Flexible Environmentally Friendly Thermoelectric Material Made of Copper (1) Iodide and Nanocellulose for Green Energy

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Herein, we have developed a new efficient flexible hydrophobic thermoelectric (TE) material with increased thermal stability and mechanical strength for green energy production. The 8 µm thick flexible nanocellulose (NC) substrate was obtained from stalks of common reed by TEMPO-mediated oxidation. It has a high crystallinity index of 88 % and the amount of coherent scattering of nanocrystals in the range from 2 to 3 nm. A CuI film with a thickness of $4.3 \ \mu m$ was deposited on the NC substrate by the Successive Ionic Layer Adsorption and Reaction (SILAR), and thus a CuI/NC thin film thermoelectric material was obtained. The average size of the CuI coherent scattering regions is 25 nm. CuI nanocrystals contain dislocations $(1.6 \cdot 10^{15} \text{ lines/m}^2)$ and tensile microstrains of $6 \cdot 10^3$ arb. units. The optical band gap E_g for direct allowed transitions in the CuI film is about 3.0 eV. The high hydrophobicity of the CuI/NC material is a useful feature for applications in humid environments. The CuI/NC material contains the same number of copper and iodine atoms. In addition, a small amount of sulfur (<1 at.%) is present in the copper iodide film, which increases the thermopower coefficient of CuI/NC to 6.7 μ W/(m K²) at T = 340 K. Its positive Seebeck coefficient $S = 108 \,\mu\text{V/K}$ confirmed the *p*-type conductivity of CuI. The change in the resistivity upon initial heating and subsequent cooling demonstrated the electrical conductivity crossover typical of films of nanocrystalline degenerate semiconductor CuI. A CuI/NC sample in the form of a 3 cm × 1 cm strip was tested as a planar thin film TE element. The output power density of a CuI/NC TE element 0.123 W/m² was experimentally recorded at a difference between its hot and cold edges of 40 K.

Keywords: Thermoelectric element, Thin film, Nanocellulose, SILAR, CuI.

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1. INTRODUCTION

Awareness of the problem of thermal environmental pollution has led to a surge in research concerning development of clean energy sources. Thermoelectrics employs waste heat to generate power and thus can be termed as green energy source [1, 2]. However, today the vast majority of commercial thermoelectric (TE) devices are based on heavy rare elements such as bismuth and tellurium or highly toxic elements such as lead [2]. To be truly green, thermoelectric materials must have a minimal impact on the environment and human health throughout their entire life cycle from raw material extraction to disposal. Copper (1) iodide (CuI) is a novel promising *p*-type thermoelectric semiconductor with a large thermoelectric figure of merit ZT of 0.22 [2-5]. At the same time, according to [6, 7], CuI exhibits good antibacterial activity against infections caused by broad-spectrum bacteria and can be used to destroy organic pollutants in water. In addition, CuI is used as a source of the micronutrients copper and iodine in dietary table salt, dog food, and other pet foods. Thus, copper (1) iodide can indeed be used to develop an efficient environmentally friendly thermoelectric material. It is especially interesting from the point of view of being used as a base of thin-film flexible portable and wearable thermoelectric devices that operate at temperatures below 373 K [5-7]. Thin-film thermoelectric generators based on CuI will be able to generate low power, sufficient to supply medical patches and wearable sensor networks, as well as Internet of things (IoT) wireless communication systems. To be truly environmentally friendly energy sources, substrates for copper (1) iodide films in thin-film thermoelectric elements and generators can be made from nanocellulose (NC) biomaterial, which has many attractive properties. According to [8], nanocellulose is a new class of renewable and biodegradable biocompatible nanomaterials with high elastic modulus, nanoscalability, optical transparency, and low thermal expansion. The low thermal conductivity of nanostructured NC films (~ 0.22-0.53 W m $^{-1}$ K $^{-1}$ [9] will help to reduce heat losses in the CuI/NC thin-film planar TE elements of in-plane TE generators. Herein, to obtain a flexible environmentally friendly thermoelectric material CuI/NC, a nanocellulose film 8 µm thick was used as a substrate, obtained by TEMPO-mediated oxidation of organosolv pulp from reed stalks in accordance with the technology described in [8]. A 4.3 µm thick copper (1) iodide film was deposited on the NC substrate by the Successive Ionic Layer Adsorption and Reaction (SILAR) method using a simple setup and aqueous solutions of precursors. According to [10, 11], SILAR is a very successful method for applying nanocrystalline coatings due to its inherent simplicity, low cost, and ability to work at atmospheric pressure. In our recent N.P. KLOCHKO, V.A. BARBASH, S.I. PETRUSHENKO, ET AL.

