SYNTHESIS OF Co AND Ni-DOPED TiO_2 FOR ENHANCED FUNCTIONAL PROPERTIES: A SOL-GEL APPROACH

Musaev Kh.B.
Institute of Fundamental and Applied Research under TIIAME National Research University
E-mail: musaevkhusniddin90@gmail.com
Jumaeva M.E.
Institute of Material Sciences of the Academy of Sciences of the Republic of Uzbekistan
Baglov A.V.
Belarusian State University
Khoroshko L.S.
Belarusian State University

Annotation. This study investigates the synthesis and characterization of titanium dioxide (TiO_2) nanomaterials doped with cobalt (Co) and nickel (Ni) metals, both individually and in combination. The sol-gel method was employed for the synthesis of these nanomaterials. The influence of metal doping on the crystalline structure, particle size, surface morphology, band gap energy, and magnetic behavior of TiO_2 nanoparticles is discussed. The results indicate significant alterations in the properties of TiO_2 upon doping, highlighting the potential of these modified nanomaterials for a variety application such as photocatalysis, energy storage, and magnetic devices.

Keywords: nanomaterials, titanium dioxide, sol-gel, chemistry.

Аннотация. В данной работе исследованы синтез и характеристики наноматериалов диоксида титана (TiO_2), легированных кобальтом (Co) и никелем (Ni) как по отдельности, так и в комбинации. Для синтеза этих наноматериалов использовался золь-гель метод. Обсуждается влияние легирования металлами на кристаллическую структуру, размер частиц, морфологию поверхности, ширину запрещенной зоны и магнитное поведение наночастиц TiO_2. Результаты свидетельствуют о значительных изменениях свойств TiO_2 при легировании, что подчеркивает потенциал этих модифицированных наноматериалов для различных применений, таких как фотокатализ, накопление энергии и магнитные устройства.

Ключевые слова: наноматериалы, диоксид титана, золь-гель, химия.

Annotatsiya. Ushbu tadqiqot kobalt (Co) va nikel (Ni) metallari bilan qo'shilgan titan dioksidi (TiO_2) nanomateriallarining alohida va kombinatsiyalangan sintezi va tavsifini o'rganadi. Ushbu nanomateriallarni sintez qilish uchun sol-gel usuli qo'llanilgan. Metall dopingning kristalli tuzilishga, zarrachalar hajmiga, sirt morfologiyasiga, tarmoqli bo'shliq energiyasiga va TiO_2 nanozarrachalarining

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magnit harakatlariga ta'siri muhokama qilinadi. Natijalar doping paytida TiO_2 xususiyatlarida sezilarli o'zgarishlarni ko'rsatadi, bu o'zgartirilgan nanomateriallarning fotokataliz, energiyani saqlash va magnit qurilmalar kabi turli xil ilovalar uchun potentsialini ta'kidlaydi.

Kalit so‘zlar: nanomateriallar, titan dioksidi, sol-gel, kimyo.

Introduction.

TiO_2 is a promising material for various applications, but its wide band gap (~3.2 eV) limits its light absorption to the UV region, reducing its photocatalytic efficiency under visible light. Additionally, rapid electron-hole recombination also reduces its photocatalytic activity and narrows the application scope [1-6]. To overcome the limitations and tailor the properties of TiO_2 for specific applications, various modification strategies have been explored. Among these, doping with metal ions has emerged as an effective technique to alter the electronic structure, optical absorption, and surface characteristics of TiO_2 nanoparticles [7-10]. Transition metal doping, in particular, has shown promising results in enhancing photocatalytic activity, introducing magnetic properties, and modifying the band gap energy.

Synthesis. The sol-gel method was employed to synthesize cobalt (Co) and nickel (Ni) co-doped titanium dioxide nanomaterials. This approach is widely recognized for its simplicity, cost-effectiveness, and ability to precisely control the composition and structure of the material. Titanium isopropoxide (TTIP) served as the titanium precursor, while cobalt nitrate and nickel nitrate were used as doping agents. The aqueous dopant solution was then added dropwise to the TTIP solution, maintaining continuous stirring to ensure uniform mixing. The resulting mixture was stirred at room temperature until gel formation occurred. The gel was aged to increase its stability, then dried at 100 °C to remove residual solvents. Finally, the dried gel was calcined at 450–600 °C in a muffle furnace to achieve crystallization and integrate Co and Ni ions into the TiO_2 lattice (Fig. 1).



