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RESEARCH ARTICLE

A green synthetic method for cobalt(II,III) oxide nanoparticles with high surface activity

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Abstract

Objectives. *To develop a new green method for the synthesis of nanosized materials of cobalt(II,III) oxide, with improved surface activity, using environmentally friendly precursors and solvents.*

Methods. *A green method was proposed, in order to isolate Co_3O_4 nanoparticles with high surface activity. Instead of the usual organic solvents, three different natural sugars, including glycogen, sucrose, and glucose were used for the first time as templates. Water as a green solvent was used in all the steps. The polymorphic composition of the synthesized samples was determined by means of X-ray phase analysis. The morphology of the obtained crystallites was studied from micrographs of the oxide phases. Image Pro Plus 6 software was used to measure the size of nanoparticles. The surface activity of the isolated samples was studied using the Brunauer–Emmett–Teller method and the Langmuir method. The Barret–Joyner–Halenda method was used to determine the diameter, volume, and distribution of pores.*

Results. *The crystallite sizes of the samples are 23 nm, 36 nm, and 30 nm for glucose, glycogen, and sucrose templates, respectively. Adsorption–desorption isotherms for samples obtained from complexes of glucose and sucrose correspond to type IV, indicating a strong interaction between the adsorbent and the adsorbed sample. The isotherm for the sample isolated from the complex with glycogen is of a different type and most likely indicates that this sample is almost completely mesoporous. The pore radii are found in the interval 1.2–1.6 nm.*
Conclusions. *A new green method for the synthesis of nanosized particles of Co(II,III) oxide using natural saccharides and deionized water was developed. The composition, morphology, structure, and surface activity of the samples obtained were studied. It was shown that due to the polymeric structure of their metal complexes and the ability to bind active carbon on the surface of nanoparticles, natural saccharides can be used as matrices in the synthesis of nanosized metal oxides with high surface activity.*

Keywords: *nanoparticles of cobalt(II,III) oxide, synthesis, surface activity, X-ray phase analysis, Fourier transform IR spectroscopy, electron spectroscopy*

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НАУЧНАЯ СТАТЬЯ

«Зеленый» метод синтеза наночастиц оксида кобальта(II,III) с улучшенной поверхностной активностью

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Аннотация

Цели. *Разработать новый «зеленый» метод синтеза наноразмерных материалов оксида кобальта(II,III) с улучшенной поверхностной активностью, используя неопасные для окружающей среды прекурсоры и растворители.*
Методы. *Предложен новый метод выделения наноразмерных частиц Co_3O_4 с высокоразвитой поверхностью. В качестве матриц впервые применены природные сахариды — гликоген, сахароза и глюкоза. В роли экологически чистого растворителя на всех стадиях процесса используется вода. Полиморфный состав синтезированных образцов определяли с помощью рентгенофазового анализа. Морфологию полученных кристаллитов изучали по микрофотографиям оксидных фаз. Для измерения размера наночастиц использовалось программное обеспечение Image Pro Plus 6. Поверхностную активность выделенных образцов изучали методом Брунауэра–Эммета–Теллера и методом Ленгмюра. Для определения диаметра, объема и распределения пор применялся метод Баррета–Джойнера–Халенды.*

Результаты. *Размеры кристаллитов синтезированных образцов составляют 23, 36 и 30 нм для матриц глюкозы, гликогена и сахарозы соответственно. Изотермы адсорбции–десорбции для образцов, полученных на основе комплексов глюкозы и сахарозы, соответствуют IV типу, что свидетельствует о сильном взаимодействии между адсорбентом и адсорбированным образцом. Изотерма для образца, выделенного на основе комплекса с гликогеном, относится к другому типу и, скорее всего, указывает на то, что этот образец почти полностью мезопористый. Радиус пор составляет 1.2–1.6 нм.*

Выводы. *Разработан новый «зеленый» метод синтеза наноразмерных частиц оксида кобальта(II,III) с использованием природных сахаридов и деионизированной воды. Исследованы состав, морфология, строение и поверхностная активность полученных образцов. Показано, что природные сахариды благодаря полимерной структуре их металлокомплексов и способности связывать активный углерод на поверхности наночастиц, могут быть использованы в качестве матриц при синтезе наноразмерных оксидов металлов с большой поверхностной активностью.*

