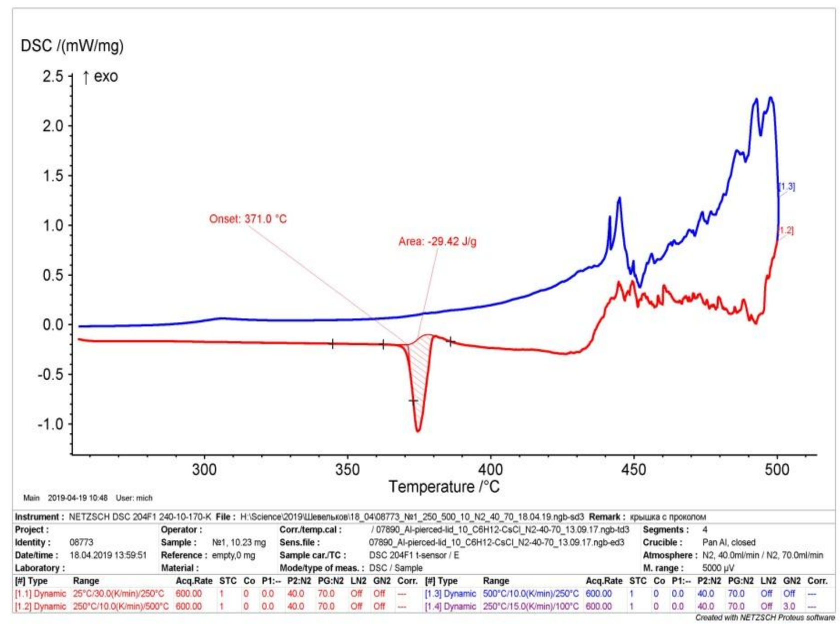
The following image shows 25%:75 %, 50% silver chloride and silver orthophosphate. Compared with the other 100% substances and the rest, the difference is clearly visible. Here too, it is assumed that homogeneous composites have been synthesized.

DSC results of AgCl / Ag_3PO_4 nanoparticles

At first, all powders were studied for purity. And as the chart shows the powders are clean and dry from moisture. A change in the composition to 0.5% is normal for powders.
As can be seen here, the melting point of silver chloride is 455 degrees. And the graph clearly shows that silver chloride and another substance (in our case, silver orthophosphate).





