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**SYNTHESIS AND CHARACTERIZATION OF COBALT OXIDE NANOSTRUCTURES
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The newest achievement in the synthesis of cobalt oxide nanoparticles are considered. Cobalt oxide nanoparticles have attracted a great attention due to their uncommon properties and application in a supercapacitor, optoelectronic device, Li-ion battery gas sensor and electrochromic devices. Recently, nanostructured transition metal oxides with valuable properties have become a new class of materials for many technological fields. Cobalt oxide nanoparticles obtained from various precursors show different size distribution as well as different optical, electrical, magnetic, and electrochemical properties. A reduction in particle size to nanometer-scale leads to changes in properties compared to bulk ones due to quantum size effects. Depending on the application area, the choice of an appropriate synthesis method for nanoparticles with desirable properties is a crucial factor. This work aims to provide additional information on the synthesis methods and properties of cobalt oxide nanoparticles.

Keywords: cobalt oxide, crystallite size, supercapacitor.

doi

Introduction

Cobalt oxide nanoparticles (NP_s) have numerous uncommon physical and chemical properties due to their quantum size effect and large surface area, in comparison with bulk counterparts. Cobalt has two stable oxides such as cobalt(II) oxide (CoO), with a rock salt structure, and spinel cobalt (II, III) oxides (Co₃O₄), in which Co²⁺ ions occupy the tetrahedral 8a sites and Co³⁺ ions occupy the octahedral 16d sites. Co₃O₄ is a *p*-type antiferromagnetic oxide semiconductor with two band gaps and it is of great importance due to its optical, catalytic, and magnetic properties. The wide application areas of cobalt oxide nanostructures are known such as anode material in Li-ion rechargeable battery, catalyst, gas sensor, supercapacitor, electrochemical sensor, solar absorbing material, pH sensor, electrochromic devices, smart windows, photovoltaic devices, and magnetic materials [1–11]. Co₃O₄ with a variety of morphologies such as wires, cubes, fibers, tubes, sheets, flowers, and hollow microspheres [12–18] have been reported in the literature. It is possible to change the properties of the particles by control size and morphology; therefore, minimizing the total surface energy has always been the focus of the researchers.

Synthesis methods of cobalt oxide nanoparticles

Owing to its unique physical and chemical properties and wide applications in many technological fields, cobalt oxide has attracted much attention. The most widely employed, effective synthetic techniques of cobalt oxide nanostructures are summarized, and their advantages and disadvantages are highlighted by us.

Precipitation chemical method is one of the most used methods for the synthesis of cobalt oxide nanoparticles. It consists of a two-step process: at the first stage, precipitation of different cobalt salts (sulfate, nitrate, acetate, chloride) occurs with various precipitating agents. Cobalt hydroxide [Co(OH)₂], cobalt oxyhydroxide [CoOOH], cobalt carbonate (CoCO₃) or cobalt oxalate (CoC₂O₄) forms at this stage, cobalt oxide being obtained as a result of decomposition of these intermediate products at above 300⁰C temperature at the next stage. This method is simple, inexpensive; does not require a long reaction time and complicated equipment. Wadekar et al. [19] synthesized the amorphous structure of Co₃O₄ nanoparticles with an average crystallite size of 25.62 nm utilizing cobalt nitrate and sodium hydroxide (NaOH) as precur-

sors. Viljoen and co-workers [20] learned on the influence of anion type in cobalt salt on the size and shape of synthesized Co_3O_4 nanoparticles. They demonstrated that when cobalt nitrate was used as precursor spherical nanoparticles with a size of 6.3 nm were obtained while using cobalt acetate cubic nanoparticles with a size of 5.1 nm were obtained. pH is also a key factor in preparing cobalt oxide nanoparticles. Allaedini and Muhammad [21] obtained Co_3O_4 nanoparticles by this method in various pH conditions. Uniform and smaller nanoparticles were observed at a low pH value (pH=8–9) than higher pH values (pH=10–11). This is explained to the fact that the growth rate of particles is faster than the nucleation rate at high pH values. Sharifi et al. synthesized Co_3O_4 nanoparticles using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and potassium hydroxide (KOH) in the presence of polyvinylpyrrolidone (PVP) subsequent calcination at different high temperatures [22], which causes the aggregation of smaller particles into bigger ones and the average diameter increased from 2 nm to 80 nm. Xu et al [23] obtained porous Co_3O_4 with different morphologies using cobalt nitrate, cobalt acetate as cobalt source, and NaOH and ammonia as precipitating agents followed by calcination of formed $\text{Co}(\text{OH})_2$. They investigated gas-sensing action to acetone and ethanol and compared them with each other. As a result of numerous research works, it has been determined that the obtained nanoparticles show mainly spherical morphology, which is difficult to control the morphology with this method.

