Synthetic analogs of minerals as advanced Cu-based solid-solution photocatalysts

A key challenge of the present decade worldwide is to get rid of increasing environmental contaminants. The exponential growth of the world's population has led to increased energy demand and environmental destruction due to significant amounts of colored wastewater discharged into the environment from various industries such as textiles, paper, food and pharmaceutical plastics. The presence of dyes in wastewater (even in very small amounts) is undesirable due to their hazardous influence and dangerous effects on human health and other living species, as they affect the food chain and aquatic life. Dyes hinder water from being exposed to the sunlight hampering the photosynthetic activity. Additionally, they cause serious water pollution due to their non-biodegradability and toxicity.

Some conventional physical and chemical techniques can efficiently remove dyes from wastewater, however, these methods have limitations. Photocatalytic degradation has been regarded as a more effective method for remove dyes from wastewater. The purification process takes place as a simple reaction: when a semiconductor is irradiated with photons with energy greater than its band gap energy, electron-hole pairs are formed. In aqueous system, holes react with water or OH−adsorbed on the surface of the semiconductor to produce OH·radicals, and electrons trapped at surface sites react with O_2 to form superoxide anion radical O_2 · (or HO_2·at lower pH). The oxidizing species undergo a series of reaction to convert the dye to biodegradable intermediates and finally to CO_2, water, and salts of mineral acids.

For several decades, TiO_2 has been considered as one of the most promising candidates for photocatalysts due to its suitable energy band position (valence and conduction bands for oxidation and reduction), low cost, chemical stability, and high photoactivity. However, TiO_2 as a photocatalyst is inefficient because of its wide bandgap (3.2 eV). TiO_2 only works when exposed to the UV portion (<400 nm) of the solar spectrum. In terms of energy, sunlight consists of 3–5% UV (<400 nm), 42–43% visible (Vis) light (400–700 nm), and 52–55% infrared radiation (>700 nm). The development of visible light response semiconductor photocatalysts is required.

The use of mineral-based semiconductors as photocatalysts has been the focus of recent attention since it aims at the destruction of contaminants in water and air. Synthetic Cu-based minerals have attracted attention recently as a photocatalyst for reactions with visible light. They can be a promising alternative to TiO_2 which the photoabsorption spectrum is in the range of ultraviolet (UV) light due to its large bandgap, which accounts for only 5% of the sunlight with low overall efficiency.

The objective of the study is synthesis and photocatalytic characterization of series of substances which are solid solutions of Cu-based minerals. It is hypothesized that intermediate solid solutions exhibit better photocatalytic properties than pure end members. This will be accomplished by laboratory synthesis of two types of materials, analogs of natural minerals: stannite sulfosalts $Cu_2(Fe_xMn_{1-x})SnS_4$ solid solutions (semiconductors) and various 3D hierarchical superstructures of libethenite Cu_2PO_4OH – olivenite Cu2AsO4OH solid solutions. The structural and chemical properties of as prepared photo-catalyst samples will be characterized by X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and UV-visible absorption spectroscopy techniques. The photo-degradation of methylene blue has been chosen as a model reaction to evaluate the photocatalytic activities of the phases in question and their solid solutions. The effect of isomorphic substitution in the structures on photocatalytic properties will be determined to optimize the procedure of synthesis. The possible photocatalytic activity enhanced mechanism will be proposed.

The project will be concerned with fundamental research which is designed to generally increase mineralogical and geochemical sciences but also important from the point of view of environmental protection and material science. In contrast to multiple experiments and research carried out on synthetic and pure minerals, in the proposed project the author focuses on completing and updating the state of knowledge in the field of photocatalytic properties of isomorphic series Cu_2MnSnS_4 - Cu_2FeSnS_4 and $Cu_2(AsO_4)OH$ - $Cu_2(PO_4)OH$. Additionally, the properties of olivenite [$Cu_2(AsO_4)OH$] have not been investigated in terms of the degradation of organic dyes so far. Additionally, exploration of substitution effect to inner structure is crucial of understanding the path of crystallization these minerals in environmental and geologic processes. Vast number of recent publications reports about photocatalytic properties pure members of stannite and olivenite minerals group. For this reason, it is so important to understand the mechanism of substitution of elements in these isomorphic series and the influence of these substitutions on photocatalytic properties.

Therefore, the importance of the project includes three areas:

- the results will advance basic knowledge of an intensively studied group of minerals
- the proposed methodology contributes to the development of experimental and analytical techniques that can be widely used in the future in mineralogical, geochemical, environmental sciences and materials science
- some research results may be used in the future in technology and nanotechnology