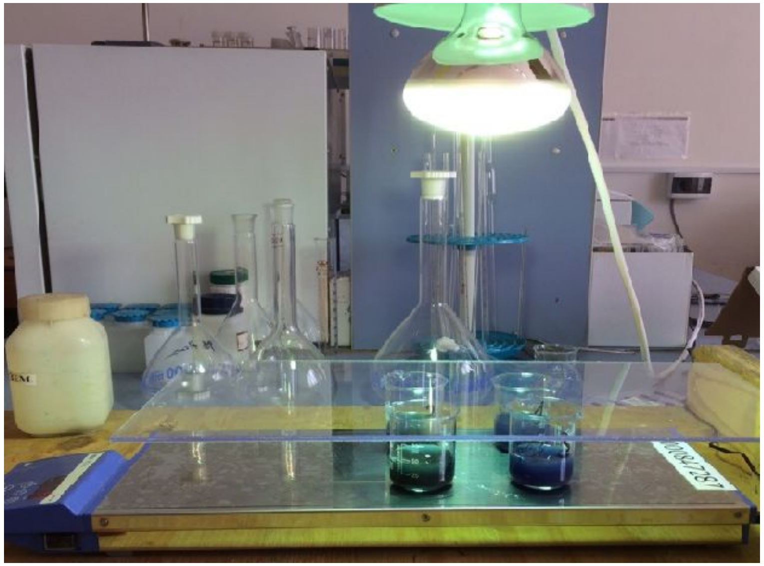


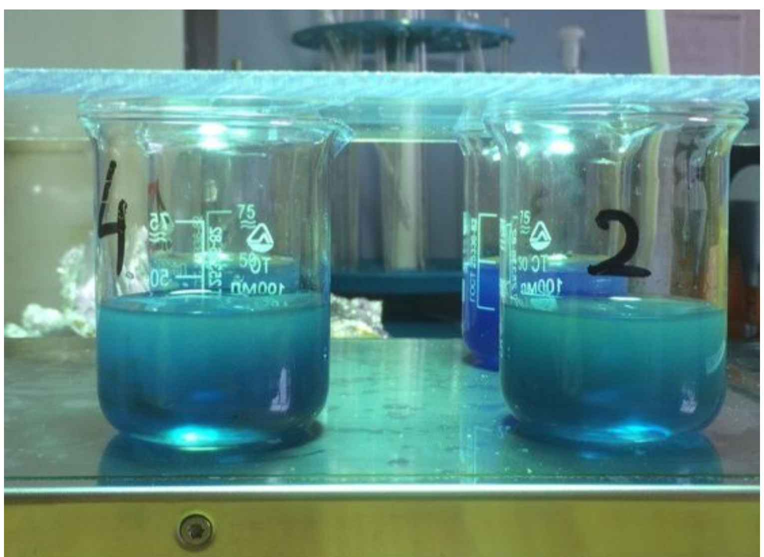
Washing products MA with distilled water and obtaining nanoparticles in pure form

The next stage of this work was continued by washing with distilled water and ethanol, since the simplest and easiest method of washing with distilled water and ethanol was used to remove the non-target product in the powder.

Refrigerated Centrifuge HETTICH Rotina 380R

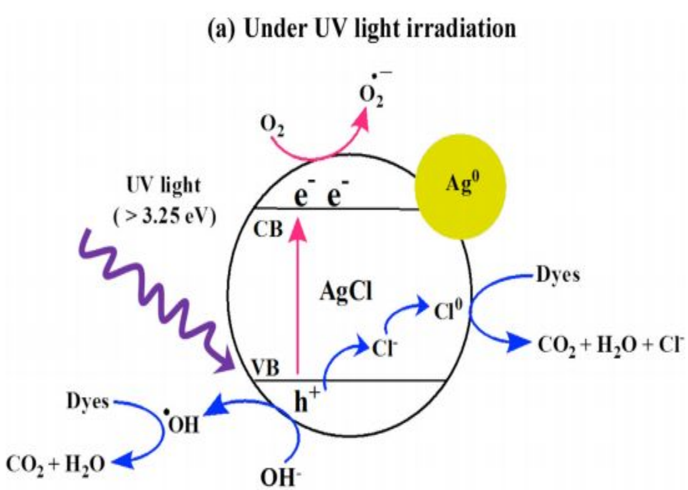
Verification of the photocatalytic activity of the obtained AgCl / Ag3PO4 nanoparticles



