

Fe₃O₄'s Phase Composition and Magnetic Properties are Affected by in-situ Oxidation: Suggestions for Zinc Hydrometallurgy

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Abstract

The removal of iron in zinc hydrometallurgy results in the production of a significant amount of hazardous waste, which poses a serious and enduring environmental threat. As of late, an imaginative magnetite (Fe₃O₄) strategy for iron precipitation has been proposed. However, the oxidizing conditions in the pregnant leach solution from zinc hydrometallurgy cause Fe₃O₄'s magnetic separation performance and phase composition to be sensitively altered. A variety of in-situ Fe₃O₄ samples with varying degrees of oxidation were created in this study. We found that oxidation didn't demolish the Fe expulsion and that all examples have a moderately high iron substance (>42.3%). In the meantime, although the samples' magnetic properties decreased from 32.31 to 6.56 emu/g, they were still able to be recovered (10.60 emu/g) by controlling the oxidation to some extent. As the degree of oxidation increases, there is a correlation between this and the phase transition of iron oxides. Raman and Fourier transform infrared spectroscopy measurements have also shown that the change in Fe-O bond length is the mechanism by which oxidation affects magnetic properties. This work gives another technique to the commonsense ramifications of the "attractive iron" rather than the magnetite precipitation strategy in zinc hydrometallurgy.

Keywords: Steel swarf; Recycling; Leaching selectively; Dissolving fluid; Ferric chloride; Hazardous materials

Introduction

With a relatively lower energy cost than pyrometallurgy, hydrometallurgy uses aqueous solutions to leach metals from battery waste. Strong acids cause valuable metals like Co and Ni to be leached, then they are extracted separately or simultaneously with organic solvents, and finally they are (co-)precipitated into solid-state salts [1]. The extraction efficiency, the quantity and composition of the corresponding (co-)precipitates, and ultimately the electrochemical performance of regenerated cathodes are all influenced by the composition of the leaching solution. For this reason, a high-efficiency hydrometallurgy process for recycling waste LIBs requires the rapid and sensitive detection of metal ions in a leaching solution. This must be a difficult task due to the complexity of the sample matrix, which necessitates extensive pretreatments and a wide range of prior knowledge, given the numerous components of cathode active materials like LiCoO₂, LiFePO₄, LiNi_xMnyCozO₂, and LiNiO₂. Specifically, the ordinary metal particle fixation in corrosive filtering arrangement from the hydrometallurgy cycle of waste LIBs is in the reach among μM and mM , which is a long ways past the interest and capacity of the regular strategies.

One of the most common methods for compositional analysis of metal ion-containing aqueous solutions is inductively coupled plasma mass spectrometry (ICP-MS); However, when the specimen is at a high concentration that is more than 10³ times greater than its maximum detection limit (hundreds of M), an extreme pre-dilution is necessary, implying a high risk of error caused by dilution. Otherwise, ionization suppression, the space charge effect, and spectral interference from matrix elements frequently result in a significant loss of sensitivity to a target metal ion when there is a high level of sample matrix [2]. Also, ICP-MS depends on unsafe synthetics, for example, water regia, nitric corrosive, and sulfuric corrosive to get ready homogeneous examples, delivering the discovery cycle more mind boggling and perilous. These issues likewise go with an extra test by changing the substance harmony of an objective metal where its prevalent stage at balance is profoundly reliant upon temperature, tension, focus, and pH.