work [11], in order to obtain an efficient thermoelectric material CuI/NC, we used as a substrate a 12 μm thick nanocellulose film obtained from the stalks of the perennial Miscanthus × giganteus by acid hydrolysis. However, as was established in [11], planar CuI/NC thermoelectric elements cracked during energy dispersive X-ray mapping due to the thermal degradation of nanocellulose from miscanthus under the action of successive scans of 32 s each with an electron beam with an energy of 30 eV for 30 min. In this work, by studying the crystal structure, morphology, chemical composition, optical, electrical and thermoelectric properties, we confirmed the creation of a planar TE element with a nanostructured CuI layer on a nanocellulose substrate obtained from reed using TEMPO-mediated oxidation, which demonstrated improved thermal stability and thermoelectric efficiency.

2. EXPERIMENTAL DETAILS

To prepare NC film we used stalks of common reed grown in the Cherkassy region, Ukraine. First, the reed stems were extracted with an aqueous solution of NaOH (50 g/l) for 120 min at a temperature of 97 ± 2 °C, the ratio of liquid to solid phase was 10:1. The second stage was cooking reed pulp for 120 min at a temperature of 97 ± 2 °C in an aqueous solution containing glacial acetic acid and 35 % hydrogen peroxide at a volume ratio of 7:3 and a liquid to solid ratio of 10:1. At the third stage, to obtain a stable nanocellulose hydrogel by TEMPO-mediated oxidation, the organosolv pulp was treated with an aqueous solution of 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (its acronym is TEMPO) in the TEMPO/NaBr/NaClO system at room temperature for 24 h, pH was controlled within 10-11 with the addition of NaOH solution followed by ultrasound treatment. To stop TEMPO-mediated oxidation, ethanol and 0.5 M HCl were added to the suspension to pH 7. Then, the resulting nanocellulose suspension was purified from TEMPO, salts and other compounds present in the oxidizing mixture by centrifugation with the addition of distilled water three times at 4000 rpm for 30 min, followed by treatment of the pure suspension with ultrasound for 10 min. The resulting homogeneous hydrogel of pure nanocellulose was poured into a Petri dish and air-dried at room temperature, obtaining an 8 um-thick NC film.

To create TE material CuI/NC we employed 40 cycles of CuI deposition through the SILAR method by using 0.075 M NaI aqueous anionic precursor at 30 °C, in accordance with described in [11]. The averaged thickness of the obtained CuI film 4.3 μ m in the CuI/NC material was determined gravimetrically taking for a calculation the bulk CuI density 5.67 g/cm³.

The surface morphology of the CuI/NC thermoelectric material was observed by scanning electron microscopy (SEM) using a Tescan Vega 3 LMH SEM device operating at an accelerating voltage of 10 kV. Chemical analysis of the $50 \times 50 \ \mu m$ CuI/NC region was performed by X-ray fluorescence (XRF) microanalysis using a Bruker XFlash 5010 energy-dispersive X-ray spectrometer (EDS). Quantitative evaluation of the XRF spectrum was carried out in the mode of a selfcalibrating detector. In addition, SEM imaging capabilities were combined with EDS X-ray measurements to obtain X-ray mapping of elemental distribution (EDS mapping). Each EDS map was a superposition of the signal received from the backscattered electron detector (colored in white) and the intensity of the Cu or I characteristic line (colored in shades of the corresponding color). The scanning time was 32 s, and the information was accumulated over a series of successive scans for 30 min. The resolution of the EDS map was 500×500 pixels.

