

## Report of Alexey Shavel

### Water-based synthesis of non metallic plasmonic nanomaterials.

The aim of this 8 week exchange grant was a attempt to prepare aqueous thiol-stabilized  $\text{Cu}_2\text{S}$  and  $\text{Cu}_5\text{FeS}_4$  nanocrystals for the plasmonic and photovoltaic applications . Using short chain thiols as a NPs stabilizer in a water, can potentially allow direct preparation (without sophisticated ligand exchange procedure) of the highly conductive solids and films made of plasmonic nanoparticles.

More precisely, during the 8 week of this project, we study the methods of the preparation of the plasmonic copper and copper-iron sulfides in a aqueous media. Thioglycolic acid (TGA) was chosen as a a one of the most popular and well studied stabilizers for the aqueous NPs [2].  $\text{CuCl}_2$  and  $\text{FeCl}_3$  were used as a metal precursors. All synthesis was conducted at a basic (pH 12) condition.

Unfortunately, very little is known about the iron and copper complexes with thioglycolic acid. Such complexes has been firstly proposed in 50<sup>th</sup> for the colorimetric determination and separation of the iron and copper from other metals [3-4]. No reliable information about composition and stability constant of the possible TGA-Cu and TGA-Fe complexes is available (data from ref. 4 is obviously incomplete). This makes impossible preliminary calculation of the concentration of the complexes in solution depending on the concentration and pH as we did previously for the Cd-TGA system [5]. Such calculation can allow making rational choice of synthetic condition. The only two iron complexes are known in a pH range between 9 and 10: i) yellow  $\text{Fe}[\text{OH}][\text{RS}]^-$  and ii) red  $\text{Fe}[\text{RS}]_2^-$  (where RS is  $[\text{S}-\text{CH}_2-\text{COO}]^{2-}$ ).[4]. Any information about composition and stability constants of the copper complexes is unavailable at the moment.

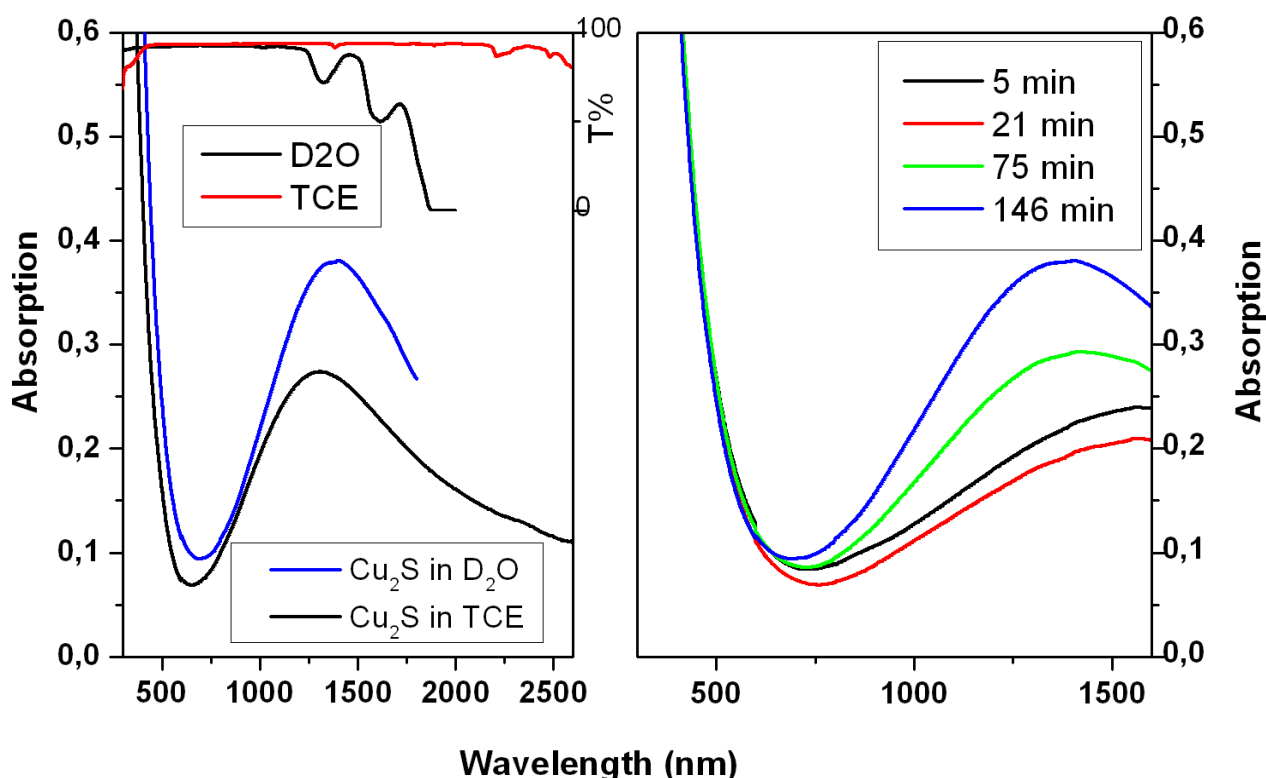
Note that Fe(III) and Cu(II) ions can rapidly oxidize TGA at the basic conditions by following equation:



So, it is important to avoid back oxidation of the Cu(I) and Fe(II) to the Cu(II) and Fe(III) by the oxygen because such cyclic process (oxidation by the oxygen and immediate reduction by TGA) will consume TGA and influence the composition and

concentration of the metal complexes in the solution.