Ключевые слова: *наночастицы оксида кобальта(II,III), синтез, поверхностная активность, рентгенофазовый анализ, ИК-спектроскопия, электронная спектроскопия*

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INTRODUCTION

At the present time, due to their unique properties, nanoscale materials are widely used in everyday life and various industries, such as medicine, ecology, and the paint and varnish industry [1–4]. However, a significant drawback in their synthesis is the use of environmentally hazardous precursors and solvents. Therefore, an urgent task is to find an environmentally friendly and highly effective method for isolating metal oxide nanoparticles with high surface activity.

Cobalt(II,III) oxide is interesting due to its specific properties. Materials based on Co_3O_4 have the properties of *p*-type semiconductors and exhibit magnetic properties [5, 6]. They are used as molecular detectors, electrochemical storage devices, magnetic storage media, solar energy converters and in the electronics industry, as well as catalytic systems for various purposes, including organic synthesis and environmental purification from toxic impurities [7–14].

Co_3O_4 nanoparticles are stable structures of various morphologies [15] (rods [16], sheets [17], tubes [11, 18], cubes [19], and spheres [20, 21]). Ordered structures isolated by the hydrothermal method were studied by Hu *et al*. [22], and spinel Co_3O_4 nanoparticles were shown to have lower crystallinity and smaller crystallite size.

Previously we synthesized and studied nanoparticles of 3d metal oxides using organometallic complexes based on alkyl and benzylnitrosohydroxylaminates [23], biphenolic compounds [24–26], and polyhydroxybenzoic acids [27, 28] as precursors.

This work reports a new green method for the synthesis of Co_3O_4 nanoparticles using deionized water and natural saccharides and the study of their surface. It is shown that this method can be considered as a promising method for the synthesis of various nanocrystalline materials.

EXPERIMENTAL

The sucrose, glycogen, and glucose used in the work are pure grade, and cobalt(II) chloride hexahydrate is chemical grade purchased from *Sigma-Aldrich*, USA.

Method for the synthesis of Co_3O_4 nanoparticles. 10 g of the corresponding saccharide was dissolved in 50 mL of deionized water and stirred. At the same time, 2.96 g of cobalt(II) chloride hexahydrate was dissolved in deionized water in a second glass and stirred until a homogeneous solution was obtained. The saccharide solution was then slowly poured into the cobalt salt solution and stirred at 75°C for 1 h. The solution was kept at 20°C until a gel formed. The resulting gel was transferred to a pre-calcination oven at 120°C. The dried sample was calcined at 650°C, in order to obtain the corresponding cobalt oxide. The yields of the final products are 60–70%.

Elemental analysis for cobalt content was carried out by means of complexometric titration [29]. Carbon content was determined using micromethods [30]. Elemental analysis results:

Sample 1 (derived from a complex with sucrose). Found: Co — 73.15%; C — traces (<0.5%). For Co_3O_4 it was calculated as: Co — 73.42%.

Sample 2 (derived from a complex with glycogen). Found: Co — 73.38%; C — not detected. For Co_3O_4 it was calculated as: Co — 73.42%.

Sample 3 (derived from a complex with glucose). Found: Co — 73.18 %; C — traces (<0.5%). For Co_3O_4 it was calculated as: Co — 73.42%.

X-ray diffraction patterns of oxide phases were obtained using a GNR automatic diffractometer (*GNR Analytical Instruments Group*, Italy) in continuous mode. Operating wavelength was 1.541 Å (Cu-K_a). X-ray diffraction patterns were interpreted using the GNR Explorer program (*GNR Analytical Instruments Group*, Italy)[1].

The surface activity of the synthesized samples was determined by means of the Brunauer–Emmett–Teller (BET) method at 77 K on a Belsorp-mini II micrometer device (*Microtrac Retsch*, Germany). The Barrett–Joyner–Halenda (BJH) method was used to evaluate mesoporosity and pore size distribution. In order to prepare and dry the material before measuring and removing water vapor, carbon dioxide, or other molecules that may occupy the volume of the material's cavities, the sample was placed in an oven for several hours at high temperature. The dehydration temperature was 393.15 K. The dehydration time was 2 h at a saturated water vapor pressure of 84.737 kPa.