Optical transmittance and reflectance of the CuI/NC TE material in the wavelength (λ) range 400-800 nm were studied on an SF-2000 spectrophotometer with an SFO-2000 attachment to obtain the total reflectance $R(\lambda)$. $R(\lambda)$ was the sum of specular reflectance and diffuse reflectance $R_d(\lambda)$ at an angle of incidence of light 8° relative to the normal to the surface. The optical band gap E_g for direct allowed transitions in the CuI film was determined, as described in [12], from the Kubelka-Munk function F(R):

$$F(R) = \frac{(1 - R_d)^2}{2R_d},$$
 (1)

A plot of $(F(R) hv)^2$ versus hv gives the direct band gap E_g CuI by extrapolating the linear part of $F(R) hv)^2$ to hv.

To analyze the crystal structure of thin NC and CuI films in the CuI/NC thermoelectric material, X-ray diffraction patterns (XRD) were taken on a Shimadzu XRD-6100 X-ray diffractometer with Bragg-Brentano focusing (θ -2 θ) (CuK α radiation, $\lambda = 1.54060$ Å). The average size D of the regions of coherent scattering in the direction normal to the reflecting planes, usually called as the crystallite size, was determined by X-ray line broadening using the Scherrer equation, as in [11].

To determine the relative amount of the crystalline cellulose phase in the nanocellulose film, we used the X-ray diffraction pattern of the pristine NC substrate. The crystallinity index (CI) was calculated by the Segal method in accordance with [11] as:

$$CI = [(I_{200} - I_{am})/I_{200}] \times 100 \%,$$
(2)

where I_{200} is the intensity of the (200) reflection for the crystalline phase of NC at $2\theta \approx 22.6^{\circ}$, I_{am} is the intensity of amorphous scattering at $2\theta \approx 19.9^{\circ}$. Thus, CI was calculated from the height ratio between the intensity of the crystal peak ($I_{200} - I_{am}$) and the total intensity I_{200} after subtracting the background signal.

The lattice parameter *a* of γ -CuI was calculated from the X-ray diffraction positions by the Nelson-Reilly graphical extrapolation (N-R) method and refined by the least squares method using the UnitCell (UC) program in accordance with [11]. The lattice microstrains were obtained from the relationship $\varepsilon = \Delta d/d$ (where *d* is the interplanar spacing of the γ -CuI crystal in the JCPDS reference database, and Δd is the difference between the corresponding experimental and reference interplanar spacing). The dislocation density was estimated in terms of $1/D^2$ as described in [11].

The Seebeck coefficient S, defined as the ratio of the thermal electromotive force (thermoelectric voltage) to the temperature difference ΔT between the hot and cold edges of a 3 cm × 1 cm CuI/NC sample, was measured

using a homemade setup. In this setup, the CuI/NC sample was suspended between gold ring contacts that were placed 2.3 cm between the hot plate of the Peltier module as a heat source and the cold aluminum plate as heatsink.

The resistivity ρ of the CuI film in the CuI/NC sample was measured using a four-point collinear probe method. The measurements were carried out in the temperature range of 305-335 K. The resistivity was calculated according to [13] as follows:

$$\rho = (\pi t \delta V_{23})/(I_{14} \cdot \ln 2), \tag{3}$$

where t is the CuI film thickness; V_{23} – voltage drop between two internal (second and third) probes; I_{14} – current between first and fourth probes; δ is a correction factor based on the ratio of probe dimensions to sample dimensions; $\pi\delta/\ln 2 \approx 4.04$.

According to [14], thermoelectric power factor PF of the CuI/NC sample was calculated as S^2/ρ . The output thermoelectric voltage U and the output power P of the planar thin-film CuI/NC TE element were obtained at some temperature gradients ΔT in the range of 5-40 K between its hot and cold edges, provided by resistive heating of one edge of the CuI/NC sample using a Peltier module. To obtain output thermoelectric characteristics, the CuI/NC sample with an area of 3 cm × 1 cm was connected through gold ring contacts to an external load with adjustable resistance R_{load} and two multimeters for recording U and output current I. From the dependence of U on I, the values of open-circuit voltage U_{oc} at load resistance $R_{load} = \infty$, and short-circuit current I_{sc} at $R_{load} = 0$ were obtained. From the dependence of P on I, the maximum output power P_{max} was obtained when the load resistance and the internal resistance R_{int} of the TE element CuI/NC were equal. In accordance with [14], the output power density P^*_{max} was estimated for the obtained CuI/NC sample according to the following equation:

$$P_{\max}^* = P_{\max} / (w \times t), \qquad (4)$$

where w is 1 cm.