Fluorescent chemosensors could be a potential option in contrast to the customary procedure because of high responsiveness, basic activity without pre-treatment, speedy and continuous reaction, and cheap instrumental set-up. They act as a device for the specific and delicate discovery of metal particles in the ecological and organic frameworks to screen pollution and explain the component of arising poisonous impacts, separately [3]. Broad investigations have been centered around the advancement of fluorescent test particles fitting for the location of follow measures of metal particles under different conditions. These incorporate exploration endeavors to plan 1) an organizing ligand that includes a tunable proclivity and selectivity toward an objective metal particle and 2) a fluorophore showing an adjustment of fluorescence signal at a particular frequency upon the limiting occasion. A wide range of fluorescent sensor platforms have been established for the detection of environmentally (Cd²⁺, Hg²⁺, and Pb²⁺) and biologically (Ca²⁺, Cu²⁺, Fe³⁺, and Zn²⁺) important metal ions thanks to the remarkable advancements in coordination and fluorophore chemistry over the past fifty years. However, the hydrometallurgy process's wider use of fluorescent sensor platforms has not yet been achieved. Supposedly, there are a couple of reports in regards to the (quantitative) discovery of high-moved metal particles in watery arrangements, particularly without outrageous pre-weakening. This is because most fluorescent sensors no longer depend on concentration in the low concentration range. In typical acid-leaching solutions, the amount of metal ions far outweighs the amount of ligand and/or fluorophore molecules, leading

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to early saturation. The inability to maintain their functions with high population density and quality while forming close-packed arrays of alternating ligand and fluorophore molecules presents a challenge. They frequently conflict with one another: Fluorophore loses its optical property as a result of severe aggregation, and metal ions are unable to sterically bind to ligand molecules.

However, traditional treatments that lack on-demand and precise antibacterial capabilities face issues such as uncontrolled drug release, inadequate concentration of nanomaterials in infected sites, and toxicity to healthy organs and tissues. Plus, the wide range medicines of general nanomaterials consistently lead to the advantageous microbes passing and low bactericidal productivity of pathogenic microscopic organisms, but with phenomenal antibacterial effectiveness [4]. To deal with the multi-microorganism contaminated locales and the muddled physiological and biochemical climate in vivo, on-request and exact procedures assume fundamental parts. In the absence of stimuli, nanomaterials based on an on-demand strategy typically remain in a "turn off" state and are unable to release antimicrobial agents or exert antibacterial effects; however, once they reach the appropriate location, they may suddenly switch to a "turn on" state. As a result, on-demand nanomaterials boost antibacterial efficacy while minimizing harm to healthy tissue from antibacterial effects or agents. Because targeting nanomaterials only bind to specific sites, they can be concentrated in bacterial infectious tissue, reducing the toxicity of extravasation drugs and allowing the antibacterial effect of nanomaterials to work precisely in close proximity to bacteria. To combat side effects and increase sterilization rates, nanomaterials should be designed to precisely target bacteria or respond to infectious locations based on the original antibacterial effect.

There are fewer reviews of the development and implementation of on-demand and precise strategies than there are of antibacterial properties, functions, and activation mechanisms of nanomaterials. This review therefore began with a discussion of nanomaterials based on precise and on-demand strategies. The design of various NPs was then completed. Following that, specific classifications and applications of these nanosystems were discussed. The purpose of this review is to improve comprehension of the design mechanisms, benefits, and disadvantages of various nanomaterials based on precise and on-demand antibacterial strategies, as well as the current applications challenges. In conclusion, we offered our viewpoints and direction regarding the development of nanomaterials in the future based on precise and on-demand strategies. Several highly regarded reviews on the use of stimuli-responsive and targeting nanomaterials to combat bacterial infection have been published up to this point. Sheshala et al. comprehensively analyzed the role of nanomaterials that respond to stimuli in infectious diseases.

The strategies and mechanisms of stimuli-responsive nanomaterials were summed up by Ji's group. Geng and co. provided a list of traditional targeting groups and a summary of the antibacterial mechanisms of various materials. The advantages, disadvantages, and difficulties of targeting nanomaterials for antimicrobials were delicately discussed by Adam's group [5]. Based on on-demand and precise antibacterial strategies, these reviews have provided a comprehensive summary of antibacterial nanomaterials and promoted novel approaches to the treatment of bacterial infections. However, the majority of the aforementioned works primarily focus on describing the findings and conclusions of studies without offering any suggestions for the future development of more advanced nanomaterials. The mechanisms, advantages, disadvantages, difficulties, and perspectives of various on-

demand and precise antibacterial strategies were summarized in this review after in-depth examination and analysis of previous works. More importantly, this review provided researchers with a more precise understanding of the increased antimicrobial efficacy of nanocomposites with on-demand and precise strategies over benchmarked systems.

