

# Advances in Functional Inorganic Materials Prepared by Wet Chemical Methods (Volume II)

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Functional inorganic materials are an indispensable part of innovative technologies, which are essential for development in many fields of industry. The use of new materials, nanostructures, and multicomponent composites with specific chemical or physical properties promotes technological progress in electronics, optoelectronics, catalysis, biomedicine, and many other areas that are concerned with aspects of human life. Due to the broad and diverse range of potential applications of functional inorganic materials, the development of superior synthesis pathways, reliable characterization, and a deep understanding of the structure–property relationships in materials are rightfully considered to be fundamentally important scientific issues. Only synergetic efforts of scientists dealing with the synthesis, functionalization, and characterization of materials will lead to the development of future technologies. This Special Issue on “Advances in Functional Inorganic Materials Prepared by Wet Chemical Methods (Volume II)” covers a broad range of preparation routes, the characterization and application of functional inorganic materials, and metal–organic materials that are important in the fields of catalysis, electronics, optics, biomedicine, and others.

Metal phosphates are a family of inorganic compounds that are widely used in different areas such as medicine, catalysis, sensors, water treatment, the development of optical materials, etc. Calcium hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) is probably the most popular member of the calcium phosphate (CP) subfamily, whose solubility, specific surface area, surface wettability, and adsorption characteristics strongly depend on the morphology and crystallinity. Karalkeviciene et al. [1] investigated the effects of different organic solvents on the formation of hydroxyapatite via the hydrolysis of  $\alpha$ -tricalcium phosphate under solvothermal conditions. The syntheses were performed with different proportions of water–organic solvents: ethylene glycol, methyl alcohol, ethyl alcohol, isopropyl alcohol, and butyl alcohol. The influence of the solvothermal conditions, the nature of the solvent, and the effect of the organic solvent fraction in the solution on the phase purity and morphological features of HA were investigated. It was demonstrated that methyl alcohol and ethylene glycol had a stronger inhibitory effect on the hydrolysis process. The morphology of the obtained samples varied from plate-shaped to rod-shaped depending on the reaction medium and synthesis conditions. Out of all the solvents analyzed, ethylene glycol had the highest impact on the sample morphology. A different efficient way to modify the morphology of hydroxyapatite considers the usage of various organic additives. A comprehensive experimental study was carried out to compare the effects of sodium lauryl sulfate and three amino acids (DL-aspartic acid, dodecanedioic acid, and suberic acid) on the formation of calcium-deficient hydroxyapatite via the hydrolysis of  $\alpha$ -tricalcium phosphate [2]. The study revealed that higher concentrations of sodium lauryl sulfate and dodecanedioic acid induced the formation of impurities in addition to hydroxyapatite, whereas aspartic and suberic acids did not affect the phase purity. The morphology of the samples varied from plate- to rod-like depending on the concentration of the specific organic additive.



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Another member of the CP group is brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ), which is a material that can be synthesized in aqueous medium by using simple wet precipitation. Alshaaer et al. [3] studied the feasibility of full-scale substitution of  $\text{Ca}^{2+}$  by  $\text{Ni}^{2+}$  ions and its influence on the crystal structure of brushite. The authors concluded that the substitution level is limited, and that the replacement of 20% of  $\text{Ca}^{2+}$  leads to the formation of a mixture of compounds.

Rare-earth phosphates are another group of phosphate-based materials that recently have gained much scientific interest, especially in the field of luminescent materials. Ezerskyte et al. [4] reported the hydrothermal synthesis of  $\text{GdPO}_4:\text{Eu}^{3+}$  nanoparticles by varying different synthesis parameters: pH,  $\langle\text{Gd}\rangle:\langle\text{P}\rangle$  molar ratio, and  $\text{Eu}^{3+}$  concentration. It was shown that the nanoparticle length can be adjusted from hundreds to tens of nanometers by changing the pH. Increasing the  $\langle\text{Gd}\rangle:\langle\text{P}\rangle$  molar ratio resulted in a decrease in nanoparticle length and an increase in its width. The temperature-dependent measurements in the 77–500 K range revealed that the  $\text{GdPO}_4:50\%\text{Eu}^{3+}$  sample maintains half of its emission intensity, even at room temperature.