Sol-gel method is one of the simplest and cost-effective methods for the synthesis of metal oxide nanostructures. Co_3O_4 nanoparticles with an average crystallite size of 45 nm by Luisetto et al. [24] using cobalt nitrate and ethyl acetate followed by thermal treatment at 450°C for 2h. Ethanol was used as a solvent. Abdelhak and colleagues [25] reported on the synthesis of Co_3O_4 thin film by the method of sol-gel dip-coating on glass substrates. Sinko et al. [26] described the synthesis of cobalt oxide nanoparticles by this method using various solvents (ethanol and 1-propanol) and surfactants [citric acid, ethyl acetate, and polydimethylsiloxane (PDMS)]. The effect of solvents and surfactants

on the particle size and their size distribution were investigated. The smallest size (about 85 nm) with narrow polydispersity (70–100 nm) were observed in the presence of ethyl acetate and 1-propanol. Using CTAB as surfactant Co_3O_4 nanorods with a particle size of 50 nm (determined by Scanning electron microscopy) were successfully synthesized by Shadrokh et al. [27]. Devi et al. [28] synthesized spinel Co_3O_4 nanoparticles by this method utilizing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, urea, CTAB, and reported to a capacity of 620 mA h g^{-1} . Cobalt nitrate was used in most experiments related to the synthesis of Co_3O_4 nanoparticles by the sol-gel route; the use of cobalt acetate is metrarely because due to low the solubility of cobalt chloride and cobalt sulfate in alcohol solvents.

Hydrothermal/solvothermal method is widely used for the synthesis of cobalt oxide nanomaterials of specific sizes and shapes. Wang et al. employed a this method to synthesize nanoporous Co_3O_4 nanorods, which demonstrated a high capacitance of 280 F/g [29]. Hashemi Amiri et al. [30] described the synthesis of $\beta\text{-Co}(\text{OH})_2$ particles by this method with subsequent calcination at three different temperatures such as 300°C , 600°C , and 900°C to obtain Co_3O_4 . The specific surface area of nanoparticles decreased from $134 \text{ m}^2/\text{g}$ to $13 \text{ m}^2/\text{g}$ and particle size increased with rising calcination temperature. For comparison, they obtained Co_3O_4 nanoparticles in the presence of H_2O_2 as an oxidizing agent with different amounts without the need for further heating. Nassar reported the synthesis of cubic Co_3O_4 nanoparticles with an average crystallite size of 25 nm by thermal decomposition of cobalt carbonate at 300°C for 2 h with high yield and high purity [31]. Nugroho et al. [32] proposed supercritical hydrothermal synthesis and investigated the effect of the concentration of KOH acting as a reducing agent on the structure and morphology. Significant changes in morphology and particle size were observed, so that morphology of cobalt oxide changed from well faceted to irregularly shaped particles and specific surface area increases from $6.7 \text{ m}^2/\text{g}$ to $26.5 \text{ m}^2/\text{g}$ upon the addition of KOH. Elhag et al. [33] reported

the synthesis of cotton-like Co_3O_4 nanostructures for sensing cholesterol using sodium dodecyl sulfate (SDS) as a template. The use of template had a significant impact on morphology, when not using SDS wire-like structure and the larger size was observed, but using SDS synthesized nanostructures possess enhanced properties. Finger-like Co_3O_4 nanorods were prepared by this eco-friendly method in the presence of cobalt acetate tetrahydrate ($\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$), urea, and CTAB at 100°C for 24 h followed by calcination of the final product at 400°C for 2h [34]. This nanostructure was considered a potential electrode for a supercapacitor application and exhibits a specific capacitance of 265 F/g at 2 mV/s. Another astonishing case is the successful synthesis of Co_3O_4 nanocrystals by a solvothermal reaction in an alcohol-water solvent at 160°C from common Co_2O_3 powder as a precursor for the first time [35]. It was concluded that reaction time, type, and concentration of solvent affect the structure and nanoparticle size. When the reaction time extended from 6 to 24 h nanoparticle size increased from 30 nm to 38 nm, crystallinity also increases. When using pure ethanol, the nanoparticles composed of Co_3O_4 and CoO with a smaller size (about 25 nm) were observed due to the reducing ability of alcohol. Nassar et al. [36] used Co(II)-1,3-*bis*(Salicylaldimine)urea complexes as a new precursor prepared by the solvothermal reaction of urea, salicylaldehyde, and cobalt chloride at 120°C for 2h. The porous mixed-phase CoO/ Co_3O_4 nanocomposites with an average diameter of 5 ± 2 nm have been prepared using ethanol as solvent at 160°C for 8h without further calcination and show a high capacitance of 451 F/g at a current density of 1 Ag^{-1} as an electrode for supercapacitor application [37].

