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Synthesis and Properties of Nickel Copper Phosphorus ($Ni_xCu_yP_z$) Catalyst

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Abstract

Nowadays, scientists around the world are paying more attention to renewable hydrogen fuels. There is a growing need for precious metal catalysts to calculate the cost of obtaining renewable energy, an efficient method of producing H2 by electrolysis of water, as well as to facilitate the decomposition of water into its elemental parts. Today, due to the increase in the problem of the shortage of energy resources and the growing of CO_2 emissions into the atmosphere, attention is being paid to hydrogen energy. However, the production of H2 requires low-cost, efficient catalysts that facilitate hydrogen/oxygen separation reactions in the water splitting. For this purpose, intermediate metal phosphides (Fe, Co, Ni, Cu, Mo, W) were used as effective electrocatalysts for water decomposition. The catalytic activity of intermediate metal phosphides to form hydrogen is largely dependent on the phosphorus content, but the P atoms play an important role in increasing efficiency. The production of hydrogen by electrolysis of water on the basis of bifunctional catalysts has good prospects for use in the energy industry. In the article, the one-step hydrothermal synthesis method and physico-chemical (electronic structure and conductivity, structure morphology) of double metal phosphide with NixCuyPz composition were studied.

Keywords

Bimetallic phosphide, electrocatalyst, water splitting, hydrogen generation, hydrothermal synthesis, structural morphology, electrocatalyst.

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Introduction

Recently, there is a shortage of energy in the world and the increase in CO_2 emissions into the atmosphere attracts the attention of scientists. However, producing carbon-free H_2 through water electrolysis is a promising but expensive method. It requires inexpensive, efficient catalysts to facilitate the hydrogen/oxygen dissociation (HER/OER) reactions in water splitting (Walter et al., 2010; Man et al., 2011). Although intermediate metal oxides (OMO) demonstrate impressive activity as inexpensive, non-toxic, native metal-free catalysts, their low HER activity and poor conductivity limit their universal application in practical hydrogen production technologies. In such cases, the presence of an electrocatalyst with a corresponding electron structure, adapted using various methods, plays an important role, for example, doping with heteroatoms, surface control, and the formation of anion vacancies in catalysts based on transition metal compounds. Phosphorus doping also provides a direct modification of the electron state of catalysts, especially (HER), which has been found to change. For example, some intermediate metal phosphides (Fe, Co, Ni, Cu, Mo, W) are known to be effective electrocatalysts for water splitting (Nguyen & Blum, 2015; Götz et al., 2016).

Today, due to the growing problem of energy resource scarcity and the increase in CO_2 emissions into the atmosphere, attention is increasingly focused on hydrogen energy. However, the production of H_2 requires low-cost, efficient catalysts that facilitate hydrogen/oxygen separation reactions in water decomposition. For this purpose, the use of intermediate metallic phosphides, which are effective electrocatalysts for the decomposition of water, has been introduced (Dau et al., 2010). Although intermediate metal oxides (OMO) demonstrate impressive activity as cheap, non-toxic, non-precious metal catalysts, their low HER activity and low conductivity limit their universal application in practical hydrogen production technologies. In such cases, the existence of an electrocatalyst with the appropriate electronic structure, adapted using various methods, plays an important role, for example, doping with heteroatoms, surface control, and formation of anion vacancies in catalysts based on transition metal compounds. Phosphorus doping has also been found to change the electronic state of the catalysts, specifically providing proper modification of (HER). For instance, some intermediate metal phosphides (Fe, Co, Ni, Cu, Mo, W) are known to be effective electrocatalysts for water splitting. Moreover, in this work, a polyfunctional electrocatalyst based on nickel phosphide of mixed metals (Ni-Co-P) was synthesized (McCrory et al., 2013; Du & Eisenberg, 2012). Properties of bifunctional catalysts were considered in works of (Hong et al., 2015). Studies have used phosphorus doping method to obtain Ni_2P-CoP bimetallic phosphides as bifunctional electrocatalysts for the synergistic effect of bimetallic phosphides and hydrogen and oxygen decomposition reactions (HER and OER) in water electrolysis (Liu et al., 2019). Currently, the interest of scientists around the world is increasing in renewable hydrogen fuels. This topic is becoming global, mainly because of the growing energy shortage. However, the promising carbon-free method of producing H_2 via water electrolysis is still an expensive method, requiring inexpensive, efficient catalysts to facilitate hydrogen/oxygen separation (HER/OER) reactions in water splitting (Hong et al., 2015; Mo et al., 2019).

