Creation of complex composites from Metal-Organic Frameworks with pure metal nanoparticles under electronic irradiation

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Abstract. Metal-organic frameworks (MOFs) are unique materials with high porosity and flexibility utilized widely in chemistry and physics. However, they could be used as initial materials for creation new types of composites with nanoparticles. The creation of NPs inside MOFs crystals is related with different types of outer stimuli (temperature, light, and electron irradiation). Here we report about a new approach of the creation complex composites from MOFs’ crystals using the electron irradiation of the transmission electron microscope (TEM) as a highly precise method for the growing of different types of Ni and Cu nanoparticles and discuss about the dynamical process of NPs growth using the classical kinetic theory.

1. Introduction
Metal-organic frameworks are the astonishing compounds in materials science due to their high crystallinity, hierarchy, and porosity. In the last few decades these compounds became well-known in such areas as catalysis, absorption, storage, etc. Moreover, such compounds could exhibit different types of structural changes under outer stimuli as pressure, temperature, light, and magnetic or electric field. This is achieved by various types of interactions between building blocks of the compound. It plays a crucial role for observation dynamical response of MOFs’ structure under different outer stimuli (temperature, pressure, light, magnetic or electric field, etc.) such as reversible/irreversible structural changes, phase transition and bistability effects. These behaviors so important for new MOFs’ areas like for sensing or electronic and communication devices [1].

Moreover, the outer stimuli as temperature or light can be utilized for creation new types of complex materials from MOFs [2-4]. In this way, MOFs could be used as initial precursors. Such nanocomposites demonstrate better catalytical, optical and sorption properties. The amorphous carbon particles, pure metal or metal oxide nanoparticles, chalcogenides, phosphides, and carbides have become obtained employing these stimuli [4-6]. However, low precision of modification and thermal degradation are huge disadvantages of all these stimuli.

Here we report about the new advanced and precisely method for creation complex nanocomposites from MOFs as initial precursors under the electronic irradiation and discuss about the dynamics of the growth process of nanoparticles. Such approach helps to modify MOFs’ crystals in situ with high resolution and precision and with absence of thermal decomposition [7, 8].
2. Results and Discussion
In this work we utilized two compounds: HKUST-1 and Ni-BTC (BTC, benzene-1,3,5-tricarboxylate). HKUST-1 has been purchased from Sigma-Aldrich; Ni-BTC has been synthesized by solvothermal synthesis under 110°C in the oven for 24 hours and further cooling at room temperature [9]. These two compounds are composed of Cu(II) and Ni(II) ions, respectively, which are coordinated with benzene-1,3,5-tricarboxylate ligand. Recently it was found that HKUST-1 is unstable under electronic irradiation and this behavior ultimately leads to the creation of pure copper NPs within initial crystals [7, 8]. For Ni-BTC such behavior has been shown for the first time.

All major experiments have been carried out using a transmission electron microscope MET-ACCEL ARM 200F at 200 kV with variation of current density of the electron beam and magnification. Frequently, due to unstable MOFs in TEM [10], we observed absolutely amorphous crystals of HKUST-1 and Ni-BTC. However, EDX mapping revealed uniform distribution of elements in the volume of MOFs’ crystals.

![Figure 1. TEM images of MOFs’ composites with pure metal NPs: a) pure copper NPs inside crystals of HKUST-1; b) pure nickel NPs inside a crystal of Ni-BTC.](image_url)

Under electronic irradiation HKUST-1 and Ni-BTC exhibit the fast growing process of pure metal nanoparticles with high crystallinity (Figure 1). EDX mapping confirmed the creation of pure metal NPs inside initial crystals. However, the investigation of the growth process of NPs inside MOFs’ crystals revealed several interesting dependences. Firstly, the NPs growth process for HKUST-1 and Ni-BTC has a strictly dependance with parameters of the electronic beam: pure copper NPs with the average size of 9 nm inside HKUST-1 crystals could be created in 40 s and 5.5 s under magnification of 60k and 80k, respectively, and permanent current density; pure nickel NPs with the average size of 4.5 nm could be created in 15 s and 40 s under 250k and 800k, and current density of 120 and 65 pA/cm², respectively. Secondly, the experiment with HKUST-1 revealed that under permanent current density, the magnification plays a crucial role for the final size of obtained pure copper NPs. It means the bigger magnification increase the electron density on a crystal, and the biggest NPs can be observed. For Ni-BTC we observed the same result but in a different way: increasing electronic density on a crystal by current density leads to have the bigger nickel NPs inside. And thirdly, we analyzed the dynamics of growth process of pure copper NPs inside HKUST-1’s crystals. The experimental results of the nucleation and growth of pure copper NPs shown a high consistency with a classical model of Johnson-Mehl-Avrami-Kolmogorov (JMAK). It means that such complex process...
of the growth of pure copper NPs inside MOFs’ crystals could be explained well by the growth theory [8].

3. Conclusions
We found a new approach for in situ creation of complex composites with pure metal nanoparticles inside the organic matrix from metal-organic frameworks. We selected the best way for creation such complex composites under the electron irradiation, operating with such parameters as magnification and current density. It has been revealed for the first time that Ni-BTC exhibit the same behaviour under the electron irradiation as HKUST-1. Dynamical processes of NP’s growth in time revealed a good correlation with a classical model of Johnson-Mehl-Avrami-Kolmogorov (JMAK).

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