Sonochemical method is a promising route for the preparation of various metal oxide nanostructures. It is based on the acoustic cavitation phenomenon such, as nucleation, growth, and collapse of a large number of microbubbles in a liquid medium, that can cause causes local hot spots with a temperature of around 5000°C under pressures of 500 atm, heating and cooling

rates of more than 10^{10} K/s. These extreme conditions lead to an influence on the structure, morphology, and size of synthesizing materials. The main advantage of this method is that it is possible to control size by altering the sonication time, ultrasonic power, current density, and concentration of precursors. Al-Qirby et al. [38] reported the synthesis of Co_3O_4 nanoparticles by an ultrasound-assisted method in the presence of ionic liquid 1-Ethyl-3-methylimidazolium tetrafluoroborate [EMIM] $[\text{BF}_4]$ as a reaction medium for the first time. They also investigated sonication time and different molar ratios of the ionic liquid affect the nanoparticle size, chemical, and physical properties. The formation mechanism of oxide was proposed. Askarinejad and Morsali proposed the synthesis of Co_3O_4 nanocrystals with different sizes and morphologies by a one-step sonochemical method [39]. Cubic shape Co_3O_4 nanocrystals with an average size of 19 nm were observed using 0.1 M $\text{Co}(\text{CH}_3\text{COO})_2$ and 0.2 M tetramethylammonium hydroxide (TMAH) as precursors at 1h sonication time and 15–18 W ultrasound power. Irregular shapes between spherical and facet with poor crystallinity were observed from transmission electron microscopy (TEM) measurements when lower ultrasound power (6–9 W) was applied and using cobalt salt and NaOH with the same concentrations (0.1 M). Kamar et al. [40] obtained Co_3O_4 /graphene nanocomposites for application as a counter electrode in dye-sensitized solar cells.

Chemical bath deposition method (CBD) is one of the simplest and cheapest techniques to prepare transition metal oxides. Xia and co-workers deposited a highly porous cobalt oxide thin film on indium tin oxide (ITO) substrate at room temperature using cobalt sulfate, potassium persulfate, and ammonia. The porous structure and large surface area of thin films enhanced electrochromic performance since it can facilitate the contact between the electrolyte and the oxide surface [41]. Using the same synthesis method Li and colleagues employed Co_3O_4 thin film for an electrochemical capacitor which shows a maximum specific capacitance of 227 F/g at the specific current of

0.2 Ag⁻¹ [42]. Lokhande et al [43] reported on the synthesis of cobalt oxide on glass and copper substrates using cobalt chloride and ammonia, in which transformation of oxyhydroxide to oxide occurs at 350°C. It has been concluded that the nature of the substrate has significantly affected the structural properties, crystallinity and morphology of films. Interconnected flack morphology was observed on the glass substrate, while nanoworm morphology was observed on the copper substrate. In another work, they used cobalt oxide thin film prepared on copper substrate by this method for supercapacitor application, which exhibited the highest specific capacitance of 118 F/g [44]. In another work, they also employed these thin films for the detection of acetaminophen [45]. The electrode modified with Co₃O₄ obtained using cobalt chloride demonstrated the high electrocatalytic properties. Ezema et al. deposited Co₃O₄ thin films on glass and FTO substrates at 70°C bath temperature changing the pH between 10 and 12 [46]. It was observed that a sample of pH 12 showed a maximum specific capacitance of 1576 F/g, an energy density of 245.98 (Wkh/kg), and a power density of 2.08 (W/kg).

Properties of cobalt oxide nanoparticles.

Cobalt oxide nanoparticles have tunable physical and chemical properties with enhanced performance over their bulk counterparts. We will selectively summarize the main and general properties of cobalt oxide nanostructures.

Optical and electrical properties. Martínez-Gil et al. [47] studied the influence of annealing temperature on the Co₃O₄ thin films synthesized using cobalt sulfate and triethanolamine. The amorphous phase was observed in all the samples and annealing temperature did not affect the morphology. Optical and electrical properties vary with increasing annealing temperature. The resistivity of the films changed between $4.29 \cdot 10^3$ and $1.32 \cdot 10^7$ Ω·cm. These results and band diagram behavior of thin films suggest potential application in supercapacitors as electrode and optoelectronic devices. Valanarasu et al. [48] deposited Co₃O₄ thin films on a glass substrate at various pH values. pH influences the thickness, optical and electri-

