The effect of MgO additive on the g-C$_3$N$_4$ performance in electrochemical reforming of water-ethanol solution

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In this work, a simple wet-chemical route was proposed to synthesize g-C$_3$N$_4$/MgO (5% wt.) with enhanced electrocatalytic activity toward hydrogen evolution from water-ethanol (10% vol.) solution. It was found that synthesized nanocomposite is a single phase and chemically pure, consisting of graphitic carbon nitride (g-C$_3$N$_4$) and cubic magnesium oxide (MgO, periclase) with an average crystallite size of 15.5 nm and 9.5 nm, respectively. It was shown that magnesium nanoparticles are evenly distributed on the surface of g-C$_3$N$_4$ nanosheets and uniform distribution of components is observed over the nanocomposite volume. It was found that this feature leads to an improvement in the electrocatalytic characteristics of the synthesized nanocomposite. So, the g-C$_3$N$_4$/MgO-coated electrode has an overpotential of $-251$ mV, which is better than for a g-C$_3$N$_4$-coated ($-264$ mV) or pure nickel ($-293$ mV) electrode. Moreover, the nanocomposite-based electrode possesses a low Tafel slope (106.7 mV/dec) and high cyclic and chronopotentiometry stability.

Keywords: graphitic carbon nitride, magnesia, nanopowders, electrocatalytic reforming, hydrogen evolution reaction.

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1. Introduction

Currently, the production of hydrogen using photo- and electrocatalytic conversion of solar energy into chemical energy seems to be a rather promising solution for main problems associated with environmental and energy crises [1]. The key task, in this case, is the search for an inexpensive and effective photo- and electrocatalysts exhibiting activity under the influence of visible light and effective electron transfer. Among them, the graphite-like carbon nitride (g-C$_3$N$_4$) stands out, which is a semiconductor with high stability, and photo- and electrocatalytic activity [2–4]. At the same time, in its pure form, graphite-like carbon nitride is characterized by a low specific surface area, a lack of active centers on its surface, rapid recombination of photogenerated electron-hole pairs, and a wide bandgap (2.7 eV), which all together causes insufficiently high photo- and electrocatalytic activity [5, 6].

But the synthesis of heterogeneous structures based on graphite-like carbon nitride and some oxide can neutralize the disadvantages mentioned above. For example, it was shown that the preparation of the g-C$_3$N$_4$/MgO nanocomposite allows one to achieve a high rate of hydrogen evolution – up to 30.1 $\mu$mol/h in the photoinduced hydrogen evolution reaction (HER) process, which is almost 6 times higher than for pure graphite-like carbon nitride [7]. The authors explain this by the fact that in this case, the presence of a heterojunction possesses quick transfer of photoinduced electrons from the conduction band of g-C$_3$N$_4$ to the conduction band of MgO, which contributes to a significant separation of photoinduced electrons and holes and effectively suppresses the recombination of electron-hole pairs. Moreover, it can be assumed that the intercalation of magnesium oxide into the interlayer space of graphite-like carbon nitride may lead to the enhanced specific surface area providing higher catalytic activity of obtained nanocomposite.

However, another important direction of hydrogen production is through the electrocatalytic reforming of aqueous-ethanol solutions using catalysts based on graphite-like carbon nitride nanocomposites is still largely unexplored. In the case of g-C$_3$N$_4$/MgO nanocomposite, the mesoporous g-C$_3$N$_4$ can be tuned by different amounts of MgO to significantly enhance its electrocatalytic performance and reduce the absolute value of its overpotential. However, previously it was shown that an excessive amount of second component (MgO) may also decrease the activity and stability of g-C$_3$N$_4$ [8]. Based on this work 5 wt%. can be considered as optimal MgO content for g-C$_3$N$_4$/MgO electrocatalyst production. Thus, this work aimed to synthesize and complex study the structural, morphological, and electrochemical features of the g-C$_3$N$_4$/MgO nanocomposite. A simple wet-chemistry technique is proposed to synthesize a nanocomposite of graphitic carbon nitride and magnesium oxide as a promising material for hydrogen production from water-ethanol solution. A comprehensive study of the structure and morphology of g-C$_3$N$_4$/MgO was
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carried out using the complex physicochemical analysis to better understand the origin of its enhanced electrocatalytic activity.

2. Experimental section

2.1. Synthesis procedure

The nanopowder of the initial graphitic carbon nitride (g-C₃N₄) was synthesized by heat treatment of urea ((NH₂)₂CO) under aerobic conditions. A detailed description of its synthesis procedure and preparation of a g-C₃N₄-based colloidal solution was previously given in [9, 10]. After homogenization, 1.5 mg of magnesium acetate tetrahydrate (Mg(CH₃COO)₂·4H₂O or Mg(Ac)₂·4H₂O) was dissolved in 10 ml of distilled water using magnetic stirring. The mixture then was evaporated at 100°C and calcined at 350°C for 30 minutes followed by grinding. As a result, initial g-C₃N₄ powder and g-C₃N₄/MgO nanocomposite (mass fraction of magnesia is 5%) were prepared. MgO to g-C₃N₄ proportion was selected based on [8] work. The generalized synthesis scheme of both g-C₃N₄ and g-C₃N₄/MgO shown in Fig. 1. All the chemicals used were of analytical grade.