TEM images were obtained using a model LEO 912AB microscope (*Leitz-Opton*, Germany) in low vacuum mode using ethanol as a dispersant.

FTIR spectra of the samples were recorded using an AVATAR 370 spectrometer (*Thermo Nicolet*, USA) at a temperature of 20°C in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} in KBr pellets.

Electronic absorption spectra were recorded on a Cary-50 spectrophotometer (*Agilent Technologies Inc.*, USA) in the wavelength range 200–800 nm.

RESULTS AND DISCUSSION

Synthesis and Co_3O_4 nanoparticle properties

A diagram of the new green method for the synthesis of Co_3O_4 nanoparticles is shown in Fig. 1.

The polymorphic composition of all synthesized samples was determined using X-ray phase analysis ($15° < 2\theta < 80°$) (Fig. 2). Analysis of X-ray diffraction patterns of samples obtained using various precursors shows that the spinel modification of Co_3O_4 (ICDD: 96-900-5889) of high purity (peaks 19.02°, 31.31°, 36.73°, 44.67°, 59.35°, and 65.02°) is the main crystalline structure of the products obtained from thermolysis of all precursors: the highest purity characteristic of Co_3O_4 being obtained from the decomposition of a solution containing glycogen. Based on the data from literature, the presence of low-intensity peaks in the region of about 26° and 44° in the X-ray diffraction patterns of cobalt oxide samples obtained from glucose and sucrose may indicate the presence of carbon impurities in the samples [31].

The size of crystallites (coherent scattering regions) D_c was calculated using the Scherrer equation (1):

$$D_c = k\lambda/\beta\cos\theta, \quad (1)$$

where k is the shape factor (approximately 0.9), λ is the wavelength of the X-ray source (1.5406 Å), and β is the width of the observed diffraction line at its half-maximum intensity (400).

Based on the results obtained, the sizes of crystallites (coherent scattering regions) of the samples are 23, 36, and 30 nm for precursors based on glucose, glycogen, and sucrose, respectively.

Microphotographs of oxide phases obtained by calcination of cobalt complexes of sucrose,

[1] Explorer: G.N.R. srl – Analytical Instruments Group (gnr.it). Accessed May 23, 2022.

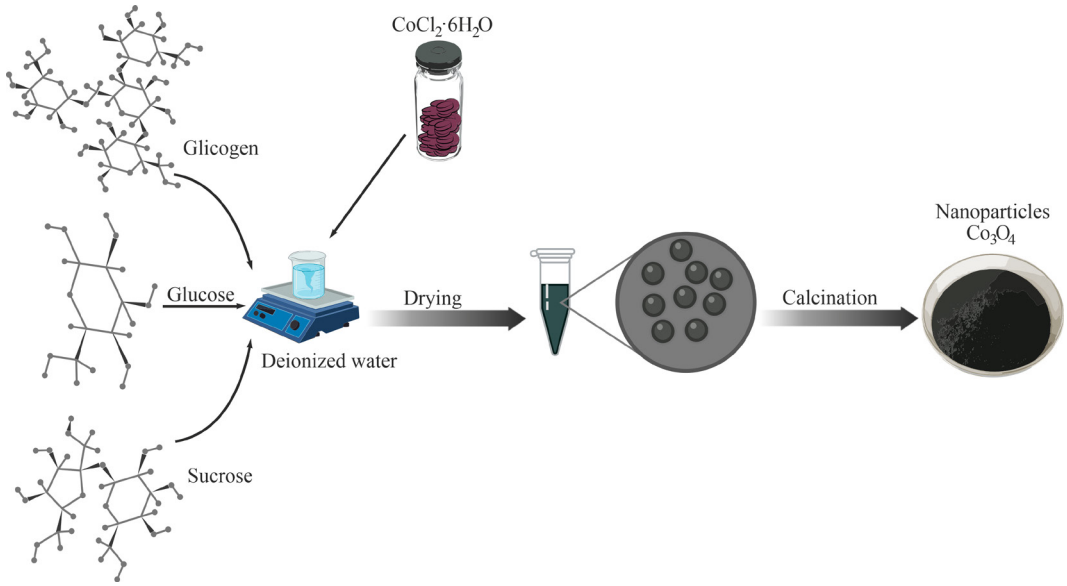


Fig. 1. Synthetic scheme for Co_3O_4 nanoparticles.