cal properties of thin films. The film growth rate and thickness increase, the optical band gap decreases from 2.31 to 2.16 eV with increasing pH value. To improve optical and electrical properties thin films were doped with different transition metals (Ni, Mn, Cu) and significant changes were observed [49]. The band gap values decreased compared to undoped Co₃O₄. Patil et al. [50] investigated the influence of temperature on the physical properties of Co₃O₄ thin film deposited on a glass substrate using a sol-gel spin technique. The crystallinity and mean crystallite size increases from 53 to 69 nm; the optical band gap and film thickness decrease with increasing annealing temperature from 400 to 700°C. Khansari et al. [51] described the synthesis of Co₃O₄ nanohexagonales (30 nm) thermal treatment of Co(salen) precursor at 500°C for 5h. Khalaji prepared Co₃O₄ nanoparticles with one direct band gap of 2.3 eV thermal decomposition of mononuclear acyclic cobalt(II) complex [CoL](NO₃)₂ (L = 3,3'-dimethoxy-2,2'-(propane-1,3-diylidioxy)dibenzaldehyde) at 450°C for 3h in air [52]. Co₃O₄ nanoparticles with two band gaps (2.20 and 3.55 eV) were obtained from carbonatotetra(amine)cobalt(III) nitrate complex, [Co(NH₃)₄CO₃](NO₃)·H₂O at low-temperature decomposition (175°C) [53]. Nanoporous Co₃O₄ hierarchical nanoflowers with band gaps of 1.49 eV and 1.98 eV have been prepared by the hydrothermal method using Co(NO₃)₂ and urea [CO(NH₂)₂] [54]. Co₃O₄ nanocubes with band gaps of 1.58 eV and 3.40 eV were prepared by a one-step hydrothermal process in the presence of sodium dodecylbenzene sulfonate (SDBS) at 160°C reaction temperature for 36 h [55]. Recently, Turan et al. investigated the change in Co₃O₄ optical and electrical properties by varying the bath temperature and deposition time [56]. They prepared films on microscope glass substrate using cobalt(II)chloride as a source of Co²⁺ and aqueous ammonia solution (25 mass.%) followed by annealing of CoO(OH) at 300°C for 1h. When the bath temperature was increased from 65 to 95°C, the electrical conductivity increased from about $1.37 \cdot 10^{-6}$ to $2.40 \cdot 10^{-2}$ (Ω·Om)⁻¹. This fact was explained by enhancement in crystallinity of films. The carri-

er concentration increased with increasing bath temperature from $8.57 \cdot 10^{21}$ to $1.50 \cdot 10^{26} \text{ (m)}^{-3}$ and film thickness decreased with increasing deposition time at both temperatures. Two absorption bands (around at 400 and at 700 nm) were observed for cobalt oxide thin films deposited on glass and silicon substrates using the reactive radio-frequency sputtering method (Figure 1). The optical band gap and electrical resistivity of films increased with increasing oxygen pressure in the sputtering atmosphere [57]. The measured band gap is 1.46 eV and 1.87 eV for thin films synthesized at 10% oxygen pressure whereas it is 1.50 eV and 2.17 eV for films synthesized at 50% oxygen pressure. The optical band gap is 4.10 eV for the Co_3O_4 nanoparticles produced by the hydrothermal method using thioglycolic acid as a fuel. The synthesized nanoparticles were applied for dye-sensitized solar cells application. The shifting of absorption edge to lower wavelength and increasing of the band gap is due to the quantum size confinement [58]. Alla et al. [59] studied the improvement in electric properties of zirconium substituted Co_3O_4 nanoparticles produced by the single-step microwave refluxing method. Composition and frequency-dependent electric properties have been measured in the frequency range of 10 kHz to 20 MHz. It was noticed that Co_3O_4 nanoparticles with higher zirconium concentration ($x \geq 0.1$) showed better conductivities compared to lower ones ($x \leq 0.05$). At higher frequencies Co^{2+} ion converts into Co^{3+} ion

($\text{Co}^{2+} - 1e^- \rightarrow \text{Co}^{3+}$) by losing an electron. It made possible that the net charge on both sites is positive rather than neutral and causes high conductivity values of high concentration zirconium substituted samples. It was concluded that surface morphology, size, and shape of nanoparticles influences the electric properties. In their other research work, they produced cobalt oxide nanoparticles doping with zinc using the same method. An increase in conductivity at high frequencies was also observed for these samples. The low conducting behavior and the lowest dielectric constant for samples with Zn concentration $x=0.05$ and 0.5 are attributed to their narrow grain size distribution (Figure 2)[60]. The relative permittivity of Co_3O_4 nanolaminates grown by atomic layer deposition was found to be 30 at the applied electric field frequency of 1000 Hz [61]. Sayed and Gamal investigated the electrical and dielectric properties of sodium carboxymethyl cellulose (Na-CMC)/polyvinyl alcohol (PVA) composite films doped with Co_3O_4 at different concentrations. It has been determined that dielectric permittivity and dielectric loss increased with increasing Co_3O_4 content. This fact was explained with increasing in charge carrier density and micro-Brownian motion of long-chain segments in the amorphous regions of CMC/PVA, respectively. The enhancement in electrical and dielectric properties with Co_3O_4 doping makes possible the application of this nanocomposite film in several industrial and electronic devices [62].