Using the immune cell membrane as a target

Physical adsorption or chemical bonding were used by researchers to alter the surface of nanomaterials in order to give them good targeting properties. Notwithstanding, these techniques require reasonable material plan and muddled readiness processes, which limit the uses of these strategies. In recent years, researchers have discovered that membrane-coated NPs have numerous functions, high biosafety, and simple preparation. Multi-functional cell membranes like those from macrophages, dendritic cells, neutrophils, and platelets have been used by researchers to modify NPs to target bacteria and inflammatory sites.

Macrophages layer: As "bleeding edge warriors", macrophages perceive microbial science through the over-articulation receptors (predominantly the cost-like receptors) that can tie distinctively to microorganisms. Strangely, when various microbes initiated macrophages, the receptors on the outer layer of macrophages changed simultaneously. In order to target bacteria, Zhang's group coated gold nanocages known as Sa-M-GSNC with an *S. aureus*-treated macrophage membrane. Under NIR laser irradiation, this kind of nanosystem with a long cycle time, good biocompatibility, and a PTT antibacterial effect combined with bacteria [6]. In light of gold nanocages, the antibacterial pace of Sa-M-GSNC expanded by 25%. Sa-M-GSNC was capable of drug loading and PTT-responsive on-demand drug delivery due to its hollow nanocage structure. Xu's group developed poly lactic-co-glycolic acid (PLGA)-simvastatin-CS-metronidazole NPs coated with *P. gingivalis*-treated macrophage membranes (MM/STNPs) in another study to treat both periodontitis and atherosclerosis simultaneously. As well as being the essential microorganism of atherosclerosis, *P. gingivalis* can likewise enter veins to advance the movement of atherosclerosis. As a result, the authors came up with a creative way to coat NPs with the membranes of *P. gingivalis*-pretreated macrophages in order to target bacteria in the periodontal and intravascular environments. The "homing effect" of the macrophage membrane allowed NPs to get to the sites of the lesions, and then they released metronidazole and simvastatin to fight off bacteria, atherosclerosis, and inflammation, respectively. The antibacterial rate of MM/STNPs increased by 15% in comparison to that of NPs without the ability to target. Furthermore, the NPs-incited M2 macrophages additionally successfully checked the alveolar bone misfortune brought about by periodontitis.

Crystalline structure: Translucent pieces of swarf and filtering not entirely set in stone with X-beam diffraction (XRD, Bruker, D8 advance). The samples were analyzed using an angular range of 2° from 10° to 90°, a step size of 0.04°, and a wavelength of 1.5406. The diffraction peaks were compared to the ICDD database.

Membrane of dendritic cells: Toll-like receptors on the membrane of a dendritic cell, a type of antigen-presenting cell, are capable of recognizing pathogens. As a result, the dendritic cell can specifically target bacteria. Hou and co [7]. Allow *S. aureus* to stimulate the dendritic cell in order to coat CuFeSe₂ with a pathogen receptor membrane. Modern pathogen receptor membrane-coating technology enabled the nanoplateforms to adhere to bacteria. CuFeSe₂ used the PTT effect to generate precisely the right amount of heat to kill bacteria when NIR light was applied to it. Additionally, CuFeSe₂ with 100 and 112 crystal faces was synthesized by the authors. They discovered that the (1 0 0)

facet had a stronger nanoenzyme effect, which meant it could produce more reactive oxygen species. The sterilization rate of NPs coated with the dendritic cell membrane increased by 15% on the basis of CuFeSe₂.