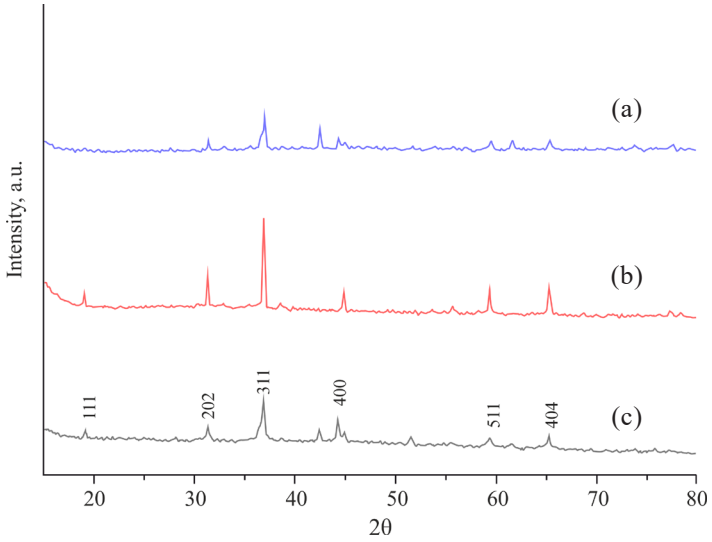


Fig. 2. X-ray diffraction patterns of oxide phases obtained by calcination of cobalt(II) complexes with sucrose (a), glycogen (b), and glucose (c).

glycogen, and glucose are presented in Fig. 3. As can be seen in Fig. 3, the shape of nanoparticles obtained by calcination of cobalt(II) complexes with sucrose, glycogen, and glucose is the same, but they differ in size. The largest size of nanoparticles was observed for the thermolysis product of the complex with sucrose, corresponding to the results obtained from the analysis of X-ray diffraction patterns. Image Pro Plus 6 software (*Media Cybernetics*, Inc., USA)[2] was used to measure the nanoparticle sizes. It was found that the average particle sizes for all samples were in the range of 5–30 nm.

[2] https://mediacy.com/image-pro/. Accessed July 05, 2022.

Surface properties

The state of the surface of products obtained from solutions containing various sugars was studied by infrared (IR) spectroscopy in the range of 400–4000 cm^{-1} (Fig. 4).

According to the data from literature, the bands at 526 and 561 cm^{-1} correspond to vibrations of the Co_3^+O bonds in the octahedral environment, and Co_2^+O in the *s*-tetrahedral environment in the spinel crystal lattice. The band at 1115 cm^{-1} is associated with stretching vibrations of CO bonds of carbonate anions, formed due to the adsorption of CO_2 on the surface of Co_3O_4. This is consistent with the basic properties of cobalt(II,III) oxides formed during calcination of saccharides. In the case of Co_3O_4 isolated from a complex with

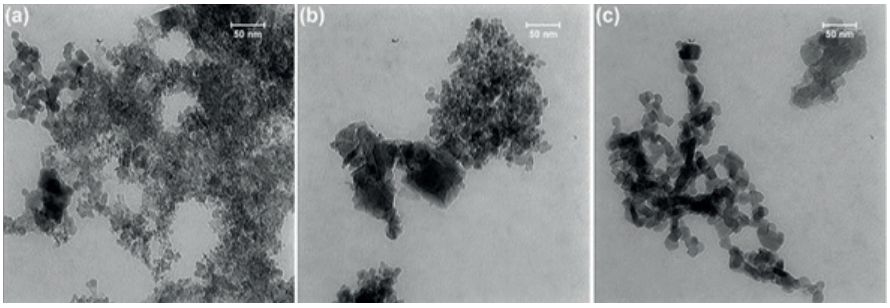


Fig. 3. Micrographs of oxide phases obtained by calcination of cobalt(II) complexes with sucrose (a), glycogen (b), and glucose (c).