Fig. 1. Absorption spectra of Co_3O_4 thin films at different oxygen pressure [57].

Fig. 2. a) Change in the AC conductivity as a function of the frequency of the electric field for $\text{Zn}_x\text{Co}_{3-x}\text{O}_4$ ($x=0, 0.01, 0.05, 0.1, 0.3$ and 0.5) samples; b) Change in the permittivity with the frequency of the electric field for $\text{Zn}_x\text{Co}_{3-x}\text{O}_4$ ($x=0, 0.01, 0.05, 0.1, 0.3$ and 0.5) samples [60].

Catalytic, Photocatalytic, Electrocatalytic properties

Co_3O_4 nanorods were prepared in the presence of cobalt chloride and urea and applied as a catalyst for the hydrolysis of sodium borohydride by Durano et al. [63]. Co_3O_4 nanoaggregates were synthesized using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and sodium carbonate as precursors, under decomposition of CoCO_3 at 500°C for 3h and proved to be an efficient catalyst for thermal decomposition of ammonium perchlorate [64]. Pudukudy et al. [65] described the synthesis of mesoporous spinel Co_3O_4 nanosheets with the mean crystallite size using Pluronic P123 triblock copolymer as a stabilizing agent and it has been applied as photocatalyst for the degradation of methylene blue under UV light irradiation. Farhadi et al. [66] reported the synthesis of sphere-like Co_3O_4 nanoparticles with an average size of 17.5 nm using pentamminecobalt(III) complex $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_3$ at relatively low temperature (175°C). The synthesized nanoparticles have been proved an efficient photocatalyst for the degradation of methylene blue. Kang and Zhou obtained Co_3O_4 nanocubes as a catalyst for the thermal decomposition of ammonium perchlorate (AP) [67]. They investigated the effect of a mole ratio of surfactant to Co^{2+} , reaction temperature, and time on the growth mechanism of nanoparticles in detail. The molar ratio of polyvinylpyrrolidone (PVP) to Co^{2+} equal to 0.002 and 120°C reaction temperature for 27 h

was chosen as optimal reaction parameters. Ren et al. [68] described the synthesis of Co_3O_4 nanoflowers, nanoplates, nanoneedles utilizing various cobalt salts, precipitating agents, and investigated catalytic activity toward toluene oxidation. It has been determined that 3D- Co_3O_4 nanoflower exhibited better stability as catalyst compared to the other two nanostructures, achieving T_{90} at 238°C at a space velocity ($\text{WHSV} = 48,000 \text{ mL/g}\cdot\text{h}$). Kung et al. presented a chemical bath deposition method in which Co_3O_4 thin films were deposited onto conducting fluorine-doped tin oxide (FTO) substrate in the presence of different anions for hydrogen peroxide (H_2O_2) in sensor application [69]. Thin films with various morphology such as straight acicular nanorods, bending acicular nanorods, nanosheets, and net-shaped nanosheets were obtained using different cobalt sources. They found that the best electrocatalytic activity toward H_2O_2 was observed from electrode synthesized in the presence of cobalt chloride. Behling and co-workers used Co_3O_4 nanoparticles synthesized by the co-precipitation route as a catalyst for sonochemical oxidation of vanillyl alcohol to vanillin. They also discussed the influence of reaction parameters, catalyst loading, and hydrogen peroxide concentration on the yield and selectivity of vanillin product. It has been determined that vanillin was not formed in the absence of Co_3O_4 catalyst and vanillin yields decreased with an increasing amount of

catalyst due to the overoxidation. When used 2 mass.% Co_3O_4 , maximum yields of vanillin were observed [70]. Dong et al. explained that the catalytic property of the as-prepared Co_3O_4 nanofibers towards glucose oxidation in alkaline solution is related to CoOOH and CoO_2 , which reversible

reactions are described in research work [71].

Liu et al. [72] employed a one-pot hydrothermal method for the synthesis of flower-like Co_3O_4 /graphitic carbon nitride ($\text{Co}_3\text{O}_4/\text{g-C}_3\text{N}_4$) nanocomposite and its electrochemical behavior was investigated using cyclic voltammetry.