Fig. 1. Steps in obtaining nanomaterials

Characterization techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), FTIR, and UV-Vis spectroscopy were employed to confirm the successful co-doping of TiO_2 with Co and Ni, as well as to evaluate the structural, morphological, and optical properties of the synthesized nanomaterials.

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Scanning electron microscopy (SEM) is one of the most powerful and versatile techniques for investigating the surface morphology and microstructural features of materials. Scanning Electron Microscopy (SEM) plays a crucial role in investigating the properties of nanoporous semiconductor materials. Due to its high magnification and depth of focus capabilities, SEM allows for the direct observation of the microscopic structure and morphology of these materials. SEM helps in determining essential morphological features of the nanopores, such as their shape, size, distribution, and interconnectivity [11-12]. This is vital for understanding the overall structure of the material and its impact on its properties. For instance, SEM can visualize how the pore size and density affect the material's surface area, adsorption capacity, and optical properties. SEM enables the visualization of the internal and surface structure of nanoporous architectures (Fig. 3).

The increase in absorption range with different doped materials was registered. The saturation magnetization (MS) was higher for TiO_2 relative to doped materials. Cobalt and nickel co-doping effectively modified the structural, optical, and photocatalytic properties of TiO_2, enhancing its activity under visible light irradiation.

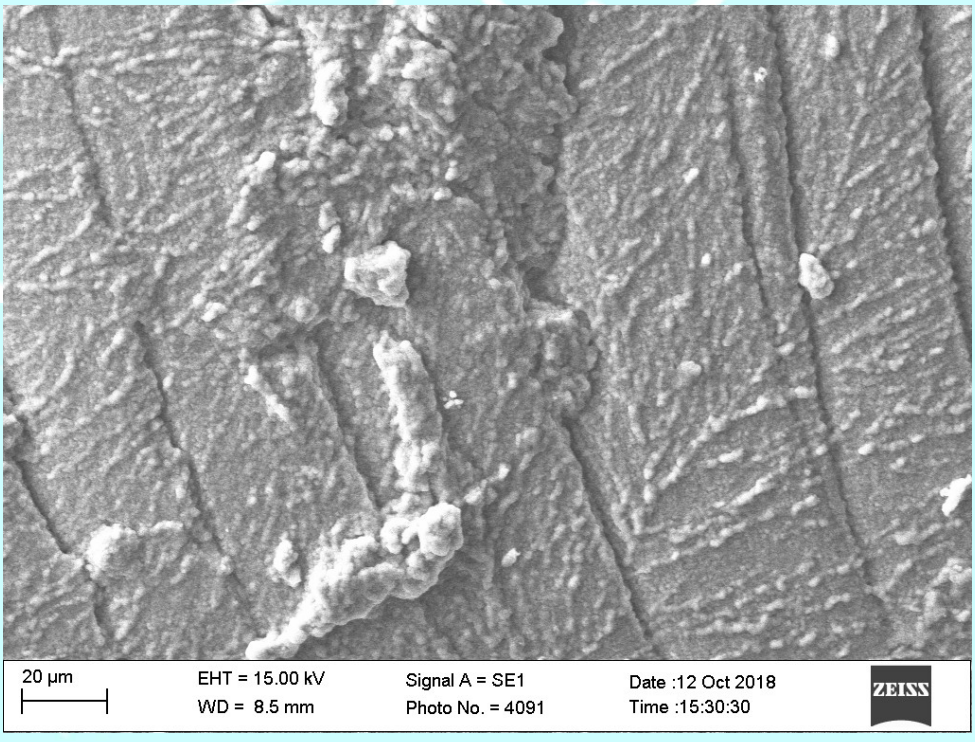


Fig. 2. SEM analylisis of Ni doped TiO_2

The co-doping could lead to unique surface properties and thus a different profile of surface hydroxyl groups compared to undoped or single-doped TiO_2. The intensity and position of the O-H bands might be altered in a way that is not simply additive of the effects of individual doping. The simultaneous presence of two different dopant ions could create new types of lattice defects or influence the

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concentration of existing defects, potentially leading to the appearance of new weak bands or changes in the intensity of defect-related bands. The IR spectrum might provide indirect evidence of interactions between Ni and Co ions within the TiO_2 lattice or on its surface if the observed band positions or intensities deviate significantly from what would be expected from a simple mixture of the effects of single doping. Comparing the Ni-Co-TiO_2 spectrum with the individual Ni-TiO_2 and Co-TiO_2 spectra can reveal if the co-doping leads to effects that are more than or less than the sum of the individual doping effects (Fig.3).