3. RESULTS AND DISCUSSIONS

Fig. 1 (a, d) presents results of studying the surface morphology of the copper iodide film in the CuI/NC sample by SEM using a secondary electron detector. It can be seen that nanostructured CuI film completely covers the surface of the NC substrate. The EDS maps demonstrate a fairly uniform distribution of copper (Fig. 1 b, e) and iodine (Fig. 1 c, f) atoms in the CuI film. It is important to note the absence in Fig. 1 visible damage or cracks on nanocellulose substrates obtained by TEMPO-mediated reed oxidation, which were visible when using SILAR deposition of CuI films of NC substrates obtained by acid hydrolysis of perennial miscanthus herb [11].



Fig. 1 - Top view SEM images of the CuI/NC sample in two magnifications (a) and (d); EDS maps of the CuI/NC sample (b), (c), (e), (f)

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Analysis of the chemical composition of the CuI/NC sample by XRF revealed (Fig. 2) the same content of copper and iodine atoms in the CuI film. A small amount of sulfur in the copper iodide film is due to the partial decomposition of thiosulfate in the cationic precursor used in the SILAR method [11]. According to [16], CuI films doped with sulfur have increased electrical conductivity due to an increase in the hole density; accordingly, sulfur enhances their thermoelectric power factors. Small quantity of aluminum in the X-ray fluorescence spectrum belongs to the equipment of the vacuum chamber in which the studies were carried out. Data of the energy-dispersive X-ray spectrometry analysis of CuI/NC in the inset in Fig. 2 includes 20 % carbon atoms, since carbon is the main component of cellulose molecules.



Fig. 2 – X-ray fluorescence spectrum of the CuI/NC sample and its chemical composition according to the EDS data in the inset

Fig. 3 (a) shows an X-ray diffraction pattern of the nanocellulose substrate. It mainly refers to the monoclinic structure of cellulose $(I\beta)$, which, according to [15], is a stable and dominant polymorph of cellulose nanocrys-

tals. The broad peak at 2θ around 19.9° refers to the amorphous phase of cellulose. According to the calculations of the crystallinity index using equation (2), NC is highly crystalline (CI = 88 %). Comparison of the data on the crystallinity index of NC obtained in this work from reed by TEMPO-mediated oxidation with NC obtained in [11] from miscanthus by acid hydrolysis explains the better thermal stability of reed-derived nanocellulose by a low content of the amorphous phase (its crystallinity index is higher by more than 11 %).

The regions of coherent scattering *D* of nanocrystals in the reed-derived NC were estimated from the broadening of the (110) peak at $2\theta \approx 15.8^{\circ}$ and the (200) peak at $2\theta \approx 22.6^{\circ}$ in the X-ray diffraction pattern in Fig. 3 (a). The values of *D* obtained in this way for reed-derived NC were between 2 and 3 nm. The *D* values of nanocrystals in nanocellulose prepared in [11] from miscanthus by acid hydrolysis were in the range of 3-4 nm. Due to smaller nanocrystals of the reed-derived NC, the area of boundaries of nanocellulose particles increased, which contributed to mechanical strengthening.

Fig. 3 (b) is an X-ray diffraction pattern of the CuI/NC sample with the polycrystalline copper iodide film having a cubic crystal structure (zinc blende, γ -CuI, JCPDS #06-0246). The average D value of the CuI film is 25 nm. CuI nanocrystals contain dislocations (1.6 $\cdot 10^{15}$ lines/m²) and tensile microstrains $\varepsilon = 6 \cdot 10^3$ arb. units. This is consistent with the reduced CuI lattice parameter (a = 0.604 nm according to N-R and a = 0.602 nm according to UC) compared to the reference value a = 0.6051 nm. An additional peak in the X-ray diffraction pattern of the CuI/NC sample at $2\theta \approx 23^\circ$ corresponds to the (200) plane of the NC.



Fig. 3 – X-ray diffraction patterns of the reed-derived NC substrate (a) and the thin-film CuI/NC sample (b). Inset (a) shows an X-ray diffraction pattern of the reed-derived NC substrate at small 2θ angles

The results of optical studies in Fig. 4 (a) confirm the low transmittance and high predominantly diffuse reflectance of the CuI/NC sample. The optical band gap E_g for direct allowed transitions in the CuI film, determined from the Kubelka-Munk function, is approximately 3.0 eV, which is a typical value for bulk copper iodide (Fig. 4(b)). As can be seen in the photograph of a water drop on the CuI/NC surface in Fig. 3(b), the CuI/NC material is waterproof. The high hydrophobicity of the material is a useful property for applications in humid environments.



