

## Colloids for Inkjet Printing of Highly Photoactive Thin Films

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Creating of photovoltaic cells with high conversion of solar light – promising trend in the field of solar energy. In this paper, we proposed the use of inkjet printing technology of photoactive films based on MOF-entrapped and pure TiO<sub>2</sub> thin films. For this application we develop a unique low temperature sol-gel synthesis using physically activated sol of crystalline phases based on the titanium dioxide produced in the process of co-crystallisation with MOF. It is shown that the developed technology and materials not only provide point positioning photovoltaic layers with high efficiency, but also to promote self-cleaning properties, exhibiting photocatalytic properties.

**Keywords:** Sol-gel, Photovoltaic, Titanium dioxide, Inkjet printing.

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### 1. SCOPES AND OBJECTS

The development of low-temperature sol - gel method allows you to create completely new materials. This study examined a new concept for the creation of highly physically activated colloid phases based on crystalline silica for multifunctional hybrid nanomaterials. For this physically activated matrix of colloidal titanium dioxide was used to create hybrid high photoactive coatings by metal-organic framework structures (MOF) in an inorganic matrix. Particular attention is paid to the study of the impact of the structural organization of the media, in order to increase surface area and finding the optimal content of crystalline phases. So as the regularities of nucleation and crystal growth in a soft synthetic describes the features of self-organization of doping agents in the inorganic matrix, studied the processes of resuspension xerogels metal oxides in the aqueous medium and analyzed the connection structure of the synthesized materials with sorption and photophysical properties.

### 2. AIMS AND RESULTS

#### 2.1 Aims and achievements

Preparation of Nanostructured materials by soft chemistry is one of the most promising areas of inorganic materials science. The most popular, for example, simple oxides acquire approaches which allow the transition from an amorphous state to a crystalline substance without resorting to an additional exposure to high temperatures. The main drawback of low temperature methods is the low crystallinity of the resulting materials, and as a consequence, low activity of obtained samples. The basic approach, able to compete in solving this problem may be a sol-gel method. As stated previously, the formation of crystal nuclei in the aqueous solution is complicated by the formation of stable complexes with aqua oxolation the reactions. Prevent this possible in several ways. The most popular approach is considered based on Raman effects strong protonating agent (usually an acidic peptizing agent)

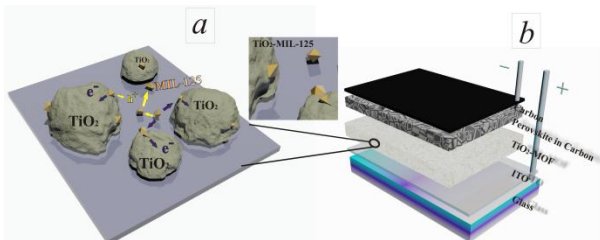
and a temperature close to the boiling point of the solvent, for promoting the dehydration process temperature. However, chemical approaches that of the crystal growth phase during polycondensation reaction, because of the high degree of protonation of the surface of the particles will contribute to the high water solubility of the compounds, significantly limiting the functionality of the resulting products. To solve these problems, the most interesting and fair approach can be based on a physical external influence to activate the phase transition from an amorphous to a crystalline structure. This allows obtain high-purity materials, predicting and managing their structure as well as to adjust pH of the medium in a wide range, which simplifies the process of co-crystallization and modification of various organic compounds. However, chemical approaches that provide crystal growth phase during polycondensation reaction, because of the high degree of protonation of the surface of the particles will contribute to the high water solubility of the compounds, significantly limiting the functionality of the resulting products. To solve these problems, the most interesting and fair approach can be based on a physical external influence to activate the phase transition from an amorphous to a crystalline structure. This makes it possible to obtain high-purity materials, predict and control their structure, and also adjust the pH of the medium in a wide range, which simplifies the process of co-crystallization and modification of various organic compounds. During research was designed for new approaches to the synthesis of functional materials based on traditional ceramic objects with controlled properties: a variable phase composition, surface area and controlled degree of crystallinity, controlled shape and measures of time-pores. To control the structural transformations and interfacial interaction of colloidal structures used physical (hydro-thermal, ultrasonic, mechanical) methods of activation, including preliminary chemical (acid, salt), a modification of the molecular precursors. Furthermore, this study investigated entirely new methods of producing xerogels crystalline oxide of titanium and aluminum when manipulating power sonication and

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temperature on the hydrolysis products of alkoxides. Deposition of colloids on the surface of thermally unstable substrates was performed by using inkjet technology. As a result of 1) first studied the mechanism of co-crystallization with the framework structures organometallic MIL-125 (Ti), which not only possess high surface area (from 500-1500 m<sup>2</sup>/g), but also superior spectral and photo-catalytic properties of (MIL-125 (Ti)). In order to form stable covalent bonds, it was made whether the modification of organic ligands-containing COO-(carboxylate) functional-functional group. By adjusting the length of the hydrocarbon radicals have been picked KMOS frame structure, complementary inorganic matrix of titanium dioxide. This led to the formation of lattice-type structures «in – grid», like the 3D structures of photonic crystals. Evaluation of photocatalytic activity for environmental photocatalysis was performed during the degradation of the fluorescent dye Rhodamine B. Analysis of the composition and concentration of the decomposition products of the photocatalytic films studied according to optical microscopy and fluorescence spectral analysis in the UV-visible range.