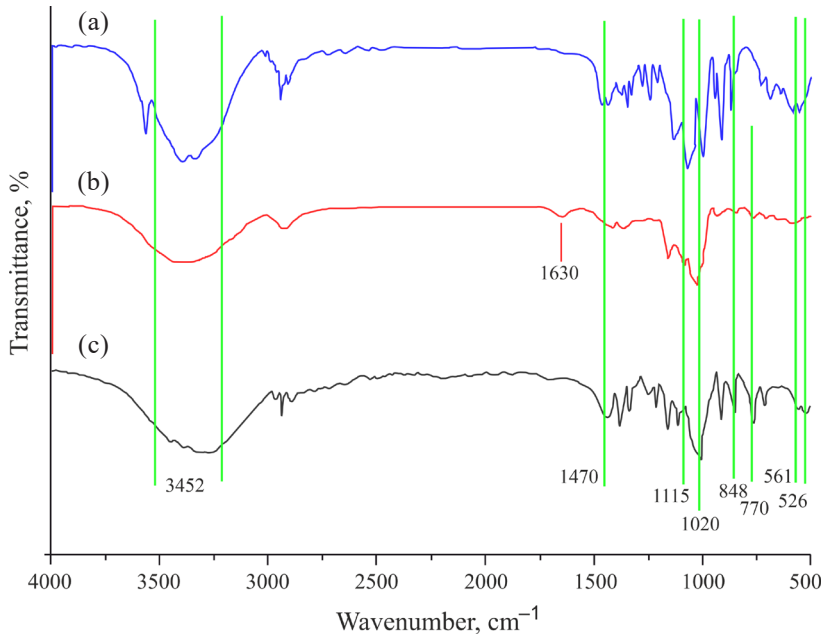


Fig. 4. IR spectra of oxide phases obtained by calcination of cobalt complexes of sucrose (a), glycogen (b), and glucose (c).

glycogen, an additional absorption band at 1630 cm^{-1} is observed in the IR spectrum which can be attributed to bending vibrations of water molecules adsorbed on the surface. In cobalt oxides isolated from solutions containing sucrose and glucose, the $\delta(H_2O)$ band is also present, but its intensity is much less. The broad band at 3400 cm^{-1} is associated with stretching vibrations of OH groups on the hydrated surface of Co_3O_4 nanoparticles. The absorption at 1470 cm^{-1} is probably due to the stretching vibrations of OCO_2. The observed band at 848 cm^{-1} can be attributed to bending vibrations of the Co–OH bond. Absorption at 770 cm^{-1} may correspond to δ(OCO), and the band at 1020 cm^{-1} corresponds to δ(C=O).

Low-temperature N_2 adsorption–desorption isotherms and the pore distribution curve of the samples are presented in Fig. 5. The surface activity of the isolated samples was studied by the BET method. The BDC method was used to determine the diameter, volume and distribution of pores. The adsorption–desorption isotherms for samples obtained from glucose and sucrose complexes correspond to type IV, indicating strong interaction between the adsorbent and the adsorbed sample (Fig. 5a and 5c). The isotherm for the sample isolated from the glycogen complex is of a different type and most likely indicates that this sample is almost completely mesoporous.

An important textural characteristic of the resulting material is the pore size distribution. Based on isotherms and average pore diameters, the porosity of nanosized particles is represented by mesopores (see Table). Type IV nanopores are confirmed by the type of adsorption–desorption isotherms and pronounced hysteresis associated with capillary condensation of nitrogen in mesopores.