The catalytic activity of intermediate metal phosphides to form hydrogen is largely dependent on the phosphorus content, but the P atoms play an important role in increasing efficiency (Akin et al., 2022). The production of hydrogen by electrolysis of water on the basis of bifunctional catalysts has good prospects for use in the energy industry (Husam et al., 2021). Mixed valence transition metal oxides such as $NiCo_2O_4$, $FeCo_2O_4$ and $CoMn_2O_4$ with a spinel structure were found to have high electrocatalytic activity due to the presence of various degrees of oxidation, high conductivity, and indestructibility of the perfect structure

(Li et al., 2022; Kuleshov et al., 2012). A flower-like nanoporous $NiCo_2O_4$ material was synthesized as a dual-functional electrocatalyst for water splitting in 1,0 M KOH electrolyte (Ren et al., 2022), in another work, samples were synthesized and studied for the decomposition of water with a nucleus (NiCo) - shell ($CoNiO_2$) structure, which showed a high mass activity with a sufficient potential value for OER and HER of 360 mV 10 mA/sm^2 and 370 Mv 10 mA/sm^2, respectively, and small Tafel slopes (150 mV/dek^{-1} and 123 mV/dek^{-1} for OER and HER respectively) have a large number of active sites and porosity due to their unique electrochemically active surface area, fast electron transfer and system stability, surface and electron lattice structure (Morales-Guio et al., 2014; Yağız et al., 2022; Joo et al., 2019). We can see the crystal structure of Ni_2P in a hexagonal structure (Cen et al., 2022; Yan et al., 2016). The crystalline structure of nickel phosphide with a hexagonal structure has shown good results in water splitting reactions (Joo et al., 2019; Li et al., 2016; Shi & Zhang, 2016).

The hydrothermal synthesis method is the most common method for producing various bifunctional catalysts among the work published in recent years. It has many advantages such as simplicity, universality, and flexibility in controlling the composition and morphology of the material (Zou & Zhang, 2015; Guo et al., 2019). The key to this method of obtaining highly efficient catalysts is the selection of appropriate precursors, including metal salts and non-metallic sources, as well as reaction conditions such as temperature, concentration, reaction time, pH, etc. For example, obtained nanocrystals of copper-cobalt oxide ($CuCo_2O_4$) and copper-cobalt sulfide ($CuCo_2S_4$) via a single reactor by hydrothermal method. The desired nanoforms can be produced by adjusting the ratio of water to ethanol, which affects the performance of the final electrocatalysts. To date, various nanoflowers electrocatalysts with high activity such as $MoS_2Ni(OH)_2$ (Liu et al., 2019), NiO-Ni_3S_2 hetero-nanoshell, hetero-structural (Ni, Fe) S_2MoS_2, NiS_2/MoS_2 have been synthesized by this method and used for water splitting (Ćurčić et al., 2018; Rashidova et al., 2023; Li et al., 2019).

Experimental Part

The calculated amount of nickel (II) and copper (II) salts for the synthesis of $Ni_xCu_yP_z$ were dissolved in deionized water and the required amount of red phosphorus was added by vigorous stirring and mixed for 1 hour. The entire reaction mixture was then transferred to a Teflon-lined stainless steel autoclave and placed in a muffle furnace for processing at 200 °C for 24 hours. After cooling, the entire mixture is collected, washed several times with deionized water and ethanol, then dried in an oven at 70°C and stored for later use. The synthesis of $Ni_xCu_yP_z$ was carried out by a hydrothermal process. It is possible to control the morphology of the structure by controlling the temperature in a hydrothermal reaction, so we conducted our work at 3 different temperatures of 140^o, 160^o, 180^o C.

The procedure for synthesizing $Ni_xCu_yP_z$ bimetallic phosphide: initially, 3,1 g of $NiCI_2{\cdot}6H_2O$, 2,22 g of $CuCI_2{\cdot}2H_2O$, and 1,61 g of red phosphorus were weighed. Then, $NiCI_2{\cdot}6H_2O$ and $CuCI_2{\cdot}2H_2O$ salts were dissolved in 20 ml of water, red phosphorus (P_4) was also dissolved in 20 ml of water. The resulting solutions were poured into a 50 ml polytetrafluoroethylene container and placed in an autoclave. The experiment was conducted at three different temperatures (140^o, 160^o, 180^o C). The resulting suspension is filtered and dried. These samples were used for our subsequent research.