Fig. 4 – (a) Transmittance spectrum $To(\lambda)$ and total reflectance spectrum $R(\lambda)$ of the CuI/NC sample. (b) – Optical band gap E_g for direct allowed transitions in the CuI film, determined from the Kubelka-Munk function. The inset (b) shows a photograph of a water drop on the surface of the CuI/NC sample

Figure 5(a) shows the change in the resistivity of the copper iodide film during initial heating and subsequent cooling. Both graphs demonstrate the electrical conductivity crossover typical of degenerate CuI nanocrystalline semiconductor films and explained by the combined quadratic temperature dependence model for the metal part and the fluctuation-induced tunneling conductance (FITC) model for the semiconductor part, reflecting the granular structure of the film [17]. Due to the presence of a thermodynamically unstable state and transient processes during heating, the semiconductor nature of the dependence of resistance on T during cooling is more indicative. According to [17], at lower temperatures, the nature of the change in resistance with temperature is more affected by the tunneling of carriers through barriers at grain boundaries. At higher T, it is mainly described by the inner part of the grains. The resulting resistivity in Fig. 5(a) is a series connection of the resistance contributions of the inner grains and grain boundaries.

The graph in Fig. 5 (b) confirms the *p*-type conductivity of the CuI film in the CuI/NC sample. The value of the Seebeck coefficient calculated as $S = U/\Delta T$ is 108 µV/K, the power factor of thermoelectric material CuI/NC *PF* is 6.7 µW/(K² m) at T = 340 K.



Fig. 5 – Plots of ρ vs. T (a) and thermoelectric voltage U induced in response to the temperature gradients ΔT along the NC/CuI sample (b)

Fig. 6 shows the output thermoelectric characteristics of the CuI/NC sample in the form of a strip with dimensions of 3 cm × 1 cm at temperatures close to room temperature. The difference between temperatures of the hot and cold edges of this planar thin-film CuI/NC TE element ΔT was 5 K, 10 K, 15 K, 30 K or 40 K. Fig. 6(a) demonstrates plots of output voltages versus output currents, and Fig. 6(b) presents output powers versus output currents. As can be seen from Fig. 6, the output parameters naturally increase with increasing ΔT . At $\Delta T = 40$ K, the CuI/NC TE element generates $U_{oc} = 4.3$ mV, $I_{sc} = 4.8$ µA and $P_{max} = 5.3$ nW. Its open circuit voltage is approximately equal to that calculated by the equation $U_{oc} = S\Delta T$.

Calculation of the internal resistance R_{int} of the CuI/NC sample according to the equation proposed by the authors [14]:

$$R_{int} = U^2_{oc}/4P_{max},$$
(5)

showed that this sample at T = 340 K has $R_{int} = 0.87 \text{ k}\Omega$. Calculations according to equation (4) gave the output power density $P^*_{\text{max}} = 0.123$ W/m² at $\Delta T = 40$ K, i.e., when heating one end of the CuI/NC sample to 340 under normal conditions of a summer day.



Fig. 6 – Graphs of output voltage U (a) and output power P (b) versus output current I for some temperature gradients ΔT along the 3 cm × 1 cm NC/CuI sample with the CuI film 4.3 µm thick deposited by the SILAR method on the nanocellulose substrate made from reed raw materials