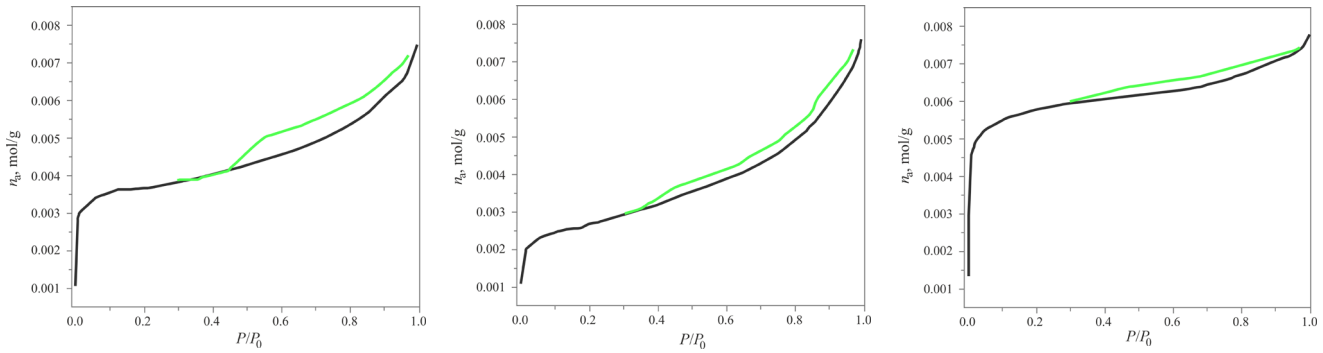


Fig. 5. Adsorption–desorption isotherms of N_2 by nanoparticles isolated from cobalt complexes of glucose (a), glycogen (b), and sucrose (c). n_a is the amount of adsorbed substance, mol·g^{-1}; P/P_0 is the relative pressure (ratio of system pressure to condensation pressure).

Table. Some characteristics of the surface of Co_3O_4 particles

Parameters	Glucose	Glycogen	Sucrose
BET analysis			
V_m, cm^3/g	71.75	49.39	73.47
$a_{s,BET}$, m^2/g	312.27	214.96	319.78
C	6366.00	1975.80	9011.80
V, cm^3/g	0.26	0.26	0.17
d, nm	3.30	4.84	2.17
BJH analysis			
V_m, cm^3/g	0.16	0.21	0.06
r_p, nm	1.64	1.64	1.21
a_s, m^2/g	79.64	119.74	41.65
Langmuir plot			
V_m, cm^3/g	65.71	45.54	69.61
a_s, m^2/g	286.00	198.20	302.98

Note: V_m is the specific pore volume, a_s is the specific pore surface area, C is the BET constant, V is the total pore volume, d is the average pore diameter, r_p is the average pore radius.

Based on the analysis of adsorption–desorption isotherms (Fig. 5), it is clear that monolayers are formed at relative pressures P/P_0 equal to 0.076, 0.05 and 0.04, and are completely formed in all samples. There is a known relationship between the shape of the hysteresis loop and the nature of the distribution of mesopores in the joint. The pores of nanoparticles obtained by thermolysis of glucose and glycogen complexes with H_4 type hysteresis are slit-like (glucose and glycogen) and conical (sucrose) [32].

BET analysis of the samples shows that the isolated Co_3O_4 nanoparticles have high surface activity with almost the same amount (Table). The large value of constant C (the ratio of the adsorption equilibrium constants in the first layer and the condensation constant) is probably associated with the nanosize of the resulting oxides, since for micro-sized samples its value usually lies in the range from 50 to 200 [33]. The significant difference in V_m values in the case of the samples obtained on the basis of glucose and sucrose when compared with that for cobalt oxide isolated on the basis of the glycogen complex can be explained by the different nature of the pores.

According to the BDH method, the pore radius of Co_3O_4 nanoparticles obtained from cobalt complexes with glucose and glycogen is the same and equal to 1.64 nm, while for nanoparticles isolated from a complex with sucrose, it is smaller and amounts to 1.21 nm (Fig. 6).

The surface activity of a monolayer of Co_3O_4 nanoparticles obtained using the Langmuir method is consistent with BET analysis; the order of surface activity in both methods is the same (Table). Thus, we can conclude that the new environmentally friendly synthesis method presented herein makes it possible to obtain nano-sized particles with high surface activity.

