CARBON MODIFIED HYBRID ELECTRODE FOR CO_2 REDUCTION REACTION

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Abstract – Electro catalytic CO_2 reduction in environmental conditions has provided a promising way to use renewable electricity for delocalized energy storage and chemical production. For an efficient CO_2 recovery process, it is necessary to create a highly efficient and stable catalyst. In this work, we propose a simple approach to the reduction of carbon dioxide using a new composite material, including catalytically active copper nano particles and carbon aerogel.

Keywords - Carbon nano fiber, Carbon aerogel, CO_2 reduction, Electrochemical measurements, Composite materials.

I. INTRODUCTION

As climate change accelerates day by day in today's reality, new technologies that can reduce or exploit excess greenhouse gas emissions play a vital role in eliminating the negative impact of human activities on the environment. One of the ways to reduce the concentration of carbon dioxide in the atmosphere is the reduction of carbon dioxide to value-added products such as hydrocarbons, alcohols, carbon monoxide, which can later be used as fuel [1-3].

A wide range of homogeneous, heterogeneous, and monoatomic catalysts is being investigated to address the challenges faced by the CO_2 electrochemical reduction (CO_2RR) reaction (high overvoltage, slow reaction kinetics, low electrode stability and selectivity).

Within the framework of this work, hybrid catalysts based on modified carbon substrates (which provide a high specific surface area) and metallic copper nanoparticles were used as catalysts for the reactions of carbon dioxide reduction. copper and copper oxide stimulate the electrolysis of CO_2 and leads to the formation of hydrocarbons and alcohols due to multistage electron transfer with a sufficiently high Faraday efficiency[4-6].

This article describes the method for creating modified electrode. Hybrid electrode is based on carbon aerogel, which was synthesized from carbon nanotubes under supercritical drying in a liquefied CO_2 atmosphere in an E3100 Critical Point Dryer. Due to the high specific surface area, developed structure and porosity of the aerogel, silver nanoparticles were deposited not only on the surface, but also penetrated the aerogel structure, which improved the catalytic activity, as well as the stability of the resulting electrode.

In this article, we report on the creation of a series of efficient and stable nanostructured electrodes for their use as electrocatalysts in CO_2 reduction reactions.

II. DETAILS EXPERIMENTAL

2.1. Materials

Hydrazine hydrate (Acros organics, 100%), copper (II) chloride dihydrate (Sigma-aldrich, 99%), hexadecyltrimethylammonium bromide (Sigma-aldrich, 99%), ammonia solution(Neva reactive, 25%), resorcinol (Sigma-aldrich, 99%), formaldehyde solution (Sigma-aldrich37 wt. % in H2O, contains 10-15% Methanol as stabilizer (to prevent polymerization)), potassium carbonate hydrogen (99,999%), argon (99,99%), propane (99%), nafion (Sigma-aldrich, 5wt%), carbon dioxide (NordGas, 99.99%), carbon nanotube (Titan-A).

III. RESULTS AND DISCUSSION

3.1. Synthesis of CuNPs

Synthesis of copper nanoparticles (CuNP) according to the previously described method [7]. To obtain CuNP, an aqueous solution of CTAB was used, which served as a stopping agent. Since the concentration of CTAB was much higher than the critical micelle concentration (CMC ~ 0.94 mM in aqueous solution), its molecules were organized in solution in the form of micelles. Copper cations (Cu2 +) were distributed over the micelle surface; after the addition of hydrazine as a reducing agent, Cu2 + was reduced to Cu0 and CuNP was formed. At the third stage, CuNP grew independently. An important feature of the synthesized nanoparticles was the ability to prevent their agglomeration and oxidation using CTAB, which suppressed the excessive growth of nanoparticles and prevented their aggregation due to the micellar steric effect. The resulting nanoparticles were used as catalysts in the CO2 reduction reaction. The morphology of these nanoparticles was studied using scanning electron microscopy (SEM) using a Vega 3 Tescan microscope (Fig. 1a). The average diameter of copper nanoparticles was determined by the dynamic light scattering method and was 95 nm (Fig. 1b). It should be noted that when synthesizing nanoparticles using surfactants, the nanoparticle diameter can be

controlled by varying the ratio of the cationic surfactant to the metal compound. Phase analysis was also performed using a D2 PHASER Bruker X-ray diffractometer. Three diffraction peaks were observed on XRD, corresponding to the planes of a cubic copper crystal at 2θ = 43.3º [111], 50.4º [200], 74.1º [220], respectively (FCC) of the crystal structure (JCPDS, 85-1326) (Fig. 1c).