Fig. 3. (a) CVs of the Nafion/ $\text{NH-Co}_3\text{O}_4$ NFs/GCE in 0.1 M NaOH solution and in 0.1 M pH 7.4 phosphate buffer solution at the scan rate of 100 mV/s; (b) CVs of the Nafion/ $\text{NH-Co}_3\text{O}_4$ NFs/GCE in 0.1 M NaOH solution at various scan rates of 20, 40, 60, 80, 100, 150, and 200 mV/s [71].

The electrochemical performance data of the Co_3O_4 nanostructures.

Methods	Typical samples	Size, nm	Electrochemical performance	Ref.
Precipitation method	Co_3O_4 nanoparticle	20–30	423 $\text{mA}\cdot\text{h/g}$ at 0.1 C after 40 cycles	[73]
Electrospinning method	Porous Co_3O_4 nanofibers	100–150	1000 $\text{mA}\cdot\text{h/g}$ at a current density of 100 $\text{mA}\cdot\text{g}^{-1}$ after 60 cycles	[74]
Solvothermal method	Co_3O_4 nanospheres	30	1262 $\text{mA}\cdot\text{h/g}$ at 0.1 C after 100 cycles	[75]
An impregnation-reduction method followed by air-oxidation	hollow structured Co_3O_4 nanoparticles	50–100	880 $\text{mA}\cdot\text{h/g}$ at 50 mA/g after 50 cycles	[76]
Hydrothermal method	Polyhedral Co_3O_4 nanoparticle	< 5	1017 $\text{mA}\cdot\text{h/g}$ at 100 mA/g after 100 cycles	[77]
Hydrothermal template method	Mesoporous perforated Co_3O_4 nanoparticles	100 ± 10	865.2 $\text{mA}\cdot\text{h/g}$ after 100 cycles	[78]
		150 ± 20	933.8 $\text{mA}\cdot\text{h/g}$ after 100 cycles	
		400 ± 50	1115.1 $\text{mA}\cdot\text{h/g}$ after 100 cycles	
Solvothermal method	Co_3O_4 nanoparticles/ nanographitic flakes	35	780 $\text{mA}\cdot\text{h/g}$ at 1000 mA/g after 50 cycles	[79]
Electrospinning and hydrothermal treatments	Porous Co_3O_4 nanofibers	< 100	900 $\text{mA}\cdot\text{h/g}$ after 50 cycles at 1000 mA/g , 600 mAh/g after 50 cycles at 5000 mA/g	[80]
Hydrothermal treatment	mesoporous Co_3O_4 nanorods	100–150	1343.8 $\text{mA}\cdot\text{h/g}$ at 500 $\text{mA}\cdot\text{g}^{-1}$ after 200 cycles	[81]
Surfactant-assisted self-assembly method	(2D) Co_3O_4 nanosheets	1.90	1868.6 $\text{mA}\cdot\text{h/g}$ at 100 $\text{mA}\cdot\text{g}^{-1}$ after 30 cycles	[82]
Wet chemical method and lyophilization	Carbon nano horn- Co_3O_4 nanoparticles	10–15	820 $\text{mA}\cdot\text{h/g}$ at 1 Ag^{-1} after 500 cycles	[83]
Template-assisted method	Co_3O_4 nanoparticles	15–30	921.2 $\text{mA}\cdot\text{h/g}$ at 0.05 $\text{A}\cdot\text{g}^{-1}$ after 60 cycles	[84]
Hydrothermal method	Co_3O_4 nanocubes	~210–230	873.5 $\text{mA}\cdot\text{h/g}$ at 0.1 Ag^{-1} after 50 cycles	[85]
Cotton template route	Carbon coated porous Co_3O_4 nanosheets	–	1735.4 $\text{mA}\cdot\text{h/g}$ at a current density of 200 mA/g	[86]

It was observed that Co_3O_4 containing a 2% mass fraction of g- C_3N_4 nanocomposite modified glassy carbon electrode shows excellent electrochemical performance towards the oxidation of hydrazine. Fu and co-workers [87] reported the synthesis of Co_3O_4 nanostructures with different morphology by adjusting the urea concentration using the microwave-hydrothermal method. They investigated the influence of morphology on the catalytic activity for oxygen evolution reaction (OER). Among three different morphologies, Co_3O_4 nanosheets exhibited superior electrochemical performance due to their high surface areas and porous structure. Wang et al. [88] enhanced the electrocatalytic activity of 2D-micro-assembly Co_3O_4 nanosheets for Li-O_2 batteries by tuning the concentration of oxygen vacancies and Co^{3+} ions and the discharge capacity was over 2000 mA h g^{-1} for 25 cycles at a current density of 100 mA g^{-1} for Co_3O_4 synthesized at 300°C hydrothermal temperature. Dhas and co-workers [89] evaluated degradation efficiencies of Rhodamine B, Methylene blue, and Methyl orange under visible light irradiation as 81, 80, and 57%, respectively, in the presence of Co_3O_4 film catalyst. Philippot and collaborators [90] prepared Co_3O_4 nanoparticles by oxidation of Co nanoparticles in the air for 6 days at room temperature and used for water oxidation. Co_3O_4 NPs covalent grafted with photosensitive polypyridyl-based Ru^{II} complexes exhibited higher catalytic performance than simple mixtures of non-grafted photosensitizers and Co_3O_4 NPs.