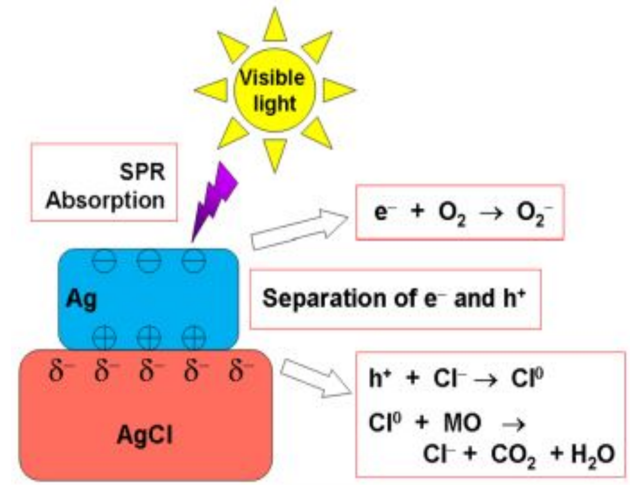


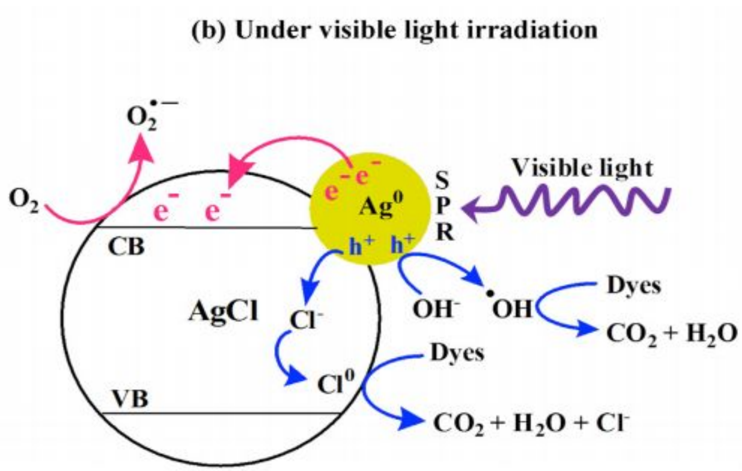
Put 40 ml of methylene blue (C - 0.1 g/l) solution into a 50 ml glass and add 0.02 g of nanoparticles there. Then mix in a magnetic stirrer.
Initially, the glass was fixed with alumina follogo paper and mixed for 60 minutes. Purpose: with good mixing with a solution of nanoparticles without sun, and also the process of absorption can occur.
The process was carried out under ultrakul radiation. Every 15 minutes the sample was removed. The experiment was carried out until the organic dye discolored.
The concentration of MK was measured by determining the optical density on the device SF-56 (spectrophotometer).

Mechanisms of the influence of Ag / AgCl nanoparticles on organic pollutants.

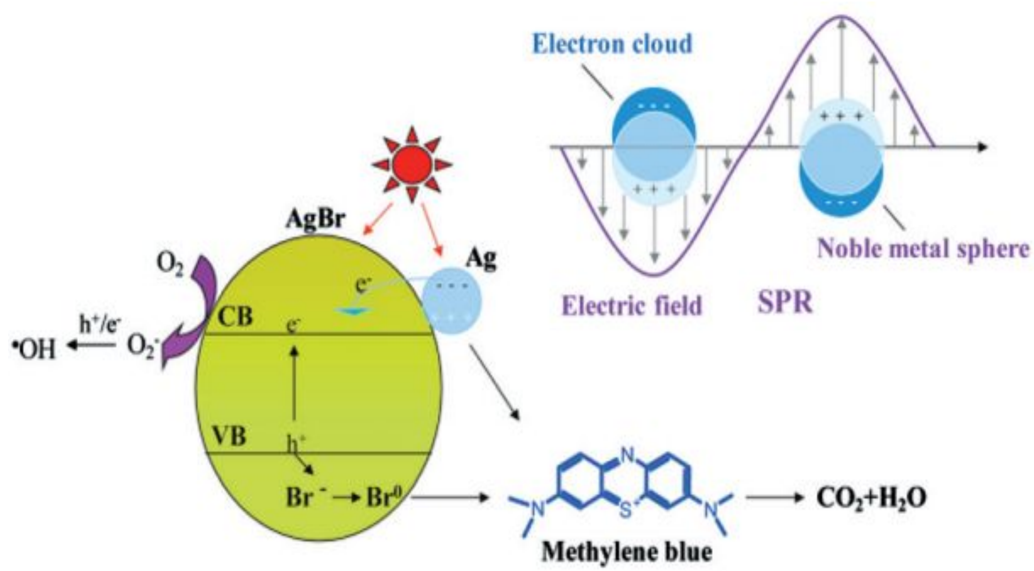


1) AgCl $^{(hv)}$□AgCl+h^++e^-
2) H^++e^-□kT
3) Ag^++e^-□Ag^0
4) O_2+e^-□O_2^-
5) Cl^-+h^+□Cl^0
6) OH^-+h^+□$^*OH$
7) Cl^0+organic compound□ CO_2+H_2O+Cl^-
8) $^*OH$ + organic compound□ CO_2+H_2O