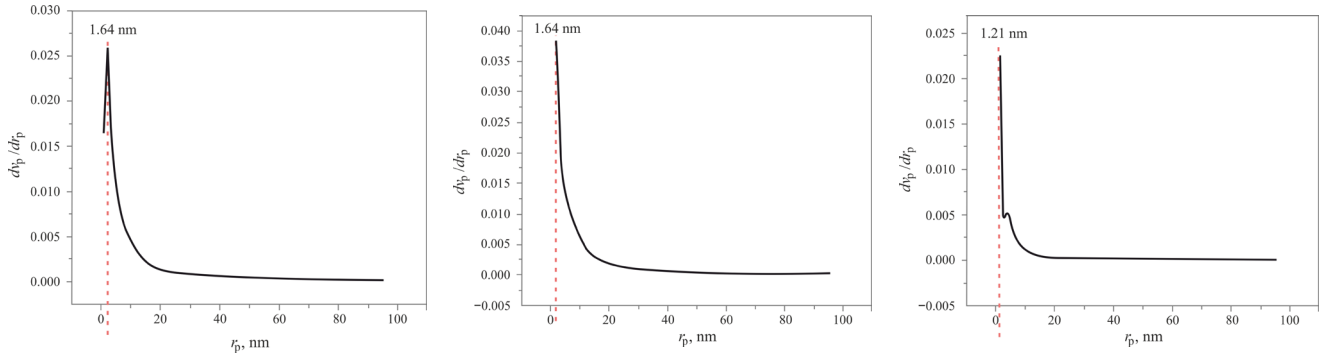
Studying the spectral characteristics of photocatalysts is one of the most important factors that determines their activity in a special region of the electromagnetic spectrum. In order to calculate the band gap of the obtained samples, electronic absorption spectra were recorded in the wavelength range from 200 to 800 nm (Fig. 7). All isolated products have optical density in a certain wavelength range: 340 nm, 500 nm, and between 800 and 850 nm, which is consistent with previously published data [34].

To find the best activating region, the Tauc method (2) was used to determine the band gap:

$$\alpha = \alpha_0(h\nu - E_g)n/h\nu, \quad (2)$$

where α is the absorption coefficient of the material, α_0 is the proportionality coefficient, $h\nu$ is the energy of the incident photon (h is the Planck's constant, ν is the frequency of the incident photon), E_g is the optical band gap, n is the refractive index. The band gap is obtained from a plot of $(\alpha h\nu)^2$ versus $h\nu$. The value of $h\nu$ at the point of intersection of the tangent and the x-axis is the band gap. Based on the result, band gap values of 1.53, 2.48, and 3.65 eV were obtained, illustrating the ability of Co_3O_4 nanoparticles to absorb in both the ultraviolet and visible regions of the spectrum.

Co_3O_4 nanoparticles isolated by the proposed synthesis method have high surface activity, exceeding that of nanoparticles obtained by other



(a) (b) (c)

Fig. 6. BJH analysis of Co_3O_4 nanoparticles isolated from cobalt complexes of glucose (a), glycogen (b), and sucrose (c); dv_m/dr_p is the derivative of the ratio of specific volume to average pore radius, r_p is the pore radius, nm.