Silver phosphate ( $\text{Ag}_3\text{PO}_4$ ) can be used as an efficient photocatalyst, which shows a very strong oxidation capacity and high visible-light catalytic activity. However,  $\text{Ag}_3\text{PO}_4$  is prone to photoelectron corrosion and becomes unstable during photocatalysis, which severely limits its application in this field. A tubelike  $\text{g-C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$  heterojunction was constructed with the chemical precipitation method by Yan et al. [5]. The photocatalytic activity of the photocatalyst was evaluated based on the degradation of RhB under visible-light irradiation. The degradation rate of the RhB was 90% under irradiation for 40 min; moreover, the recycling experiment showed that there was no apparent decrease in the activity of the heterojunction after five consecutive runs.

Precious metal-based catalysts are the most widely studied and are currently regarded as state-of-the-art electrocatalysts for formic acid/formate oxidation because of their high catalytic activity and good anti-poisoning properties. In a study by Nacys et al. [6], a platinum-coated Ni foam catalyst ( $\text{PtNi}/\text{Ni}$ ) was investigated for the oxidation of the formate reaction in an alkaline medium. The catalyst was fabricated via a two-step procedure, which involved an electroless deposition of the Ni layer and the subsequent electrodeposition of the platinum layer. The obtained composite demonstrated enhanced electrocatalytic activity compared to the Ni/Ni foam catalyst and pure Pt electrode.

Another area of application of precious metals is molecular analysis by SERS spectroscopy. Zavatski et al. [7] fabricated gold nanostructures on two different types of substrates, namely, meso- and macroporous silicon, via an electroless chemical deposition method for different time periods. SERS measurements were performed for the R6G molecules adsorbed on different Au-coated samples at a  $10^{-6}$  M concentration. The authors demonstrated the correlation of the R6G SERS spectra intensity with the morphology and structural properties of Au coverage on the silicon surface.

Carbon-based materials comprise another wide and diverse class of functional inorganic compounds, which can be modified in a variety of ways. A special subgroup of these materials, known as graphite intercalation compounds (GICs), are especially interesting due to their use in Li-ion batteries, superconductivity, catalytic activity, etc. Rimkute et al. [8] demonstrated the synthesis of GICs using three different oxidizers:  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $\text{K}_2\text{S}_2\text{O}_8$ , and  $\text{CrO}_3$ , with and without  $\text{P}_2\text{O}_5$  as a water-binding agent. The use of  $\text{CrO}_3$  resulted in a much higher structural disorder, whereas a minimal defect concentration was reached by using  $\text{K}_2\text{S}_2\text{O}_8$ . The use of  $\text{P}_2\text{O}_5$  can help to achieve more effective intercalation and has a positive effect on the formation of the stage I GIC phase.

Graphene-polypyrrole nanocomposites were synthesized via a wet-way protocol using a graphite bisulfate precursor, which was prepared in the presence of concentrated sulfuric acid and potassium periodate [9]. Three different types of graphite precursors with particle sizes of  $<50 \mu\text{m}$ ,  $\geq 150$ ,  $\leq 830 \mu\text{m}$ , and  $\leq 2000 \mu\text{m}$  were used for this purpose. The nanocomposites prepared from exfoliated graphene and polypyrrole had a core-shell structure, where the particle core is composed of exfoliated graphene covered by a polypyrrole

shell. The most relevant areas of application for these obtained nanocomposites, including energy storage and (bio)sensing, were considered.