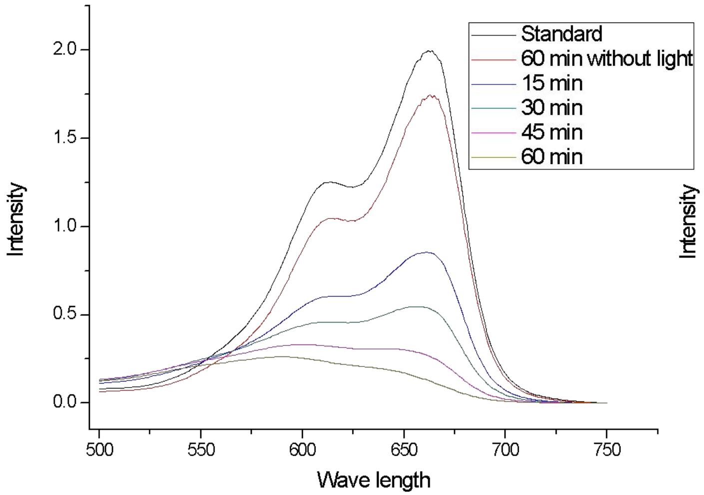


hv□e^-(electron)+h^+(hole)

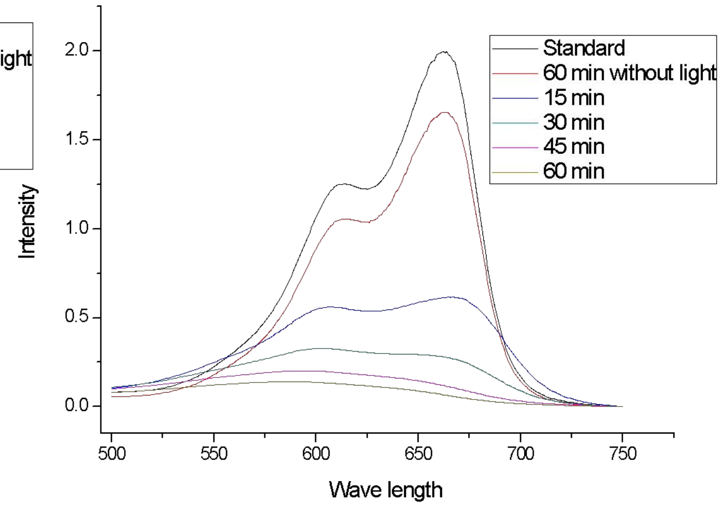


Graphs discoloration of methylene blue photocatalysts.

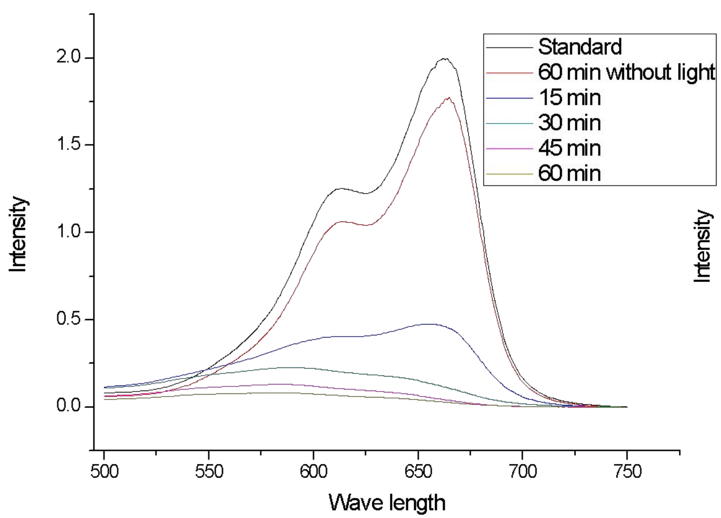
S2 Ag3PO4 (100%)



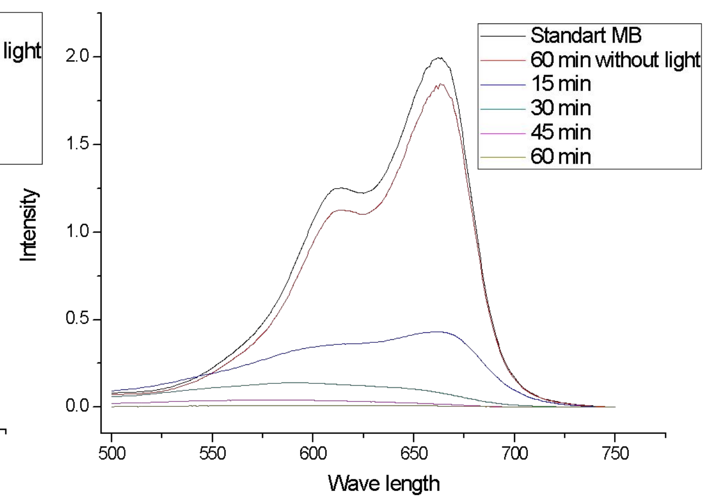
S3 AgCl (100%)