Membrane of a platelet: Proteins or plasma-bridging molecules like fibrinogen, fibronectin, and IgG, which connect bacterial and platelet surface receptors, are what bring together bacteria and platelets. Consequently, utilized a "top-down" method to enclose the platelet plasma membrane on the Van-loaded PLGA core [8]. NPs could tie microbes like platelets and accomplished a superb remedial impact in the model of fundamental bacterial contamination in mice.

Membrane hybrid: Different cell films in organic entities have various capabilities and qualities, blending different cell layers might make a multi-utilitarian "coat" for NPs. Zhang's gathering attempted to combine the erythrocyte layer and the platelet film into a new nanosystem (named [RBC-P] NP). They demonstrated that these nanoparticles possessed the properties of two kinds of cell membranes and provided an easy method for increasing the functionality of nanoparticles [9]. Bacteria and toxins may act at different locations in many bacterial infections. Perforin, for instance, acts on the membranes of erythrocytes, but bacteria stick to platelets rather than RBCs. Therefore, the erythrocyte-platelet fusion membranes were modified in the design of gold nanowires by Wang's group. The erythrocyte layer in NPs could assimilate poisons created by microorganisms, and the platelet film helped NPs in arriving at the contamination site. Gold nanowires in NPs could also mimic the long-term movement of natural cells in the complex blood environment under sound waves. A model for broad-spectrum antibacterial-detoxifying nanorobots was provided by this work.

The application of nanomaterials in biomedicine has significantly expanded thanks to the cell membrane coating strategy. Since cell membranes are complex enough to boggle the mind, this method will allow for the creation of numerous amazing NPs [10]. Hybrid membranes have become more attractive "outerwear" for multifunctional antibacterial nanosystems in recent years.

Using bacteria hunters to target

There are also some natural bacteria hunters in the ecosystem. These bacteria killers have the ability to enter the host bacteria, kill the host bacteria, and then reproduce in the host bacteria. Some "bacterial traitors" and bacteriophages are among the bacteria hunters. The representative of this bacteria hunter is *B. bacteriovorus*, which is the natural foe of Gram-negative bacteria, the primary cause of numerous diseases. When *B. bacteriovorus* spots its prey, it moves into an attacking mode and spins its flagella quickly to swim quickly (160 meters per second), then it hits the prey and spins rapidly (100 revolutions per second) [11]. *B. bacteriovorus* is able to enter and parasitize its prey at high speeds, eventually resulting in the host's death. The development of *B. bacteriovorus* can likewise scatter biofilm by annihilating the biofilm grid. In parallel, it has been demonstrated that *B. bacteriovorus* cannot invade mammalian cells, making it possible to use *B. bacteriovorus* in medical treatment. However, periodontitis has a complex microenvironment. Therefore, to get the most out of its bactericidal power, combined the surface of the piezoelectric material ZnO. ZnO is a piezoelectric material, and that implies ZnO can move mechanical strain to ROS. As a result, ZnO increases ROS production through bacterial movement and host interaction demonstrating that could swiftly swim within a biofilm and demolish its structure [12]. This sort of designed microorganism compensated for its inadequacies and accomplished great germicidal viability (the antibacterial rate expanded

by 30% in light of ZnO alone), and it has great biosafety because it can likewise be discharged through human dung. Importantly, minimizes its killing effect on beneficial bacteria in the periodontal region and prevents the imbalance of periodontal flora because *B. bacteriovorus* only targets and kills pathogenic gram-negative bacteria.

