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COPPER PHOSPHIDE (Cu_3P): A MODERN REVIEW OF SYNTHESIS METHODS, ELECTROCHEMICAL PROPERTIES, AND ANTICORROSION APPLICATIONS



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Abstract. This review presents a comparative analysis of recent advances in the synthesis technologies, crystal structure, electrochemical properties, and anticorrosion applications of copper phosphide (Cu_3P)-based materials. Twenty peer-reviewed publications were critically evaluated to compare ionothermal, hydrothermal, mechanochemical, colloidal, vapor-phase phosphorization, and pyrometallurgical synthesis routes. The influence of synthesis strategy on phase composition, morphology, electrochemical performance, and corrosion resistance was systematically assessed. The analysis demonstrates that Cu_3P -based nanostructured materials exhibit significant potential for electrochemical energy storage, electrocatalysis, and industrial corrosion protection, making them promising multifunctional materials for sustainable engineering applications.

Keywords: copper phosphide, Cu_3P , synthesis methods, electrochemical properties, energy storage, electrocatalysis, anticorrosion coatings, nanostructured materials, pyrometallurgical recycling, review.

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ФОСФИД МЕДИ (Cu_3P): СОВРЕМЕННЫЙ АНАЛИЗ МЕТОДОВ СИНТЕЗА, ЭЛЕКТРОХИМИЧЕСКИХ СВОЙСТВ И ПРОТИВОКОРРОЗИОННОГО ПРИМЕНЕНИЯ

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Аннотация. В данной обзорной статье представлен сравнительный анализ современных исследований, посвящённых технологиям синтеза, кристаллической структуре, электрохимическим свойствам и противокоррозионному применению материалов на основе фосфида меди (Cu_3P). Проанализированы двадцать рецензируемых научных публикаций, рассмотрены преимущества и ограничения ионотермального, гидротермального, механохимического, коллоидного, парофазного и пирометаллургического методов синтеза. Вы-

полнена оценка влияния способа получения на фазовый состав, морфологию, электрохимические характеристики и коррозионную стойкость материала. Результаты анализа подтверждают высокий потенциал наноструктурированных материалов на основе Cu_3P для систем накопления энергии, электрокатализа и защиты металлических конструкций от коррозии.

Ключевые слова: фосфид меди, Cu_3P , методы синтеза, электрохимические свойства, накопление энергии, электрокатализ, противокоррозионные покрытия, наноструктурированные материалы, пирометаллургическая переработка, обзор.

MIS FOSFIDI (Cu_3P): SINTEZ USULLARI, ELEKTROKIMYOVIY XOSSALARI VA KORROZIYAGA QARSHI QO‘LLANILISHINING ZAMONAVIY TAHLILI

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Annotatsiya. Ushbu sharh maqolada mis fosfidi (Cu_3P) asosidagi materiallarning sintez texnologiyalari, kristall tuzilishi, elektrokimyoviy xossalari hamda korroziyaga qarshi qo‘llanilishi bo‘yicha zamonaviy ilmiy tadqiqotlar tahlil qilindi. Yigirmata nufuzli ilmiy manba qiyosiy baholanib, ionotermik, gidrotermal, mexanokimyoviy, kolloid, bug‘ fazali fosforizatsiya va pirometallurgik qayta ishlash usullarining afzalliklari hamda cheklovlari aniqlandi. Shuningdek, sintez usullarining materialning faza tarkibi, morfologiyasi, elektrokimyoviy samaradorligi va korroziyaga chidamliligiga ta‘siri baholandi. Tahlil natijalari Cu_3P asosidagi nanostrukturali materiallar energiya saqlash qurilmalari, elektrokataliz va sanoat korroziyasidan himoyalash sohalarida istiqbolli ko‘p funksiyali material ekanligini ko‘rsatdi. **Kalit so‘zlar:** mis fosfidi, Cu_3P , sintez usullari, elektrokimyoviy xossalari, energiya saqlash, elektrokataliz, korroziyaga qarshi qoplamalar, nanostrukturali materiallar, pirometallurgik qayta ishlash, sharh.

