Design and construction of mineral-based functional nanomaterials inspired from nature-like engineering

S. Sun¹, O. Kotova², Ye. Golubev², F. Dong¹

¹Southwest University of Science and Technology, Mianyang, Sichuan, P.R. China; *shiysun@163.com*

²Institute of Geology FRC Komi SC UB RAS, Syktyvkar, Russia

Synthetic minerals, also known as «artificial minerals», refer to create the similar or analogous mineral substances by artificial methods. Synthesis of minerals or their analogues for creating functional materials for modern industries are important tasks, which solves the current demand for technological developments or overcome the limitations of natural resources [1-3]. With the advance of modern analytical technologies, especially the application of in-situ analysis technology in mineralogy at nano/molecular scale, the nanostructures and surface interface characteristics of natural nanominerals are gradually recognized. The understanding of the diversity of the mineral world has inspired construction mineral-based functional nanomaterials through natural raw minerals to improve the habitability of the earth. Based on the understanding of the genesis, composition, nanostructure and the transformation mechanism under geological conditions, the presented study focus on designing and constructing mineral-based functional nanomaterials such as two-dimensional layered nanomaterials and related microcapsule-based microreactors using clay minerals, graphite-like and talc-like matrixes as the building-blocks.

The bioinspired design and assembly of membrane-bounded semi-permeable microreactor was constructed based on spontaneous partitioning of mineral particles at water/oil interfaces to produce Pickering emulsion droplets comprising shell-like microstructures. The polydopamine-modified TiO₂ nanoparticles in clay-based colloidosomes utilizing montmorillonite as a microcapsular membrane. The PDA-TiO₂ clay colloidosomes effectively stabilized the TiO₂ NPs when compared to free aqueous dispersions. Moreover, the PDA-TiO₂ clay colloidosomes also exhibited versatility for enhancing the photocatalytic degradation of organic dyes. Our results suggest that PDA-TiO₂ clay colloidosomes can selective sequester and degrade the organic dye MB in the presence of RhB. It was found that encapsulation of TiO₂ nanoparticles within the clay colloidosomes enhanced the photocatalytic degradation efficiency. The results showed that selective degradation of methylene blue in the presence of rhodamine B was possible, with a decay constant ratio (λ MB/ λ RhB) of 2.04.

Among the various synthetic 2D graphite-like nanomaterials, graphitic carbon nitride (g-C₃N₄), a kind of non-metallic semiconductor, has garnered considerable attention due to its superior physicochemical properties such as unique band position, economic efficiency, facile preparation, and excellent chemical stability. Inspired by polydopamine (PDA) surface chemistry, a novel type of photocatalyst consisting of PDA surface-functionalized g-C₃N₄ was fabricated in this study for highly efficient visible-light-driven photocatalytic NADH regeneration. The photocatalytic performance and kinetic processes were investigated to evaluate the efficiency of NADH regeneration by the PDA/g-C₃N₄ photocatalysts. A photocurrent density 3 times higher than that of pristine g-C₃N₄ was obtained. The photocatalytic activity of the PDA/g-C₃N₄ photocatalysts showed a pH dependence, where an increase in pH from 3.0 to 9.5 substantially enhanced the NADH yield. The 20 wt. % PDA/g-C₃N₄ exhibited the highest photocatalytic efficiency, achieving a NADH yield of 94.7% with an initial reaction rate of 2.4 mmol·h⁻¹·g⁻¹, about 6 times higher than that of pristine g-C₃N₄.

Aminoclay is a novel type of synthetic Talc-like organosilicate clay, which has important potential application in the field of enzyme immobilization used as the nanostructured support. In the presented study, Lipase from *Aspergillus oryzae* was immobilized on Fe-aminoclay support via 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) as covalent crosslinking agent. The nanocomposite structure of immobilized lipase (Feclay-lipase) was characterized by XRD, TEM and FT-IR. The enzymatic properties of free lipase and Feclay-lipase were studied by enzymatic kinetics. The results showed that the optimal immobilization efficiency of Feclay-lipase was 82.88 %, immobilization capacity was 414.4 mg·g⁻¹ support, and the enzyme activity was 28.24 U·mg⁻¹, which was three times higher than that of free lipase (8.21 U·mg⁻¹). The optimum reaction temperature of Feclay-lipase increased from 45 °C to 55 °C, the optimum pH shifted to alkalinity, and the catalytic activity of Feclay-lipase did not decrease significantly after storage at 4 °C for one month.

Our study demonstrated a promising way to create smart nanomaterials from natural mineral resources with the potential for using in diverse industrial applications.

The reported study was funded by RFBR and NSFC according to the research project RFBR № 20-55-53019 and NSFC № 4191101331, 41672039.

References

1. Kotova O. B., Harja M., Kotov L. N., Ponaryadov A. V. Titanium minerals as prototypes of functional ma-

terials with pronounced electromagnetic properties ash. Vestnik of Institute of Geology of Komi SC of UB of RAS. 2018. № 4. Pp. 34—39. doi: 10.19110/2221-1381-2018-4-34-39

2. Ponariadov A. V., Kotova O. B. Phosphate sorption on leucoxene. Vestnik of Geosciences. 2020. 1(301). Pp. 19—23. doi: 10.19110/geov.2020.1.3

3. Shchemelinina T. N., Anchugova E. M., Kotova O. B., Sun S., Shushkov D. A., Gogonin A. V., Likhanova N. V., Zueva O. M., Korchagina Yu. S. Why mineral carriers are necessary for microalgae. Vestnik of Geosciences. 2020. 2(302). Pp. 24—28. doi: 10.19110/geo.2020.2.4.