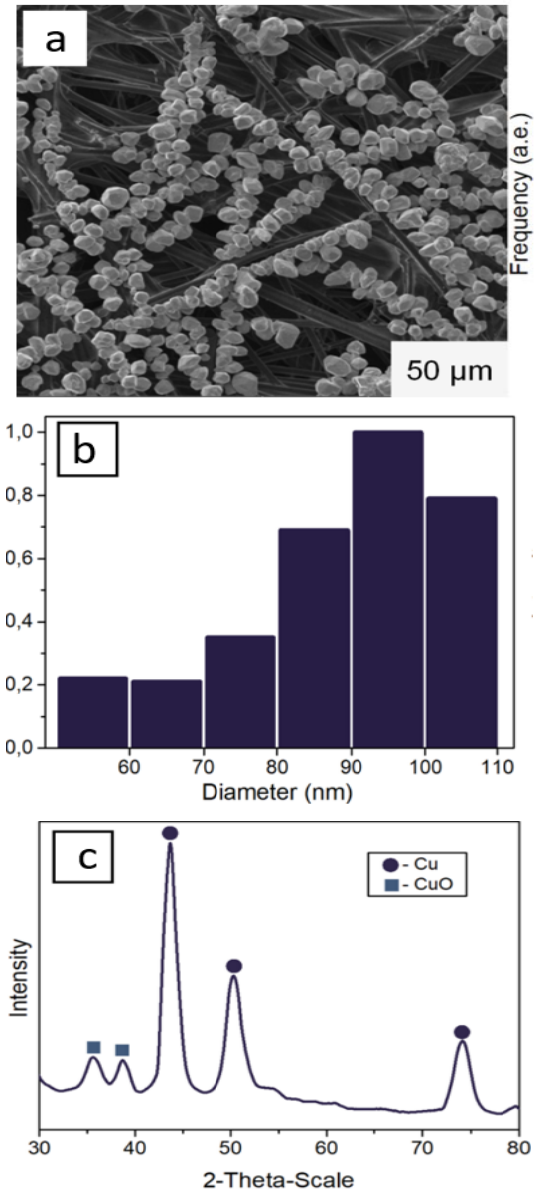

Fig.2. a - SEM image of CuNPs, b - Size distribution of CuNPs by DLSc - XRD pattern of CuNPs.

3.2. Synthesis of carbon modified hybrid electrodes

Carbon aerogels have been synthesized from carbon nanotubes using resorcinol and formaldehyde. This aerogel is widely used due to its properties: non-toxicity, highly accessible channels, and high chemical stability. The synthesized CA had the high surface area. Copper nanoparticles were deposited onto a carbon aerogel by electrochemical deposition. Due to the high porosity of the CA, copper nanoparticles not only deposited on the surface, but also penetrated the aerogel structure, this contributed to an increase in the catalytic activity and stability of the obtained catalyst, since the nanoparticles in the aerogel structure were isolated. This is evidenced not only by SEM photographs (Fig. 2a), but also by elemental analysis (Fig. 2b) obtained using a microscope with an EDX attachment.

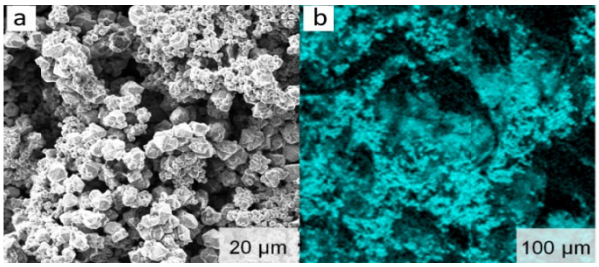

Fig.2. a - SEM image of CuNPs in carbon aerogel structure, b - EDX-distributionCuNPs in carbon aerogel structure.

3.3. Electrochemical measurements

To determine the structural stability of the obtained electrode, electrochemical experiments were carried out. The three-electrode cell consisted of a working electrode, a platinum counter electrode, and a silver wire as a reference electrode. Electrochemical measurements were performed using a computer controlled electrochemical workstation (Biologic SP-50). The electrolyte was a 0.1 M solution of potassium bicarbonate saturated with CO_2; the experiment was carried out at room temperature and atmospheric pressure. Fig. 3shows the chronoamperometric curves obtained during a continuous test of CO_2 co-electrolysis at constant potential (-0.4 V) on a hybrid electrode based on copper nanoparticles and carbon aerogel. During the five-hour test, only a slight decrease in recovery current was observed, compared to an unmodified electrode consisting of carbon fiber doped with copper nanoparticles, which deactivated after 10 minutes at the same applied potentials. CA data show excellent long-term stability of the hybrid electrode in CO_2 electrochemical reduction.

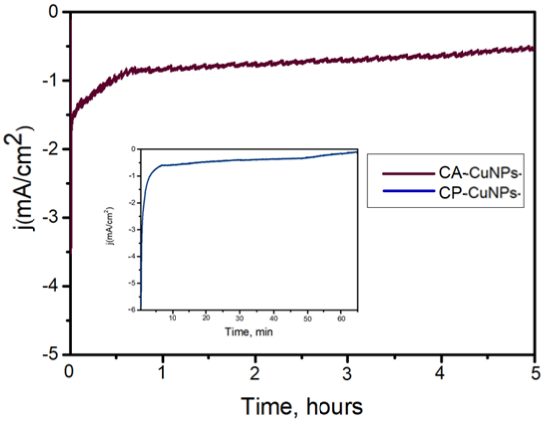

Fig.3. Chronoamperometric curves of stability test with CF-CuNPs-CNF (red line) vs RHE and CF-CuNPs (blue line) vs RHEin the CO_2-saturated 0.1 M $KHCO_3$.

IV. CONCLUSIONS

Thus, we have developed a hybrid electrode material using liquid electrochemical deposition method. The dynamic diameter of the nanoparticles is about 95 nm, the copper content is 0.6 wt%. The new electrocatalyst based on carbon airgel solves the problem of the stability of copper catalysts due to dynamic changes in material properties (aggregation, dissolution) through the growth mechanism of the nanofiber tip. Thanks to the protected carbon layer. This protection ensures the stability of the copper nanoparticles, and the active centers are not lost in the region of the substrate. This research opens up new possibilities for the development of environmentally friendly and safe electrode materials for a variety of electrochemical applications.

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