2.2. Physicochemical characterization

The elemental composition and morphology of the synthesized samples were studied by energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM) using Tescan Vega 3 SBH scanning electron microscope equipped with an Oxford INCA x-act X-ray microanalysis device. An Oxford Instruments INCA system was used for chemical analysis, including both line scan EDS and elemental mapping utilizing a 10 nm probe size. All concentration profiles were plotted using elements percentage. SEM-images of the samples were acquired in both SE (morphological contrast) and BSE (phase contrast) modes. X-ray phase analysis was performed on a Rigaku SmartLab 3 X-ray powder diffractometer (CuKα radiation, λ = 0.154051 nm, Bragg angle range 10–80°), phase analysis of the compositions was performed using JCPDS PDF-2 database. The average crystallite size (coherent-scattering regions) was calculated from the broadening of X-ray diffraction lines using the fundamental parameter method implemented in the SmartLab Studio II software.

2.3. Electrocatalytic performance

The electrochemical measurements were carried out on Elins P20X potentiostat using a three-electrode cell. The working electrode was a nickel (Ni) substrate used as a reference or initial g-C₃N₄ and g-C₃N₄/MgO nanocomposite deposited on a Ni substrate as a suspension from a 0.5% solution of Nafion in isopropyl alcohol. Ag/AgCl and platinum electrodes were used as reference and counter electrodes, respectively. The overpotentials values were calibrated with respect to the reversible hydrogen electrode (ERHE) according to the Nernst equation. All measurements were carried out at standard conditions (T=25°C, P=1 atm.) in an aqueous solution consisting of ethanol C₂H₅OH (10% vol.) and

![Diagram of synthesis procedure](image-url)
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1M KOH (pH = 14). Cyclic CV curves were taken in the potential range from open circuit potential to 1.5 V with a sweep rate of 5-10 mV/s. Qualitatively, the working overpotential of the sample was determined from the CV curves at a current density of 10 mA/cm². Electrocatalytic stability of the g-C₃N₄/MgO-based electrode was additionally characterized by cyclic voltammetry (100 cycles) and chronopotentiometry (10000 s). Electrochemical measurements were performed without IR-compensation.

3. Results and discussion

The EDS investigations were performed to obtain information about the gross chemical composition of the g-C₃N₄/MgO sample. Five different areas were selected in the sample for analysis to ensure the representativeness (Fig. 2(a)). It was shown that the typical EDS spectrum contains the lines that can be assigned to Mg, O, C and N elements (Fig. 2(b)). The quantitative elemental composition of the sample in the selected areas and on average indicates its compliance with the composition planned in the synthesis. Thus, the EDS results confirm that MgO weight fraction in g-C₃N₄/MgO nanocomposite is 5% within a method error. Further, this sample will be designated as g-C₃N₄/5%MgO.

The overview SEM image of the g-C₃N₄/MgO nanocomposite in BSE mode and the distribution of C, N, Mg and O elements on its surface are presented in Fig. 3. The BSE SEM image (Fig. 3(a)) does not show any phase contrast in the synthesized sample. The element mapping of both individual (Fig. 3(b-e)) and superposed (f) elements confirms the homogeneous distribution of all the elements in the g-C₃N₄/MgO nanocomposite without the formation of any clusters of individual MgO or g-C₃N₄ phases on a microscale.

Figure 4 shows the SEM images of g-C₃N₄/5%MgO nanocomposite at different magnification acquired in SE mode. As one can see the morphology of g-C₃N₄, which is the main component of g-C₃N₄/5%MgO nanocomposite (95% wt.), at low magnifications (Fig. 4(a,b)) is quite lumpy with a large number of micron-size aggregates. But at higher magnification (Fig. 4(c)), it becomes clear that each such aggregates consist of individual g-C₃N₄ nanosheets, some of which are gradually flaked off. Besides, in Fig. 4(b,c), it can be seen that MgO nanoparticles are also present and contrastingly differ from graphitic carbon nitride; it’s clear that these nanoparticles are evenly distributed over the surface of g-C₃N₄ nanosheets. Thus, even at the nanoscale, the synthesized g-C₃N₄/5%MgO nanocomposite is characterized by a high homogeneity of the spatial distribution of the main components.

Figure 5 shows the PXRD patterns of initial g-C₃N₄ and g-C₃N₄/MgO (5%) nanocomposite. In the case of pure g-C₃N₄, there are two distinct well-defined diffraction peaks at 13.6 and 27.7 degrees, related to the (100) and (002) diffraction planes of graphitic carbon nitride (JCPDS 87-1526). The diffraction pattern of g-C₃N₄/5%MgO nanocomposite shows additional peaks located at 36.8°, 43.2°, 62.5° that can be attributed to (111), (200), (220) planes of magnesia (MgO) with periclase cubic structure (JCPDS 78-0430). As can be seen from the inset in Fig. 5, the average crystallite size of g-C₃N₄ in pure form and nanocomposite is 16.9 nm and 15.5 nm, correspondingly. This decrease in the crystallite size can be associated with the influence of magnesium oxide, which can be formed between individual g-C₃N₄ nanosheets during the synthesis and thereby lead to partial exfoliation of graphitic carbon nitride. These results also confirmed that MgO nanoparticles with an average crystallite size of 9.5 nm are preferably formed in close contact with g-C₃N₄.