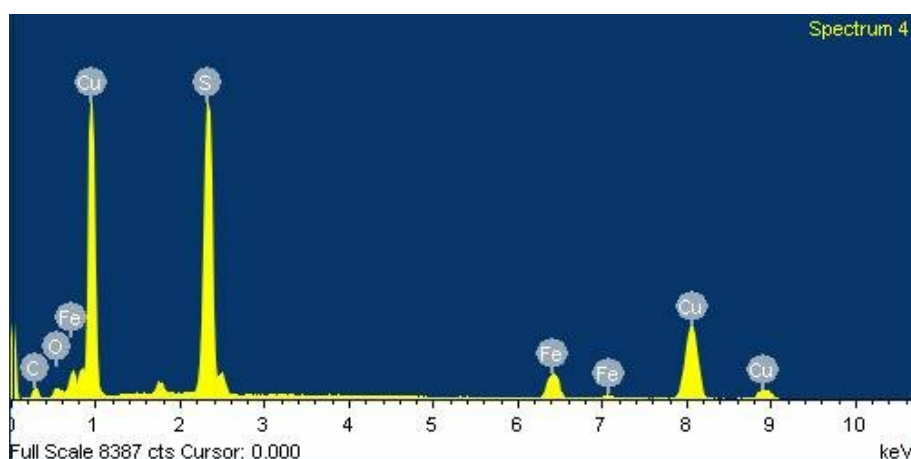
Briefly,  $\text{Cu}_2\text{S}$  and  $\text{Cu}_5\text{FeS}_4$  nanocrystals were prepared as follows. In a typical synthesis 298 mg (1.75 mmol) of  $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$  (Aldrich) and 95 mg of  $\text{FeCl}_3$  were dissolved in 100 mL of water, and an appropriate amount of TGA was added under stirring, followed by adjusting the pH by dropwise addition of a 1 M solution of NaOH. The solution was placed in a three-necked flask fitted with a septum and condenser and was deaerated by  $\text{N}_2$  bubbling for 30 min. Alternatively, only copper chloride (355 mg; 2.1 mmol) was placed to the reaction flask in order to synthesize copper sulfide. After heating the solution to  $100^\circ\text{C}$  during approximately half an hour, 1g of the 1mmol/g solution of the thioacetamide in water has been injected. NPs were allowed to growth during appropriate amount of time (in the range of 10 min – 2 h) at  $100^\circ\text{C}$  under constant flow of Ar.



**Figure 1.** Optical spectra of the typical  $\text{Cu}_2\text{S}$  nanoparticles in TCE and  $\text{D}_2\text{O}$  (left). The upper graph shows a transmittance of the corresponding solvents. Evolution of the optical spectra during the typical  $\text{Cu}_2\text{S}$  synthesis (right).

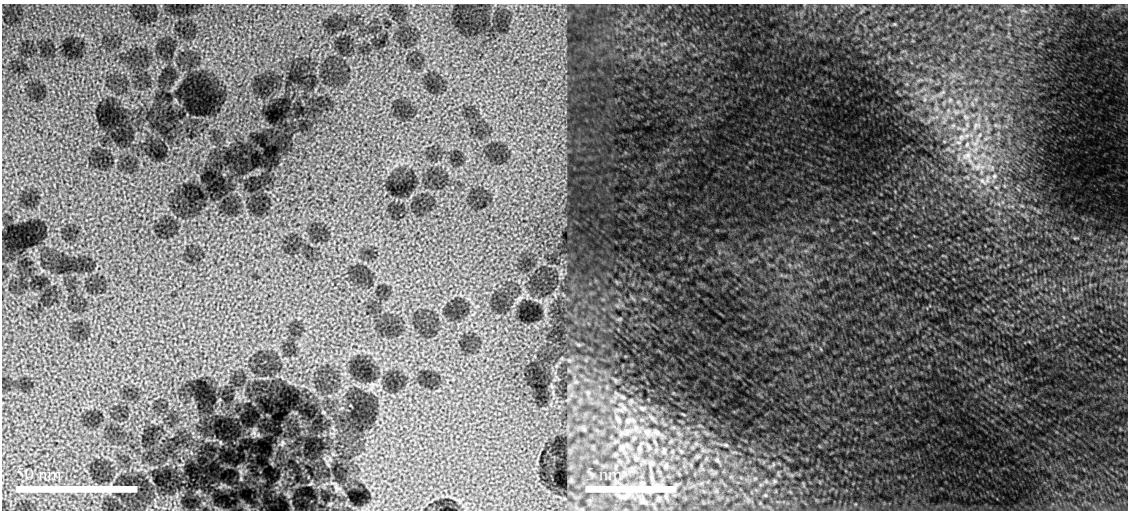
Nanoparticles were cleaned by precipitation by iPrOH and redispersion in a pure water. For optical measurements NPs were dissolved in D<sub>2</sub>O (transparent up to 1800nm) or transferred to the tetrachlorethylene (TCE) using octadecyl-p-vinylbenzyltrimethylammonium chloride (OVDAC; transparent up to 2600 nm) [6]. Typical spectra of the Cu<sub>2</sub>S in D<sub>2</sub>O and in TCE are shown in figure 1A. Spectra show plasmonic peaks at around 1400-1500 nm. Typical evolution of the optical spectra during the synthesis is shown in figure 1B. Position of the peak shifts gradually towards the lower wavelengths.