S4 AgCl/ Ag3PO4 25:75

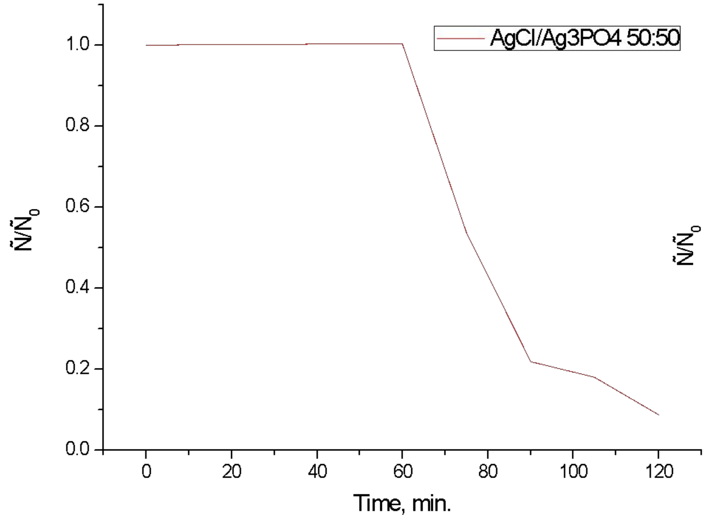


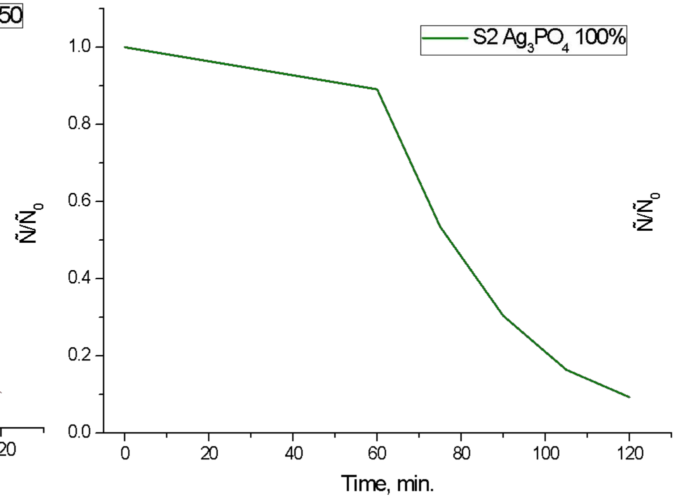
S5 AgCl/ Ag3PO4 50:50

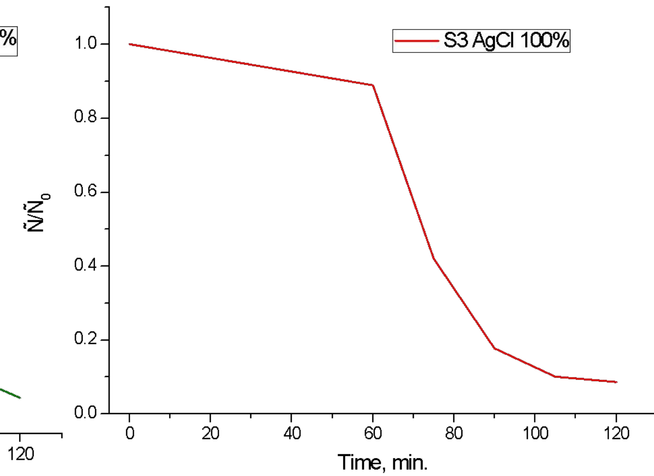


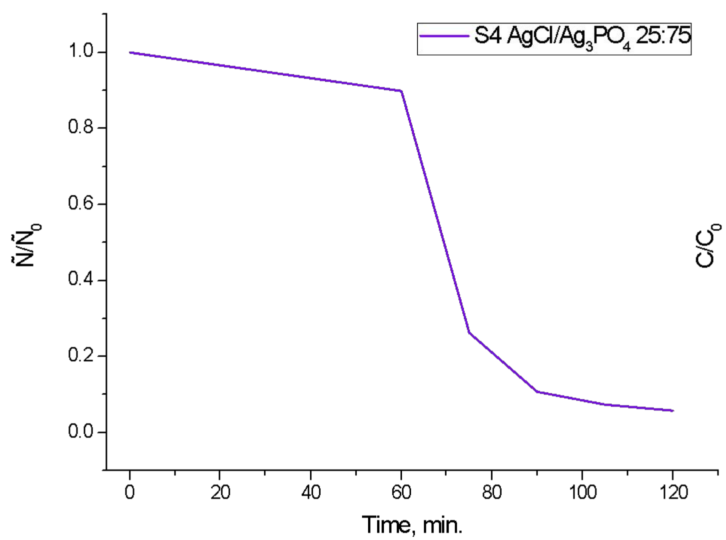
Shown here are bleaching charts for methylene blue photocatalysts. As