In recent years, scientists have shown a lot of interest in nanomaterials based on viruses or biomimetic viruses. Bacteriophage is a type of virus that can be used as a naturally targeted antibacterial agent because it only uses one or more specific bacteria as hosts and does not harm mammalian cells. However, the use of bacteriophage on its own has a subpar bactericidal effect. As a result, Gu's team combined the bacteriophage with the aggregation-induced emission photosensitizer TBTCP-PMB, which relied on the nucleophilic substitution reaction between the benzyl bromide and sulfhydryl groups in the bacteriophage's heads. This work by Gu's group gave bacteriophage therapy a more stable and effective bactericidal pathway (PDT), based on the conventional phage cocktail therapy for sepsis. The PDT effect was developed because bacteriophages reduce the distance between TBTCP-PMB and bacteria [13-20]. As a result, the antibacterial rate of a TBTCP-PMB-engineered phage increased by 30% when TBTCP-PMB was used alone. Although engineered bacteriophages could not label *S. mutans* fluorescently, other bacteria bound to the same bacteriophage had distinct red fluorescence. Researchers were able to achieve precise antibacterial therapy by further reducing the clearance of non-pathogenic bacteria and increasing the killing rate of pathogenic bacteria thanks to the imaging effect of TBTCP-PMB and the targeting capability of bacteriophages. A strong "1 + 1 > 2" bactericidal efficacy was demonstrated by this strategy. Since explicit proteins on the outer layer of bacteriophages can consolidate with other compound designs, hereditary medication can likewise be added to the genome of bacteriophages through hereditary recombination innovation.

Conclusion

Nanomaterials have advantages over antibiotics in the post-antibiotic era due to their high sterilization efficiency and adaptability. In any case, uncertain medicines generally cause lack convergence of sore destinations and high poisonousness to tissue cells. The aforementioned problems are perfectly addressed by nanomaterials based on precise and on-demand strategies. In this audit, we summed up the plan standards, focusing on and boosts reaction systems, current applications, and benefits with downsides of different on-request and exact procedures. A flooding number of these nanomaterials have been planned and applied by utilizing the physical and synthetic properties of materials, the highlights of the irresistible microenvironment, the metabolites and surface focuses of microscopic organisms, and the communication among microorganisms and cells. In terms of lowering tissue toxicity and increasing the effective drug concentration at infection sites, the on-demand and precise therapies mediated by nanomaterials have produced satisfactory results.

Be that as it may, a few difficulties actually ought to be offered more consideration and tended to before the rise of further developed nanomaterials for future applications. 1) Nanomaterials' stability must be improved because of the complex interactions between materials and humans. It's important to guarantee that the responsive and target elements of the nanomaterials are flawless until NPs show up at explicit locales. Altering the protective shells that surround the NPs or adopting a local administration strategy for the delivery of nanomedicines to infected sites is the solution. 2) Combining existing nanomaterials' repeatability because of multifaceted strides in the creation of materials

is troublesome. As a result, a promising direction is the creation of nanomaterials with easy-to-prepare components. 3) During the sterilization process, several nanomaterials sterilization tools, such as ROS, unavoidably cause side effects, aggravate inflammation, and hinder the healing of infected tissues. While sterilizing, it's worthwhile to investigate ways to reduce inflammation and speed up wound healing. The design of nanomaterials that can regulate the proliferation, differentiation, and impact of inflammatory cells like regulatory T cells and macrophages can address this problem. 4) The expense of focusing on moieties (like antibodies and macrophage cell films) used to change nanomaterials are somewhat high, and the stockpiling conditions are additionally brutal. Economic benefits must be taken into account before nanomaterials can be used in medicine or made in industry. Preferably, the building materials for NPs are inexpensive and simple to acquire and store. 5) The metabolic regularity of nanomaterials and drugs in vivo and the outcomes of diseases are unknown due to the complexity and changeability of living activities. There are still a few difficulties for the clinical use of US FDA-supported nanomaterials. As a result, in order to obtain complete data, additional animal experiments and preclinical studies are required. Despite the fact that there are many difficulties of nanomaterials for clinical application, nanomaterials in view of on-request and exact techniques are still as arising extraordinary substitutes for anti-microbials. Nanomaterials will undoubtedly have a bright future in the fight against bacterial infections thanks to advancements in technology and applicable laws and regulations.

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Conflict of Interest

None

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