Discussion of the Results

Raman spectroscopy is used primarily in organic chemistry to determine structure and molecular interactions. It is complementary to IQ spectroscopy, allowing the detection of specific structural features or groups of features. The extent, intensity, and shape of the shift are important for determining chemical bonds

and functional groups. Raman spectroscopy can also be used to determine the isomers of molecules by their polarization properties. A Raman spectroscopy analysis was performed to study the structural properties of the synthesized $Ni_xCu_yP_z$ bimetal phosphide in the sample Figure 1.

X-ray phase analysis was carried out to study the structural properties of the $Ni_xCu_yP_z$ bimetal phosphide sample obtained during the research.

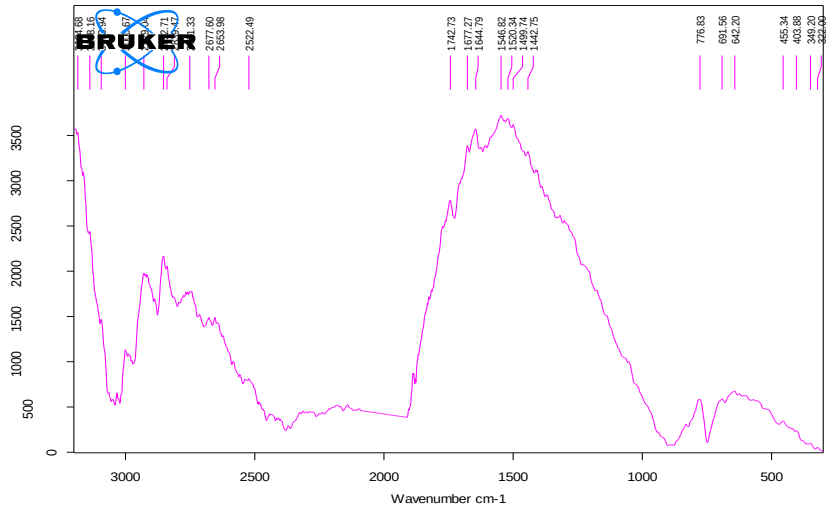


Figure 1. Raman spectrum of a sample of $Ni_xCu_yP_z$ bimetal phosphide synthesized at 160ºC

In the Raman spectrum of the $Ni_xCu_yP_z$ bimetallic phosphide sample, the signal in the region ~ 600 cm^{-1} is characteristic of Cu and represents its complex structure. The appearance of the signal spread in the region of 1442-1742 cm^{-1} was considered to belong to the Cu-P and Ni-P bonds in the sample Figure 1.

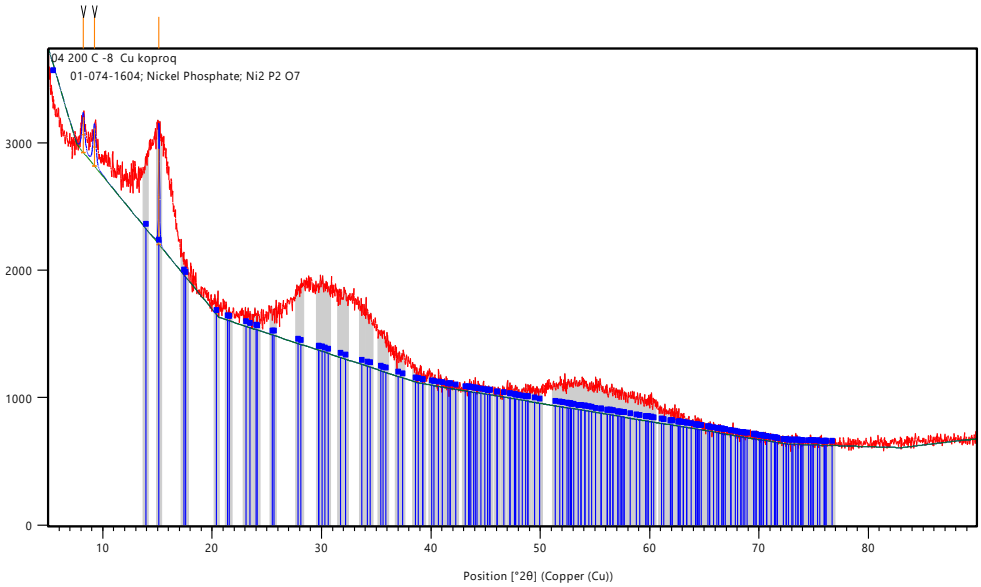


Figure 2. Diffractogram of a sample of $Ni_xCu_yP_z$ bimetal phosphide synthesized at 160ºC

The presence of intense signals (reflexes) in the 8.2167, 9.2355 va 15.1272 2θ (theta) areas was observed in the diffractogram of the $Ni_xCu_yP_z$ bimetal phosphide sample. The diffractogram is similar to the diffractogram of a crystalline substance with the composition $Ni_2P_2O_7$ (base code - 01-074-1604). Broad

peaks that correspond to the values of 30 and 55 degrees of 2θ are considered to belong to the amorphous part of the sample Figure 2.