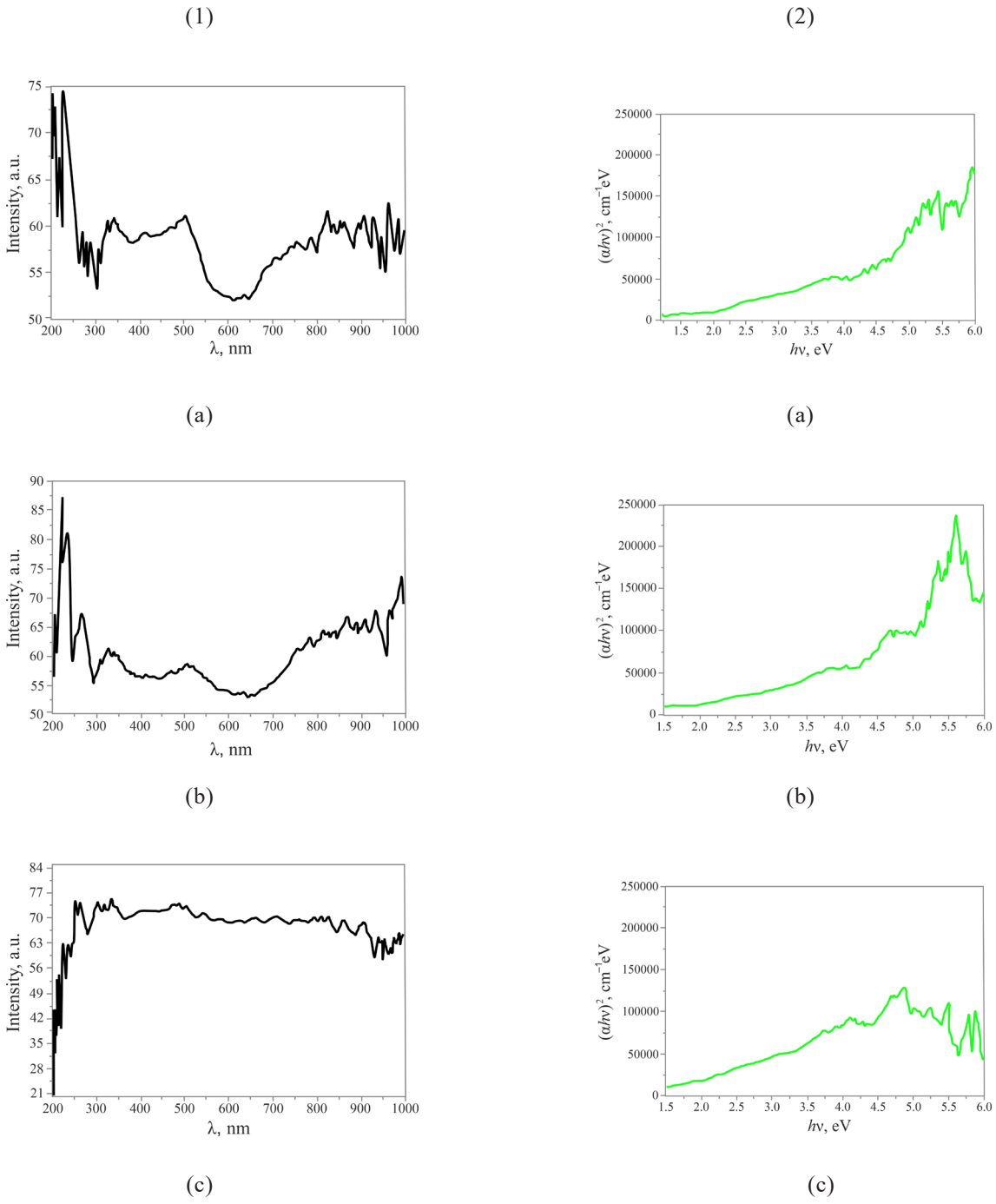


Fig. 7. Electronic absorption spectra (1) and band gap (2) of Co_3O_4 nanoparticles isolated from cobalt complexes of glucose (a), glycogen (b), and sucrose (c); $(\alpha h\nu)^2$ is the absorption coefficient squared, cm^{-1}·eV; $h\nu$ is the photon energy, eV.

methods. A possible reason is the combustion reaction of natural sugars upon ignition, leading to the formation of carbon and its possible binding with cobalt to form a carbide, the signals of which are observed in X-ray diffraction patterns. The BET constant (*C*) (see Table), exponentially related to the adsorption energy of the monolayer, is very high (>200). This also illustrates the presence of active carbon on the surface of the nanoparticles. It has been shown that a natural saccharide with a large amount of carbon in its molecular structure provides greater surface activity of the synthesized cobalt oxide nanoparticles.

CONCLUSIONS

A new green method has been developed for the synthesis of nanosized Co_3O_4 particles using natural saccharides and deionized water. It has been experimentally proven that natural saccharides, due to the polymer structure of their metal complexes and the ability to incorporate carbon on the surface of nanoparticles, can be used as matrices in the synthesis of metal oxide nanoparticles with high surface activity. In addition, natural saccharides, due to their environmental friendliness and low cost, are a good replacement for classical organic compounds used in previously developed methods for the synthesis of nanoparticles.

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Authors' contributions

Y. Absalan – planning and conducting research, research methodology, conducting research, analyzing research materials, writing the manuscript;

R. Alabada – conducting research, analyzing research materials, obtaining nanoparticles;

M.R. Razavi – conducting research, analyzing research materials, study of spectral characteristics;

M. Gholizadeh – conducting research, analyzing research materials, study of the surface of nanoparticles;

O.V. Avramenko – analyzing research materials, article editing, corresponding author;

I.N. Bychkova – conducting research, validation of research products;

O.V. Kovalchukova – formulation of the scientific concept, general management, analyzing research materials, author's supervision, reviewing and editing the article, scientific consulting.

The authors declare no conflicts of interest.

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