![Fig. 2. Results of the selected area EDS analysis of g-C₃N₄/MgO nanocomposite: (a) SEM image of the sample and selected areas, (b) EDS spectrum of area #5. The table inset in (b) shows data on the MgO weight fraction in g-C₃N₄/MgO nanocomposite by selected areas and on average](image-url)
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A linear potential sweep method with a constant sweep speed of 10 mV/s was used as the main measurement procedure to evaluate the electrocatalytic activity of the synthesized g-C$_3$N$_4$/5%MgO nanocomposite with respect to pure Ni substrate and initial g-C$_3$N$_4$ (Fig. 6). As shown in Fig. 6(a), the overpotential on a Ni substrate at a current density of 10 mA/cm$^2$ is 293 mV, which matches to the literature data [11]. In the case of g-C$_3$N$_4$ and g-C$_3$N$_4$/MgO nanocomposite, the overpotential value at the same current density is 264 and 251 mV, respectively. This overpotential value (∼251 mV) for the nanocomposite is significantly lower than for known MgO-based electrocatalysts [12]. The observed reduction in overpotential of the g-C$_3$N$_4$-coated electrodes with the MgO addition can be explained by the higher surface area and morphological features of nanocomposite which promote free removal of evolved hydrogen bubbles (kinetic factor). From the other hand, direct and numerous contact of nanoparticles of the two components (g-C$_3$N$_4$ and MgO) leads to the formation of new interfaces, where a redistribution of electron densities occurs, which makes it easier to initiate the hydrogen evolution process (thermodynamic factor). Additional information was obtained using this data recalculation to the Tafel coordinates (so-called Tafel plot), where the Tafel slope indicates a change in overpotential value with a 10-fold increase in current density. Fig. 6(b) presents the results of the voltammogram analysis in the Tafel plot. Tafel slope for g-C$_3$N$_4$ and g-C$_3$N$_4$/5%MgO samples was found to be equal to
Fig. 5. PXRD patterns of initial g-C_3N_4 and g-C_3N_4/5%MgO nanocomposite and assignment of the main diffraction reflections of graphitic carbon nitride (g-C_3N_4) and magnesia (MgO). The inset shows the average crystallite sizes of g-C_3N_4 and MgO nanocrystals of initial g-C_3N_4 and g-C_3N_4/5%MgO nanocomposite.

Fig. 6. Electrocatalytic performance of g-C_3N_4/5%MgO nanocomposite in hydrogen production via reforming of water-ethanol (10% vol.) solution: (a) HER polarization curves, (b) Tafel plot, (c) cycling stability, (d) chronopotentiometry stability.
116 mV and 106 mV, respectively. Both values are lower than for the pure nickel electrode (120 mV) which provides an economic advantage in electrochemical reforming.

Then, the standard cyclic voltammetry and chronopotentiometry techniques [13, 14] were used to estimate the electrochemical stability of the g-C₃N₄/MgO-based electrode. Fig. 6(c) shows the polarization curves obtained at a sweep rate of 5 mVs⁻¹ for the g-C₃N₄/5%MgO after 1, 10, 50 and 100 cycles of cyclic voltammetry (CVA). After 100 times cycling of the electrode, the value of overpotential slightly degrades, reaching values of about −270 mV. But, according to the results of chronopotentiometry (Fig. 6(d)), the value of overpotential for g-C₃N₄/MgO sample at a time, when the non-stationary mode ends, is 248 mV. The time-value for this sample is about 2000 s and doesn’t change, even after a 10000 s testing. These results of both cyclic voltammetry and chronopotentiometry allow us to declare the high electrochemical stability of the synthesized g-C₃N₄/5%MgO nanocomposite in a water-ethanol reforming process.

4. Conclusion

In summary, a simple wet-chemical approach was proposed and used to synthesize g-C₃N₄/MgO nanocomposite with enhanced electrocatalytic activity compared with pure g-C₃N₄. This approach allowed synthesis of a high chemical and phase purity of g-C₃N₄-based nanocomposite with 5% wt. MgO content, as well as to ensure the uniform distribution of the individual components (g-C₃N₄ and MgO) over the volume of the synthesized electrocatalyst. It was found that the electrochemical characteristics (overpotential, Tafel slope, etc) of the g-C₃N₄/MgO nanocomposite electrode was significantly improved compared to both g-C₃N₄-coated and pure nickel electrode. At the same time, it was shown that the cyclic and chronopotentiometry stabilities of the nanocomposite-coated electrode are at a high and practically significant level. Thus, it was established and confirmed that synthesized g-C₃N₄/5%MgO nanocomposite is an effective and high stable electrode material that seems to be perspective as electrode base for electrocatalytic reforming of a water-alcohol solution toward hydrogen production.

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