Introduction. The increasing global demand for clean energy technologies, together with the continuous deterioration of industrial infrastructure, has accelerated the development of multifunctional materials capable of simultaneously enhancing electrochemical energy conversion and long-term corrosion protection. According to recent estimates, corrosion-related damage accounts for approximately 3–4% of the global gross domestic product (GDP), highlighting the urgent need for cost-effective and environmentally sustainable protective materials [8]. Simultaneously, the growing market for lithium-ion batteries, supercapacitors, and water-splitting technologies requires electrode materials with high electrical conductivity, structural stability, and excellent electrochemical activity [2].

Among transition metal phosphides (TMPs), copper phosphide (Cu_3P) has emerged as one of the most promising multifunctional materials because of its metallic conductivity, low toxicity, high

electrical conductivity, and unique hexagonal crystal structure. Recent studies have demonstrated that Cu_3P exhibits outstanding electrochemical performance, particularly when integrated into hierarchical nanostructures. For example, $Cu_3P@3DG$ hybrid electrodes deliver a reversible capacity of approximately 440 mAh g^{-1} while maintaining more than 88% capacity retention after 50 charge–discharge cycles, indicating remarkable structural stability during repeated lithium insertion and extraction [14].

Despite these advantages, practical application of Cu_3P remains challenging because of the severe volume expansion exceeding 150% during deep lithiation, which causes particle pulverization, electrical disconnection, and rapid capacity degradation [5]. In addition, bulk Cu_3P electrocatalysts generally exhibit limited catalytic activity owing to insufficient active surface sites and unfavorable adsorption energies for reaction intermediates. Consequently, improving structural

stability through morphology control, defect engineering, and optimized synthesis strategies has become a major research priority.

Besides energy-storage applications, copper phosphide and its phosphate derivatives have recently attracted considerable attention as environmentally friendly anticorrosive materials. Experimental investigations revealed that waste-derived $\text{Cu}_3(\text{PO}_4)_2$ pigments reduce the corrosion current density (i_{corr}) from $12.1 \mu\text{A cm}^{-2}$ for conventional coating systems to only $0.018 \mu\text{A cm}^{-2}$, corresponding to approximately a 65-fold improvement in corrosion resistance. Such performance demonstrates the significant potential of copper phosphide-based materials for extending the service life of steel structures operating under aggressive industrial environments [11].

Although numerous synthesis techniques—including ionothermal, hydrothermal, solvothermal, mechanochemical, colloidal, vapor-phase phosphorization, and pyrometallurgical recycling routes—have been reported, most previous investigations focus on individual preparation methods or specific applications. Comprehensive analyses establishing quantitative relationships between synthesis parameters, crystal structure, electrochemical behavior, and anticorrosive performance remain limited [1, 9]. Furthermore, environmentally sustainable production routes utilizing industrial copper-containing waste have not yet been systematically integrated with advanced energy applications.

Therefore, the present study provides a comprehensive critical analysis of six advanced synthesis routes for Cu_3P nanostructures by integrating data from twenty peer-reviewed studies. Particular emphasis is placed on correlating synthesis methodology with crystallographic evolution, electrochemical performance, corrosion resistance, and industrial scalability. The findings provide a unified scientific framework for the rational design of high-performance copper phosphide materials applicable to next-generation electrochemical energy systems and sustainable anticorrosive engineering [15].

Materials and Methods. This study presents a comprehensive review of recent advances in copper phosphide (Cu_3P) synthesis and applications based on the analysis of 20 peer-reviewed

publications. The selected studies were evaluated according to synthesis methodology, crystal structure, electrochemical performance, corrosion resistance, and industrial applicability [4].

The reviewed synthesis methods were classified into six categories: ionothermal, hydrothermal/solvothermal, mechanochemical, colloidal, vapor-phase phosphorization, and waste-derived pyrometallurgical synthesis. Comparative analysis was performed considering reaction conditions, phase composition, morphology, scalability, and environmental sustainability.