you have already guessed, photocatalysts work very effectively. Samples were taken every 15 min. The differences of the peaks each 15 minutes are clearly visible.

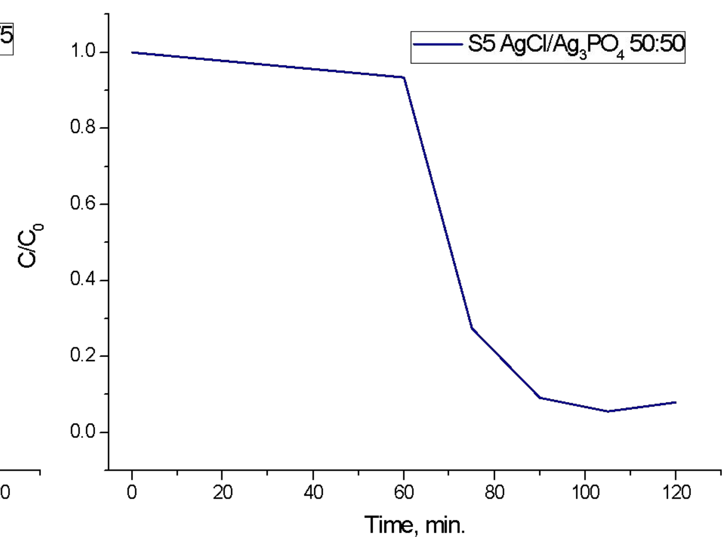
A comparative graph of the decomposition of methylene blue photocatalysts.