Composition of the prepared nanoparticles has been measured by EDX using drops of the preliminary cleaned samples on the silicon. The analysis shows that all elements (Cu, Fe and S) present in samples. Note, that NPs contain all elements starting from first minutes of the synthesis.



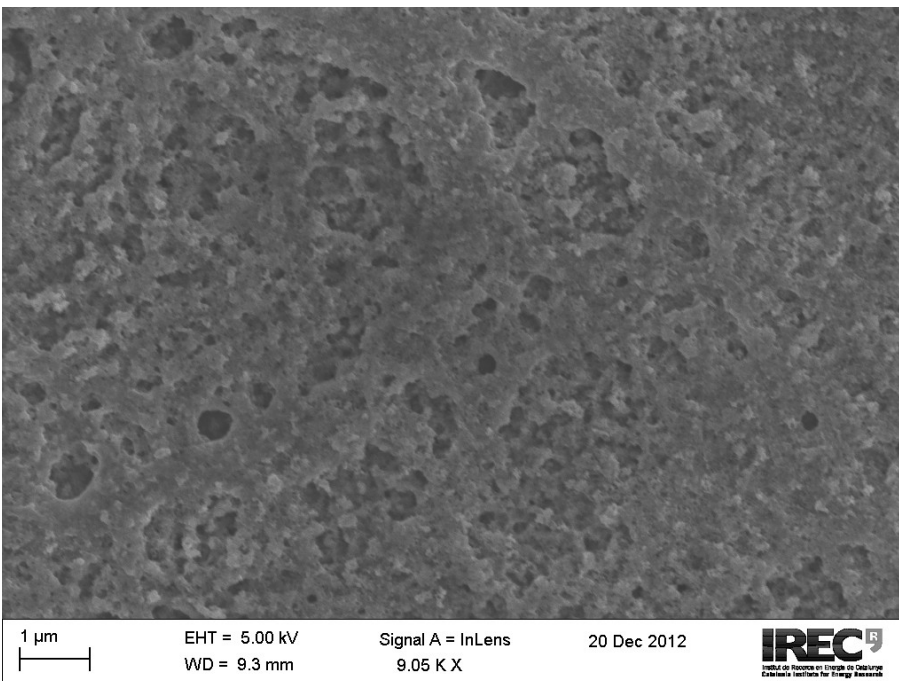
**Figure 2.** EDX spectrum of the bornite nanoparticles. Composition of the NPs is **Cu<sub>5.00</sub>Fe<sub>1.05</sub>S<sub>3.32</sub>**

Figure 3 shows TEM images of the bornite nanoparticles. Obtained NPs are polydisperse and most probably have a shape of thin plates. We can conclude it from the fact that XRD pattern of the NPs shows no distinct peaks (not shown here) while HRTEM shows clear diffraction patterns (figure 3 right).



**Figure 3.** TEM (left) and HRTEM (right) image of the prepared NPs. Scale bars are 50 nm (left) and 5 nm (right).

We made a preliminary experiment on the spraying of prepared material on the hot silicon substrate. The result of the spraying of bornite NPs on the substrate heated to 150°C shown on the figure 4. Obtained layer is quite compact and do not have a visible cracks. We are going to optimize the spraying procedure by looking for a proper formulation of the inks and conditions of the spraying.



**Figure 4.** SEM image of the bornite nanopartiles sprayed on the silicon substrate heated at 150°C

In summary, aqueous thiol stabilized Cu<sub>2</sub>S and Cu<sub>5</sub>FeS<sub>4</sub> nanoparticles have been successfully prepared at the basic condition (pH 12). Obtained nanoparticles consist of the all necessary elements (Fe, Cu and S). Prepared solution of the NPs is a stable during of at least a few weeks and can be sprayed on the hot substrate. The home made heater has been developed and adapted for using with spraying system made in TU Dresden.

## References:

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