CONCLUSIONS

The present study demonstrates a high potential of the flexible environmentally friendly thin-film thermoelectric material made of copper iodide (1) and nanocellulose for green energy due to its minimal impact on the environment and human health throughout their entire life cycle from raw materials and technology to disposal. The 8 µm thick nanocellulose substrate obtained from stalks of common reed by TEMPOmediated oxidation has a crystallinity index of 88 % and belongs to the monoclinic structure ($I\beta$), which is a stable and dominant polymorph of cellulose with increased thermal stability. Due to the small nanocellulose nanocrystals of the reed-derived NC (D between 2-3 nm), the large surface area of the nanocellulose grains contributes to the mechanical strengthening of the substrate. To obtain the CuI/NC sample, the 4.3 µm thick CuI film was deposited on the NC substrate by the SILAR method using a simple setup and aqueous solutions of precursors. According to XRD data, the copper iodide film is polycrystalline and has a cubic crystal structure of the zinc blende type *γ*-CuI. The average size of the CuI coherent scattering regions D is 25 nm. The CuI nanocrystals contain dislocations (1.6 $\cdot 10^{15}$ lines/m²) and tensile microstrains ε of $6 \cdot 10^3$ arb. units. The optical band gap E_g for direct allowed transitions in the CuI film is about 3.0 eV, which is a typical value for bulk copper iodide. The high hydrophobicity of the CuI/NC material is a useful feature for applications in humid environments. Analysis of the

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chemical composition of the CuI/NC sample by XRF revealed the same content of copper and iodine atoms in the CuI film. A small addition of sulfur to the copper iodide film (< 1 at.%) due to the partial decomposition of thiosulfate in the cationic precursor used in the SI-LAR method is favorable from the point of view of enhancing electrical conductivity of CuI by increasing the hole density. Such doping with sulfur increased the thermoelectric power factor *PF* of the CuI/NC thermoelectric material to 6.7 μ W/(K² m) at *T* = 340 K.

A CuI/NC sample in the form of a 3 cm \times 1 cm strip was tested as a planar thin film TE element. Its positive Seebeck coefficient $S = 108 \,\mu\text{V/K}$ confirms the *p*-type conductivity of CuI. The change in the resistivity of the copper iodide film upon initial heating and subsequent cooling demonstrates the electrical conductivity crossover typical of nanocrystalline CuI degenerate semiconductor films. The output power density of the CuI/NC TE element with a difference between its hot and cold ends of 40 K reached $P^*_{\text{max}} = 0.123 \,\text{W/m}^2$. Thus, in this work, we have developed a new efficient flexible hydrophobic thermoelectric material with increased thermal stability and mechanical strength for green energy production.

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Гнучкий екологічно чистий термоелектричний матеріал із йодиду міді (1) та наноцелюлози для зеленої енергетики

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Розроблено новий ефективний гнучкий гідрофобний термоелектричний (ТЕ) матеріал із підвищеною термічною стабільністю та механічною міцністю для виробництва зеленої енергії. Гнучка наноцелюлозна підкладка товщиною 8 мкм була отримана зі стебел звичайного очерету шляхом ТЕМРОопосередкованого окислення. Вона має високий індекс кристалічності 88 % і області когерентного розсіювання нанокристалів в межах від 2 до 3 нм. Плівка Cul товщиною 4,3 мкм була нанесена на підкладку NC методом послідовної адсорбції та реакції іонних шарів (SILAR), і таким чином був отриманий тонкоплівковий термоелектричний матеріал CuI/NC. Середній розмір областей когерентного розсіювання CuI становить 25 нм. Нанокристали CuI містять дислокації (1.6 ·10¹⁵ ліній/м²) і мікродеформації розтягу 6·10³ від. од. Оптична заборонена зона *E*g для прямих дозволених переходів у плівці CuI дорівнює близько 3,0 eB. Висока гідрофобність матеріалу CuI/NC є корисною властивістю для застосування у вологому середовищі. Матеріал CuI/NC містить однакову кількість атомів міді та йоду. Крім того, в плівці йодиду міді присутня невелика кількість сірки (<1 ат.%), що збільшує фактор термоелектричної потужності матеріалу CuI/NC до 6,7 мкВт/(м К²) при T = 340 К.. Його позитивний коефіцієнт Зеебека $S = 108 \mu V/K$ підтвердив *p*-тип провідності CuI. Зміна питомого опору при початковому нагріванні та подальшому охолодженні продемонструвала кросовер електропровідності, який є типовим для плівок нанокристалічного виродженого напівпровідника CuI. Зразок CuI/NC у вигляді смужки 3 см × 1 см тестували як планарний тонкоплівковий ТЕ елемент. Експериментально зафіксовано щільність вихідної потужності ТЕ елемента CuI/NC 0.123 Вт/м² при різниці між його гарячим і холодним краями 40 К.

Ключові слова: Термоелектричний елемент, Тонка плівка, Наноцелюлоза, SILAR, Cul.