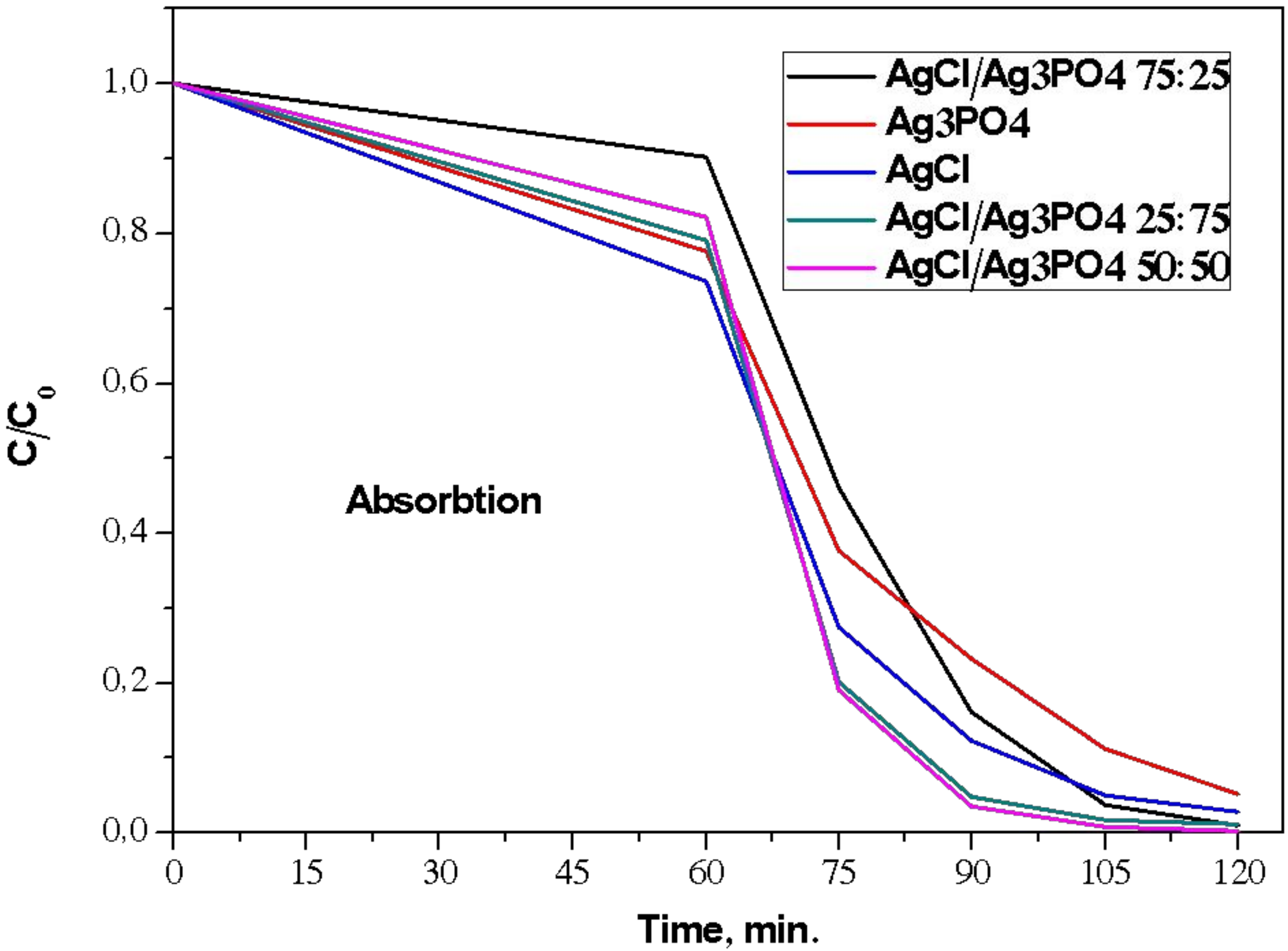




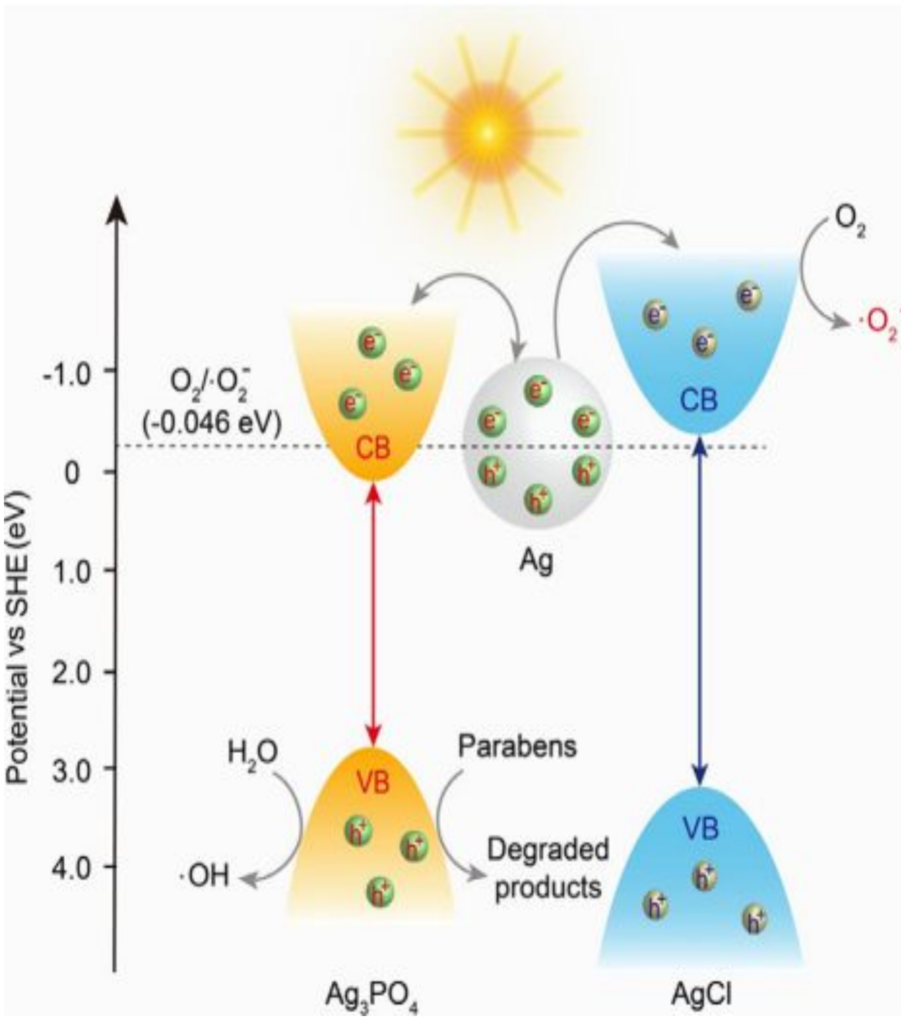


Here all photocatalysts are shown in order: S1, S2, S3, S4, S5.

The final C / C0 chart of all photocatalysts.



Photocatalytic mechanism over the $AgCl/Ag_3PO_4$ composite



A possible process of photogeneration and transfer of electron-hole pairs is shown in Figure 35. First, Ag_3PO_4 nanoparticles and Ag metal nanoparticles can absorb visible particles with the formation of photoexcited electrons and plasmon-induced electrons and holes on the surface of Ag_3PO_4 nanoparticles and metallic Ag. Then plasmoninduced electrons will be injected into the conduction band of AgCl, which can be captured by O_2 into the active particles $^*O_2$ due to the relative negative CB potential of AgCl (0.09 eV compared to SHE) to O_2 /$^*O_2$ (0.046 eV vs. SHE) [26,31,44]. These formed active substances quickly affect the degradation of organic compounds, while the holes remain on the Ag nanoparticles. Therefore, the AgCl / Ag_3PO_4 composite photocatalyst exhibits enhanced photocatalytic activity compared to pure AgCl or Ag_3PO_4.

Conclusion

1. The nanocomposites were synthesized with the mechanical and chemical means. To synthesize the following systems were selected. Metallic steel balls are used as a mobile crusher, chopper, i.e. the reaction bodies. The average mass of balls m = 1.8 g diameter is approximately d = 10 mm. The MA process was performed in the following case: Rotational speed = 400 rpm; number of balls= 18; Duration of synthesis = 10 - 20 min.3. Identified favorable conditions for washing, to avoid non-target product. Washing was carried out in a powerful centrifuge every 5 minutes.