Magnetic properties strongly depend on nanoparticle size, structure, and morphology. The magnetization of Co_3O_4 NPs synthesized by the hydrothermal method increased from 0.09 to 0.34 emu/g with the increasing amount of H_2O_2 from 5 to 45 ml due to the existence of oxygen in the spinel structure of oxide [30]. A.K.M. Atique Ullah et al. [91] implemented comparative magnetic measurements of Co_3O_4 NPs synthesized by co-precipitation method using different concentrations of NaOH (a strong base) and NH_4OH (a weak base). They reported that the value of saturation magnetization was higher for high concentration NaOH

synthesized Co_3O_4 nanoparticles than lower one, while opposite behavior was observed for NH_4OH precipitant. N.K.Yetim [92] reported that the magnetic properties of Co_3O_4 nanostructures manufactured by the hydrothermal method using different precipitating agents. The results revealed that the hysteresis curve was observed only for nanosheets-like Co_3O_4 structures synthesized using urea. This nanostructure exhibited low ferromagnetic property, while poppy flower-like, clover field-like, and nanospheres-like Co_3O_4 structures synthesized using polyvinylpyrrolidone (PVP), ethylenediamine ($\text{C}_2\text{H}_4(\text{NH}_2)_2$), and NaOH, respectively, showed antiferromagnetic behavior. It was explained by the fact that small-sized nanoparticles have small magnetic domains and this case results in low magnetic resistance. In another study [93], $\text{Co/Co}_3\text{O}_4$ nanowires were prepared by thermal annealing in the temperature range $200\text{--}600^\circ\text{C}$ of electrochemical deposited Co. The results showed that the nanostructures are completely oxidized with increasing temperature, a transition from the ferromagnetic to the paramagnetic behavior, a sharp increase in coercivity (two times), and a decrease in squareness values M_r/M_s (more than 5 times) are observed. C. Ramamoorthy et al. [94] successfully synthesized Co_3O_4 with a particle size of $\sim 25\text{--}30 \text{ nm}$ through a wet chemical route using hexadecyl-trimethyl-ammonium-bromide as a cationic surfactant. The magnetic properties characterization at room temperature revealed that this sample has ferromagnetic behavior, saturation magnetization (M_s) and coercivity is found to be 0.09 emu/g and 197 Oe , respectively. These results offered suitable features for applications in magnetic storage devices. G. Anandhababu and G. Ravi [95] investigated the influence of various surfactants, microwave reaction powers, and dopants on magnetic properties of Co_3O_4 nanostructures with hexagonal morphology synthesized by a simple microwave route. Using different surfactants such as CTAB, citric acid, and hexamine affects the nanoparticle size. The smaller size is observed when utilizing CTAB and exhibits a higher magnetization ($0.0260 \text{ emu/g}^{-1}$) than hexamine added Co_3O_4 . The ad-

dition of hexamine leads to a bigger size of particles with higher agglomeration forming a bridge between two cobalt ions and lower magnetization values were observed. The magnetization value increased from 0.010 emu/g^{-1} to $0.0225 \text{ emu/g}^{-1}$ with increasing from 300 W to 650 W microwave power due to better structure and aligned morphology but decreased to $0.0160 \text{ emu/g}^{-1}$ with a further increment of microwave power up to 900 W. In their work, Ni (similar ionic radius) and Ce (large ionic radius) were selected as dopants for Co_3O_4 . They reported that Ni-doped Co_3O_4 nanostructures showed ferromagnetic behavior due to the double exchange interaction between dopant ion and the structural defects, while Ce doped nanostructures had paramagnetic nature. Yin et al. [96] compared the magnetic properties of graphene- Co_3O_4 (G- Co_3O_4) nanocomposites synthesized by hydrothermal technique with the pure Co_3O_4 nanoparticles. They found that a small magnetic hysteresis loop was observed for pure Co_3O_4 nanoparticles at 5K with a coercivity of 300 Oe and a remanence of 0.01 emu/g , whereas, no loop appeared in G- Co_3O_4 nanocomposites. Meanwhile, graphene- Co_3O_4 nanocomposites have higher magnetization and the magnetizations increase which decreasing temperature for two samples (Figure 4).

