

favourable method due to homogenous or heterogeneous chemical reaction through a highly controlled diffusion leading to the formation of high quality nanocrystals having desired size, shape, dispersability and properties. Several approaches have been adopted by researchers to control size, shape, dispersability and in turn the properties of materials. Amongst them selective doping, precursors used, surfactants, synthesis method, etc. are important ones. Surfactants also help in modifying the surface charge of nanocrystals, such that, the material becomes either hydrophobic or hydrophilic. Experiments were carried out at 150°C with autogeneous pressure over an experimental duration of 16 hours in General Purpose autoclaves provided with Teflon liners. A variety of organic and inorganic solvents (propanol, ethanol, HCl, NaOH, HF) and also various surface modifiers (oleic acid, gluconic acid, *n*-butylamine, hexaldehyde, and benzylaldehyde) were tried. ZnO was selectively doped with molybdenum, silver, niobium, and also co-doping with silver and chromium has been carried out. The products were freeze dried and subjected to a systematic characterization using powder XRD, FTIR, UV-Vis spectroscopy, Thermal analysis, SEM, TEM, and Photoluminescence spectroscopy. The powder x-ray data shows homogeneous resultant product with high crystallinity. The FTIR spectra show the presence of various functional groups depending upon the type of surface modifier used in the *in situ* surface modification. TGA curves show the release of hydroxyl, carbonates and other organic molecules up to 500°C. UV-VIS spectroscopy study indicates the shift in the band gap depending upon the doping metal(s) and the band gap also shifts slightly accordingly. Photoluminescence spectra of pure and doped and surface modified ZnO nanocrystals show very interesting results which well correlates with the powder XRD and photocatalytic data. Higher concentration of dopants leads to structural distortion and contributes to the worsening of photocatalytic properties as well as lowering free exciton energy peaks. The application potential of products was evaluated using photocatalytic degradation of organic dyes and the ZnO nanocrystals synthesized are highly effective for the degradation of several toxic organic dyes.

[1] K. Namratha, M.B. Nayan, K. Byrappa, *Mater. Res. Innovat.* **2011**, *15*, DOS 10.1179/14330751x12922272563743. [2] K. Byrappa, K. Namratha, *Prog. Cryst. Growth Charact. Mater.* **2011** (in print).

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Growth of metal oxide – Organic hybrid nanocrystals and their interfaces in environmental applications

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Metal oxides, particularly TiO₂ and ZnO find extensive applications in modern technology including photocatalysis for environmental issues. Major breakthrough occurred during 1970s when Fujishima and Honda (1972) reported electrochemical photolysis of water at semiconductor electrode (TiO₂) [1]. With the discovery of quantization effect during the late 1970s, the size reduction in metal oxide semiconductors became a major objective to achieve higher efficiency in their applications. Difficulties in the growth of metal oxide nanocrystals were associated with the control of size, morphology, coagulation, reproducibility of results and dispersability. During 1990s several such attempts were made on the use of organic molecules as ligands or capping agents or surfactants. Also *ex situ* surface modification was tried with limited success. Thus an alternate route was envisaged to obtain high quality nanocrystals of TiO₂ and ZnO with controlled size, morphology,

dispersability and without any coagulation using *in situ* surface modification through Hydrothermal, Solvothermal and Supercritical hydrothermal routes [2]. The size could be reduced significantly to a few nanometers without any coagulation and the organic coating was so much uniform and thin, that did not alter the inherent properties of metal oxide core. The organics which are insoluble and exist as separate phases under ordinary conditions became homogeneous phases under hydrothermal / solvothermal conditions. The small size and high surface to volume ratio of the individual nanoparticles imparts distinct size tunable physical and electronic properties that have prompted some to refer to them as “artificial atoms” [3]. A highly controlled self-assembly of these hybrid nanocrystals when dispersed in organic solvents into two-dimensional and/ or three-dimensional ordered structures or superlattice structures remains a relatively unexplored area. The mechanism of formation of organic-inorganic hybrid nanocrystals is very important. Here, theory of mechanism of the formation of organic-metal oxide interface has been discussed in detail with specific case studies. Another greatest advantage of such an *in situ* modification is that the nanocrystals surfaces could be made either hydrophobic or hydrophilic. The organics could be easily removed through sintering at around 500°C, such that crystals still remain as individual nanocrystals with controlled size and morphology. Experiments were carried out within the temperature range 150 – 250°C with autogeneous pressure. The run products were characterized using powder XRD, FTIR, UV-VIS, Positron annihilation lifetime and photoluminescence spectroscopy, TEM, SEM, etc. followed by a systematic evaluation of photocatalytic properties through degradation of toxic organic industrial effluents and waste. Thus the nanohybrid metal oxide crystals could be the most effective and prospective materials for environmental issues.

[1] A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37-38. [2] T. Adschiri, K. Byrappa, In: *Nanohybridization of Organic-Inorganic Materials*, Eds: Atsushi Muramatsu, **2009**, Springer-Verlag, Germany. 217-250. [3] D.V. Shevchenko, D.V. Talapin, C.B. Murray, S. O'Brien, *J. Am. Chem. Soc.* **2006**, *128*, 3620-3637.

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Study of the intercalation of organic molecules into Hydrotalcite by fast in situ XRPD

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A new mild and fast solid state [1] for the preparation of exchanged layered double hydroxide materials (LDH), in particular, for the intercalation of bioactive molecules was extended and adapted from the intercalation of phenylbenzimidazolsulfonic acid to two other kind of compounds. The chosen organic guest were 3-carboxy-coumarin and, given their importance, a series of non-steroidal-anti-inflammatory-drugs with different pka and steric hindrance; namely Ketoprofen, Flurbiprofen, Ibuprofen, and Tiaprofenic acid.

The mechanical mixture of the LDH-NO₃ and the guest compound was put in a capillary and then dampened with a drop of NaOH solution causing the intercalation to take place. The characterization of the