2. By X-ray phase analysis, all substances are synthesized purely. The peaks in the synthesized substances accounted for the standard peaks. In this work, 1 goal was to synthesize nanocomposites in different ratios, and looking at the graph of X-ray phase analysis it is safe to say that all different percent nanocomposites were successfully synthesized. And each graph clearly shows if the percentage falls , the intensity will also fall.

Looking at the graphics of the scanning electron microscope, we can say that all nanocomposites were synthesized selectively and homogeneously. And the graph shows that the average size of nanoparticles is about 300-400 nm. But you can also see that there are nanoparticles with a size of 50-100 nm.

The results of DSK were also successful, the chloride of silver orthophosphate and silver melted in a standard temperature.

3. After silver chloride nanocomposites were successfully synthesized, the next step was to determine their photocatalytic activity. Methylene blue (10 mg/l) was used as an organic pollutant for the experiment. 20 mg of the nanocomposite was added to 40 ml solution of methylene blue. And it was put 60 minutes of darkness, while stirring in a magnetic stirrer. This is done to find out how much methylene blue is absorbed on the face of nanocomposites. Because the aim to study the clean fotoelektricheskie activity. All nanocomposites showed high photocatalytic activity. And nanocomposites with different ratios showed better photocatalytic activity than 100 silver chloride or silver orthophosphate. All photocatalysts discolored organic pollutants in about an hour.

Thanks for attention!!!