According to the results of X-ray phase analysis, the size of $Ni_xCu_yP_z$ bimetal phosphide crystallites was calculated by the Scherrer formula (1):

$$D=\frac{K\lambda}{\beta cos\theta} \quad (1)$$

Here:

D-crystalline size;

K- The constant of Scherrer;

λ-Cu-K_α wavelength of light (0.15418 nm);

β (FWHM)- half-height reflex width;

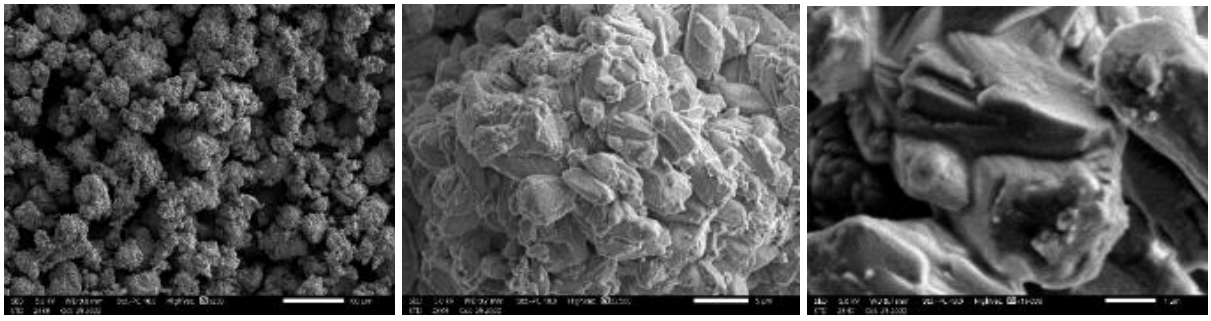
θ - angle of (Bregg) diffraction.

Table 1 shows the results of the X-ray phase analysis of $Ni_xCu_yP_z$ bimetal phosphide and the size of the crystallites calculated using the Scherrer formula.

Table 1. Results from the X-ray phase analysis of $Ni_xCu_yP_z$ bimetal phosphide and the size of the crystallites

Pos. [2θ]	Height [cts]	FWHM Left [2θ]	d-spacing [Å]	Rel. Int. [%]	r, nm
8.2167	278.26	0.3070	10.76087	37.04	27.11
9.2355	296.92	0.3070	9.57597	39.52	27.13
15.1272	751.32	0.0900	5.85214	100.00	93.04

Table 1 shows that the crystal phase sizes of $Ni_xCu_yP_z$ bimetallic phosphide are ~ 27,11 and 93,04 nm. SEM and EDS researches were conducted to characterize the synthesized $Ni_xCu_yP_z$ bimetal phosphide and determine its structural properties.



a) b) c)

Figure 3. SEM micrographs of $Ni_xCu_yP_z$ bimetallic phosphide at magnifications of x200 (a), x3500 (b) and x16000 (c).

Figure 3 shows the SEM microscopy of $Ni_xCu_yP_z$ bimetallic phosphide taken at different magnifications.

As can be seen from the micrographs presented in Figure 3, the structural morphology of bimetallic phosphide is an amorphous granular structure at low magnification (x200, Figure 3a). At the same time, significant magnifications (x3500 and x16000, Figure 3b-c) show the presence of mineral aggregates formed by the disordered accumulation of individual crystals with regular polygonal shapes.