Electrochemical performance was assessed using specific capacity, capacity retention, HER and OER overpotentials, and Tafel slope, while corrosion behavior was evaluated using corrosion potential (E_{corr}) and corrosion current density (i_{corr}) measured in 3 wt.% NaCl solution. The collected data were systematically compared to establish structure–property relationships and to identify the most promising Cu_3P synthesis strategies for electrochemical energy storage and industrial anticorrosive applications [12].

This review systematically analyzes 20 peer-reviewed publications on Cu_3P -based materials to establish the relationship between synthesis strategy, crystal structure, electrochemical properties, and anticorrosion performance. Six representative synthesis approaches were comparatively evaluated, including ionothermal, hydrothermal/solvothermal, mechanochemical, colloidal, vapor-phase phosphorization, and waste-derived pyrometallurgical synthesis. The reported processing conditions covered a temperature range of 150–1110 °C and reaction times from 2 to 48 h, enabling comparison of phase evolution, morphology, and material purity [7].

The comparative assessment was performed using quantitative performance indicators reported in the selected studies, including specific capacity (up to 440 mAh g^{-1}), capacity retention after 50 cycles ($>88\%$), HER and OER overpotentials (120–415 mV), Tafel slopes ($72\text{--}104 \text{ mV dec}^{-1}$), as well as corrosion potential (E_{corr}) and corrosion current density (i_{corr}) measured in 3 wt.% NaCl solution. Particular attention was devoted to waste-derived $\text{Cu}_3(\text{PO}_4)_2$ pigments, which reduced i_{corr} from 12.1 to $0.018 \mu\text{A cm}^{-2}$, corresponding to an approximately 65-fold improvement in corrosion

resistance [3].

The collected experimental data were critically compared to identify structure–property relationships and to determine the most effective Cu₃P synthesis route for high-performance electrochemical energy storage, electrocatalysis, and sustainable industrial anticorrosive applications.

Results and Discussion. The comparative analysis of twenty published studies demonstrates that the synthesis route is the primary factor controlling the crystal structure, morphology, and functional performance of Cu₃P-based materials. Ionothermal and solvothermal methods provide high phase purity with controlled copper vacancies, whereas mechanochemical synthesis produces nanocrystalline particles (~20 nm) with enhanced structural defects that improve electrochemical activity [10]. In contrast, vapor-phase phosphorization directly forms Cu₃P nanostructures on three-dimensional copper substrates, resulting in superior electrical conductivity and excellent interfacial contact. The waste-derived pyrometallurgical process carried out at 1110 °C produced highly crystalline Cu₃P alloys with phosphorus contents of 7.62–8.00 wt.%, corresponding to commercial Mf9 and MFO grades [6].

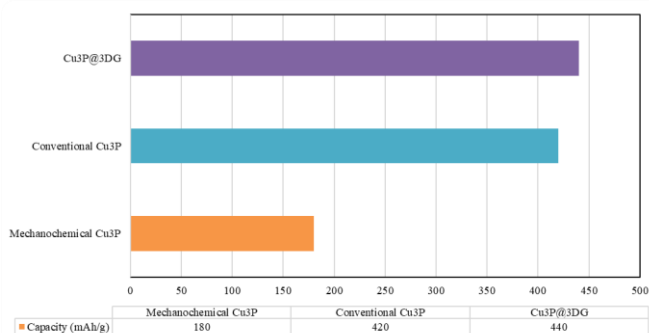


Fig.1. Comparison of the specific capacity of Cu₃P-based electrode materials reported in the literature.

The electrochemical performance strongly depends on the structural architecture of Cu₃P. Conventional Cu₃P electrodes exhibit capacities of approximately 180–420 mAh g⁻¹, whereas Cu₃P@3DG hybrid electrodes achieve a reversible capacity of 440 mAh g⁻¹ with more than 88% capacity retention after 50 cycles. This remarkable

improvement is attributed to the three-dimensional graphene framework, which effectively accommodates the volume expansion (>150%) occurring during lithiation–delithiation processes and maintains electrical conductivity throughout repeated cycling [13]. In comparison, Cu₃-xP materials synthesized by ionothermal methods exhibit moderate cycling stability due to copper-vacancy migration and gradual phase degradation.