It is reported that the M_s values varied from 0.11 to $0.06 \text{ Am}^2/\text{kg}$ with different concentrations of Zr [59]. The weak ferromagnetic behavior was observed for Zn-substituted Co_3O_4

nanoparticles due to uncompensated surface spins or finite size effect and the M_s values increased compared to unsubstituted samples [60].

Summary and perspective. There are several approaches for synthesizing cobalt oxide nanoparticles, which have been refined in recently published researches. The most widely employed techniques for the synthesis of cobalt oxide nanostructures are summarized. Among them the precipitation method is very often used to obtain Co_3O_4 nanostructures because it is a facile and cheap approach. Recent advances have proved that cobalt oxide nanostructures are great potential materials for energy conversion and storage utilization because of their unusual physical and chemical properties. Controlling cobalt oxide nanostructures with an appropriate crystal size is important. The main reaction parameters influencing the size, structure, and morphology of nanoparticles there are also described. Morphology is one of the crucial factors along with size control which affects the properties of nanostructures. For instance, surface area, the number of reaction sites, the diffusion length of ions and electrons and the volume expansion from the insertion/extraction of Li ions also depend on the morphology at the material using in a Li-ion battery. Therefore development the new synthesis methods to obtain nanoparticles with desirable properties is required because the choice of an appropriate synthesis method also affects the properties of the obtained material.

Fig. 4. Temperature dependence of the ZFC and FC magnetization curves in an applied field of 500 Oe for G- Co_3O_4 , Co_3O_4 , and Graphene, respectively [96].

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KOBALT OKSİD NANOQURULUŞLARININ SİNTEZİ VƏ XARAKTERİSTİKASI QISA İCMAL MƏQALƏ

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Son zamanlarda əla xüsusiyyətlərə malik nanoölçülü keçid metal oksidləri bir sıra texnoloji sahələr üçün yeni bir material sinifinə çevrilmişdir. Son tərəqqi göstərir ki, keçid metalların oksidləri arasında kobalt oksid nanohissəcikləri qeyri-adi xüsusiyyətlərinə və optoelektron qurğuda, yüksək tutumlu kondensatorlarda, Li-ion batareyada, qaz sensorlarda və elektroxrom cihazlarında perspektivli tətbiqinə görə geniş diqqət toplamışdır. Bu icmal məqalə kobalt oksid nanohissəciklərinin sintezi ilə bağlı son yenilikləri əhatə edir. Bu günə qədər kobalt oksid nanohissəciklərinin müxtəlif sintez üsulları mövcuddur. Müxtəlif prekursorlardan alınan kobalt oksid nanohissəcikləri fərqli ölçü paylanması, eyni zamanda fərqli optik, elektrik, maqnit və elektrokimyəvi xüsusiyyətləri göstərir. Həqiqətən hissəciyin ölçüsünün nanometr ölçüyə qədər kiçilməsi kvant ölçü effekti səbəbindən həcmli nümunələrlə müqayisədə xassələrin dəyişməsinə gətirib çıxarır. Tətbiq sahəsindən asılı olaraq arzuolunan xüsusiyyətlərə malik nanohissəciklər üçün uyğun sintez metodunun seçimi vacib amildir. Bu icmal məqalənin məqsədi kobalt oksid nanohissəciklərinin sintez üsulları haqqında geniş məlumat verməkdir.

Açar sözlər: kobalt oksid, kristal ölçüsü, yüksək tutumlu kondensator.

СИНТЕЗ И ХАРАКТЕРИСТИКА НАНОСТРУКТУР ОКСИДА КОБАЛЬТА КРАТКИЙ ОБЗОР

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В последнее время наноструктурированные оксиды переходных металлов с ценными свойствами стали новым классом материалов для ряда технологических областей. Наночастицы оксида кобальта привлекли большое внимание из-за их необычных свойств и перспективных применений в оптоэлектронных устройствах, суперконденсаторах, литий-ионных батареях, газовых сенсорах и электрохромных устройствах. Рассмотрены последние достижения в области синтеза наночастиц оксида кобальта. сегодняшний день доступны различные методы синтеза наночастиц оксида кобальта. Наночастицы оксида кобальта, полученные из различных предшественников, показывают различное распределение по размерам, а также различные оптические, электрические, магнитные и электрохимические свойства. Уменьшение размера частиц до нанометрового масштаба приводит к изменениям свойств по сравнению с объемными из-за квантовых размерных эффектов. В зависимости от области применения, выбор подходящего метода синтеза наночастиц с желаемыми свойствами является решающим фактором. Целью данной обзорной работы является предоставление дополнительной информации о методах синтеза наночастиц оксида кобальта.

Ключевые слова: оксид кобальта, размер кристаллитов, суперконденсатор.