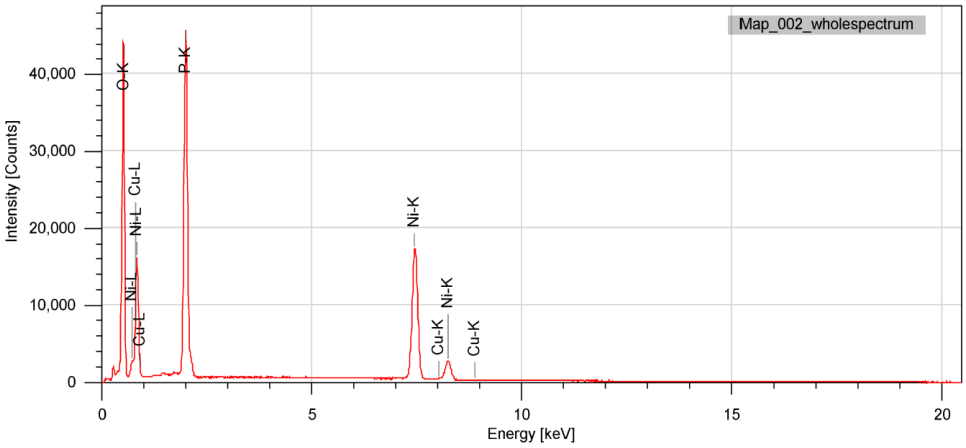


Figure 4. Energy dispersion spectrum (EDS) of $Ni_xCu_yP_z$ bimetallic phosphide

The qualitative and quantitative composition of the synthesized $Ni_xCu_yP_z$ bimetallic phosphide was determined by energy-dispersion spectroscopy (EDS). Figure 4 shows the EDS spectrum of a synthesized $Ni_xCu_yP_z$ bimetal phosphide. As you can see from the EDS spectrum, the spectrum includes peaks associated with Ni, Co, P, and oxygen atoms. The mass fraction of Ni atoms in the sample is significantly higher than the fraction of Co atoms, which are 18,10% and 1,09%, respectively.

The brightest peak in the spectrum belongs to the P atoms, their mass fraction is 37,76%. There is also a significant peak in the spectrum in the energy range of 0-1 keV associated with oxygen atoms. The mass fraction of oxygen atoms is 30,64%. It should be noted that the presence of oxygen atoms in the bimetallic phosphide Ni-Co-P and its high ratio are consistent with literature data.

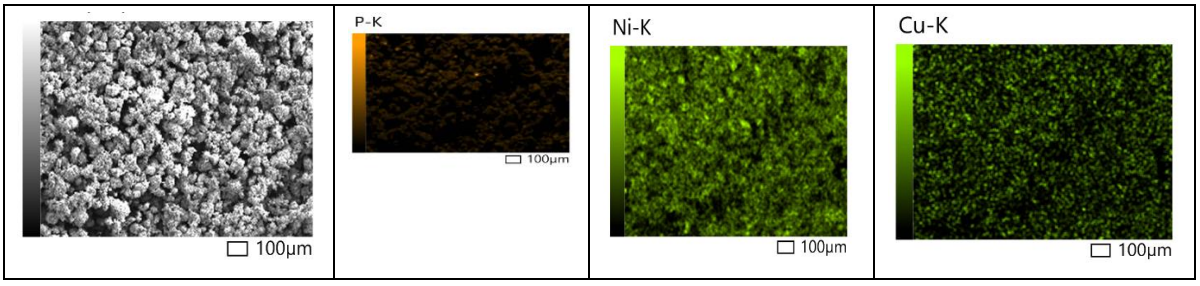


Figure 5. Distribution maps of the atoms of the main elements that make up $Ni_xCu_yP_z$ bimetallic phosphide

Figure 5 shows the distribution maps of the atoms that make up the bimetallic phosphide NixCuyPz. As can be seen from the distribution maps shown in the figure 5, the atoms of the main elements that make up $Ni_xCu_yP_z$ are evenly distributed, repeating the morphology of the sample surface. The nature of the distribution of the atoms of the elements that make up the bimetallic phosphide indicates that the synthesis process was continued uniformly throughout the entire size of the sample.

It is known that the electrocatalytic properties of semiconductor materials depend on the value of their restricted field width. An optical method was used to determine the width of the restricted area, which

involves capturing the electron diffusion reflection spectrum (EDAS) in the visible region of ultraviolet light. Synthesized $Ni_xCu_yP_z$ bimetallic phosphide was found to be ESDO in the wavelength range 380-730 nm.

Conclusion

Physicochemical methods have identified the structural properties of the synthesized bimethal phosphide Ni-Co-P. Synthesized Ni-Co-P was determined to be a phase with a clear crystalline structure, consisting mainly of nickel compounds: $Ni_2P_4O_{12}$ (59%), NiP_2O_7 (37%). At the same time, the proportion of cobalt atoms present in the sample in the form of Ni-CoP compounds is low. Ni-Co-P also contains oxygen atoms, which is explained by the synthesis process that occurs under normal conditions. In this case, all of the main atoms that make up the sample are distributed evenly throughout the volume.

Author Contributions

All Authors contributed equally.

Conflict of Interest

The authors declared that no conflict of interest.

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