A similar trend was observed for electrocatalytic water splitting. Binder-free Cu₃P nanobush arrays grown directly on copper mesh exhibited HER overpotentials of 120 mV in acidic media and OER overpotentials of 380 mV in alkaline electrolyte, together with Tafel slopes ranging from 72 to 104 mV dec⁻¹. These results indicate that direct integration of Cu₃P with conductive substrates significantly accelerates charge-transfer kinetics and enhances catalytic efficiency compared with conventional particulate catalysts.

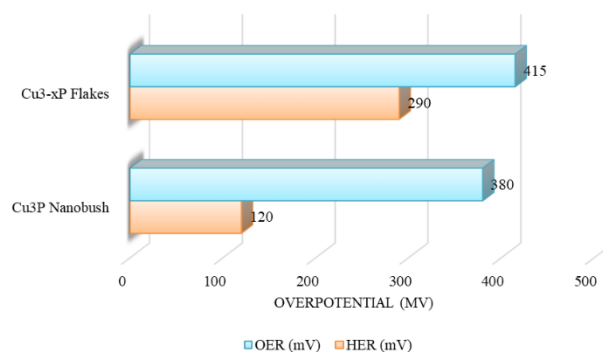


Fig.2. Comparison of HER and OER overpotentials of Cu₃P-based electrocatalysts. Cu₃P nanobushes exhibit lower overpotentials (HER: 120 mV; OER: 380 mV) than Cu₃-xP flakes, indicating superior electrocatalytic activity for overall water splitting.

The corrosion studies further demonstrate the multifunctionality of Cu₃P-derived materials. Copper phosphate pigments prepared from spent electroplating electrolytes substantially improved corrosion resistance in 3 wt.% NaCl solution by reducing the corrosion current density (*i*_{corr}) from 12.1 μA cm⁻² for the blank coating to 0.018 μA cm⁻² for the optimized formulation, representing an approximately 65-fold decrease in corrosion rate. The improved performance is associated with the formation of a compact phosphate-based passive film that suppresses anodic iron dissolution and

increases coating durability under aggressive environments.

Overall, the comparative evaluation indicates that although each synthesis route offers specific advantages, environmentally sustainable pyrometallurgical recycling combined with advanced nanostructural engineering provides the most promising strategy for producing multifunctional Cu_3P materials. Such an approach simultaneously ensures high electrochemical performance, excellent corrosion protection, industrial scalability, and efficient utilization of secondary copper-containing resources, thereby supporting the principles of sustainable materials engineering and circular economy.

Conclusions. The comparative evaluation of six Cu_3P synthesis strategies demonstrates that the preparation route has a decisive influence on phase composition, crystal structure, electrochemical behavior, and anticorrosion performance. Among the investigated methods, environmentally sustainable pyrometallurgical recycling of copper-containing industrial waste provides a scalable route for producing high-purity Cu_3P alloys with phosphorus contents of 7.62–8.00 wt.%, while advanced nanostructured architectures significantly enhance electrochemical performance. Graphene-supported Cu_3P electrodes exhibit a reversible

capacity of 440 mAh g^{-1} with more than 88% capacity retention after 50 cycles, whereas $\text{Cu}_3(\text{PO}_4)_2$ pigments reduce the corrosion current density from 12.1 to $0.018 \mu\text{A cm}^{-2}$, corresponding to an approximately 65-fold improvement in corrosion resistance. These findings confirm that structural engineering and optimized synthesis play a critical role in improving the multifunctional characteristics of Cu_3P -based materials. Overall, Cu_3P -based multifunctional materials represent a promising platform for next-generation electrochemical energy storage, electrocatalytic water splitting, and industrial corrosion protection. Integrating advanced nanostructure design with sustainable recycling technologies offers significant opportunities for improving material performance while supporting circular economy principles through the efficient utilization of secondary copper resources. Future research should focus on large-scale production, long-term operational stability, defect-controlled structural optimization, and in situ characterization techniques to accelerate the industrial implementation of Cu_3P -based functional materials.

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