Synthetic conditions for the preparation of different types of spherical amine-holding silica particles were proposed by Melnyk et al. [10]. The Stöber version of a sol-gel method of co-condensation of two alkoxy silanes was used for the one-pot synthesis of silica particles with  $\equiv\text{Si}(\text{CH}_2)_3\text{NH}_2$ ,  $\equiv\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2$ , and  $\equiv[\text{Si}(\text{CH}_2)_3\text{NH}]_2$  functional groups that had an available group content of 1.3–2.3 mmol/g. The sorption properties of these hybrid materials for nickel(II) and copper(II) ions, as well as for bovine serum albumin, were found to be dependent on the structure of the materials and the type of incorporated functional group. The maximal static sorption capacity values toward the targeted adsorbates were shown by the samples with 3-aminopropyl groups (1.27 mmol Ni/g), diamine groups (1.09 mmol Cu/g), and secondary amine groups (204.6 mg BSA/g).

The study of Pt and Pd complexes with various organic compounds is of fundamental and practical interest due to a wide range of applications, including biosensors, DNA visualization, and catalysis. Novikov et al. [11] reported the synthesis of new  $[\text{PdCl}_2(\text{HGua})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$  and  $[\text{PtCl}_5(\text{HGua})] \cdot 2\text{H}_2\text{O}$  compounds using wet chemistry methods. It was shown that the complexes have an M-N bond, and the organic ligand is included in the first coordination sphere. In the palladium complex,  $\pi$ -halogen and  $\pi$ -stacking interactions were found, whereas in analogues, such interactions were not found. On the other hand,  $\pi$ -halogen and halogen interactions were found in the structure of a platinum complex and its analogues. The same group of authors reported the synthesis of new platinum and uranium compounds with nicotinic acid [12]. The authors described the synthesis of two new anionic complexes,  $(\text{HNic})_2[\text{PtCl}_6]$  and  $(\text{HNic})_2[\text{UO}_2\text{Cl}_4]$ , using wet chemistry methods. It was determined that hydrogen bonds ( $\text{H} \cdots \text{Hal}/\text{Hal} \cdots \text{H}$  and  $\text{O} \cdots \text{H}/\text{H} \cdots \text{O}$ ) are the main contributors to the intermolecular interactions in both compounds. Other important contacts in cations are  $\text{H} \cdots \text{H}$ ,  $\text{C} \cdots \text{H}/\text{H} \cdots \text{C}$ , and  $\text{C} \cdots \text{Hal}/\text{Hal} \cdots \text{C}$ ; in anions, it is  $\text{H} \cdots \text{Hal}/\text{Hal} \cdots \text{H}$ . The Pt-containing complex has a halogen- $\pi$  interaction and halogen bonds, but this type of interaction was not observed in the U-containing compound.

Another successful synthesis of metal-organic compounds was demonstrated by Zhang et al. [13]. In this study, two different phase-pure cobalt(II) cyanoguanidine bromide coordination compounds,  $\text{Co}(\text{C}_2\text{N}_4\text{H}_4)_2(\text{H}_2\text{O})_4 \cdot 2\text{Br} \cdot 2\text{H}_2\text{O}$  (**1**) and  $\text{Co}_3(\text{C}_2\text{N}_4\text{H}_4)_8(\text{H}_2\text{O})_8 \cdot 6\text{Br}$  (**2**), were precipitated from aqueous and methanol solutions, respectively. It was shown that the magnetic susceptibility of **1** is consistent with either isolated or very weakly interacting  $\text{Co}^{2+}$  centers, whereas the magnetic susceptibility of **2** is evidence of the potential weak antiferromagnetic exchange interactions that may arise from the superexchange within the binuclear clusters.

Layered double hydroxides or hydrotalcite-like compounds are layered basic salts, whose structural features give them a number of specific properties which can be tuned by the modification of the chemical composition and partial substitution of metal ions. Nestroinaia et al. [14] employed three different wet chemical methods (co-precipitation at variable pH, co-precipitation followed by hydrothermal treatment, and co-precipitation with microwave treatment) to synthesize Mg/Ni-Al layered double hydroxides containing triply charged nickel cations. Despite the variety of synthetic approaches, the properties of the samples synthesized by the different methods were shown to be quite similar.

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