## 2.2 Results

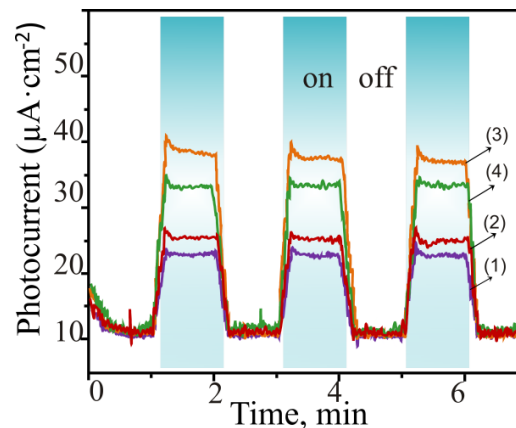
The use of photoactive MOFs in photocatalytic processes<sup>1-3</sup> and photoelectric solar energy converters has recently been reported. It has also been shown that coating the surface of titania particles with a nanoscale-thick layer of ZIF-8 resulted in a substantial increase in open-circuit voltage ( $V_{oc}$ ) due to inhibited interfacial charge recombination ( $TiO_2$ /dye and  $TiO_2$ /electrolyte) while producing dye-sensitized solar cells. However, under these conditions the environment and photocell operation time greatly affected the stability parameters. From this point of view, the application of  $TiO_2$ -MOF composites as photoactive filling material (Fig. 1a) with impregnation of methylammonium triiodoplumbate(II) ( $(NH_3Me)PbI_3$ ) crystals, corresponding to three-dimensional perovskite structures, led to formation of a depleted quasi-bulk heterojunction  $TiO_2$ /MOF-based solar cell (Fig. 1b).



**Fig. 1** – Visualization of the structure of photoactive MOF@TiO<sub>2</sub> composite(a) and structure of depleted quasi-bulk heterojunction TiO<sub>2</sub>/MOF-based solar cell (b).

Three-dimensional perovskite structures in contact with highly porous TiO<sub>2</sub>-MOF coatings possess a number of major advantages such as large absorption coefficient, high carrier mobility and high stability. In this work we have used highly photoactive MIL-125 ( $Ti_8O_8(OH)_4(O_2C-C_6H_4-CO_2)_6$ , quasi-cubic tetragonal structure) as an attractive material based on the synthetic procedure described previously. Moreover, the single-step synthesis of a TiO<sub>2</sub>-MOF composite pro-

posed in this work substantially simplifies the procedure of obtaining the corresponding materials. In the present case, the synthesis of MIL-125@TiO<sub>2</sub> was carried out by adding H<sub>2</sub>O as a limiting reactant with respect to  $Ti(OC_3H_7)_4$  (see Table S1, ESI) which resulted in step-by-step growth of a heterophase system.



**Fig. 2** – Photocurrent responses of the cells based on MOF/TiO<sub>2</sub> products containing different amounts of MIL-125 (1-2%; 2-3%; 3-4%; 4-5%).

The photocurrent response measurement was carried out under visible light irradiation to investigate the photo-induced charge separation efficiency for MOF-doped TiO<sub>2</sub> samples containing different amount of MOFs. Photocurrent response attains its maximum at 3% MOF-TiO<sub>2</sub> (39 μA/cm<sup>2</sup>). An increase in concentration to 5% does not result in an increase in photocurrent; on the contrary, we have observed a decrease (35 μA/cm<sup>2</sup>). Typically, the increase of  $V_{oc}$  is ascribed to the prohibited charge recombination due to the energy barrier effect of MOFs in titania. The suppression effect on charge recombination may be strengthened by involving a quantity MOFs, resulting in a higher  $V_{oc}$ . However, quantity of MOFs should be strictly limited, because of decrease  $J_{sc}$  significantly. The data obtained suggest that using MOFs as surface modifiers for TiO<sub>2</sub> anodes while producing quasi-bulk perovskite-based solar cells is a matter of interest due to increased adsorption capacity, hence heterojunction area. Three-dimensional structures have already been used as light harvesters for mesoscopic heterojunction solar cells. To assess the activity of the material 3% MOF@TiO<sub>2</sub>, we have constructed a depleted quasi-bulk heterojunction TiO<sub>2</sub>/MOF-based solar cell for the first time, as described in the ESI, with a carbon counter-electrode. Previously, work on modifying TiO<sub>2</sub> with perovskite nanocrystals has been performed to produce solid photocells with high stability and efficiency. We suggest increasing the area of the perovskite junction through the micro-mesoporous structure of the synthesised composite for inhibited interfacial charge recombination at the interface.

## 3. CONCLUSION

In conclusion, we have applied an inkjet printable MIL-125@TiO<sub>2</sub> composite with a highly photoactive material with good prospects for constructing quasi-bulk depleted monolithic perovskite/MOF @TiO<sub>2</sub>- heterojunction solar cells. The results of the photopolarisa-

tion measurements were employed to determine the optimal MOF concentration promoting the greatest photocurrent response. The greatest increase (39  $\mu\text{A}/\text{cm}^2$ ) was found for 3% MOF-TiO<sub>2</sub>. A MIL-125@TiO<sub>2</sub>-based heterojunction solar cell revealed high stability over time (up to 30 days), with a PCE of about 6.4%. Thus, we have shown the possibility of using MOF@TiO<sub>2</sub> composites for the successful production of solid solar cells with high stability.

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