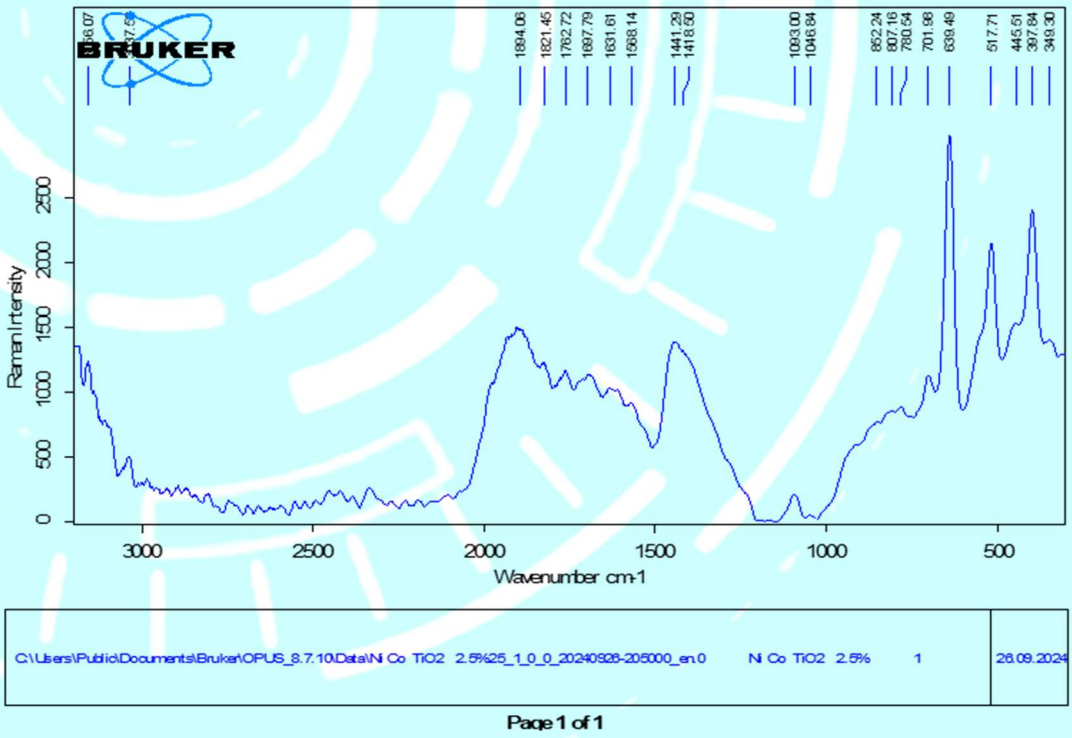


Fig. 3. Infrared spectroscopy analysis results of Ni-Co-TiO_2

X-rays are a form of electromagnetic radiation generated through the interaction of high-energy charged particles or photons with the atoms of a target material. When an energetic electron strikes the anode material, a portion of its kinetic energy is converted into X-ray radiation. The similarity between X-ray wavelengths and the interatomic spacings of crystal lattices enables the observation of X-ray diffraction in crystalline materials. As Xrays pass through a crystal, they are diffracted by the periodic arrangement of atoms across various crystal planes. X-rays are extensively used in numerous scientific antechnological fields, particularly for structural analysis of atoms, molecules, and crystalline solids. X-ray Diffraction (XRD) is a crucial technique for characterizing the structural properties of nanoporous semiconductor materials and metal-doped titanium dioxide (TiO_2).

The broadening of the diffraction peaks would be analyzed to estimate the average crystallite size of the TiO_2 nanoparticles. The co-presence of Ni and Co might have a different effect on crystallite growth compared to single doping with

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either element. It could lead to smaller crystallites due to increased nucleation sites or hinder growth more effectively (Fig. 4).

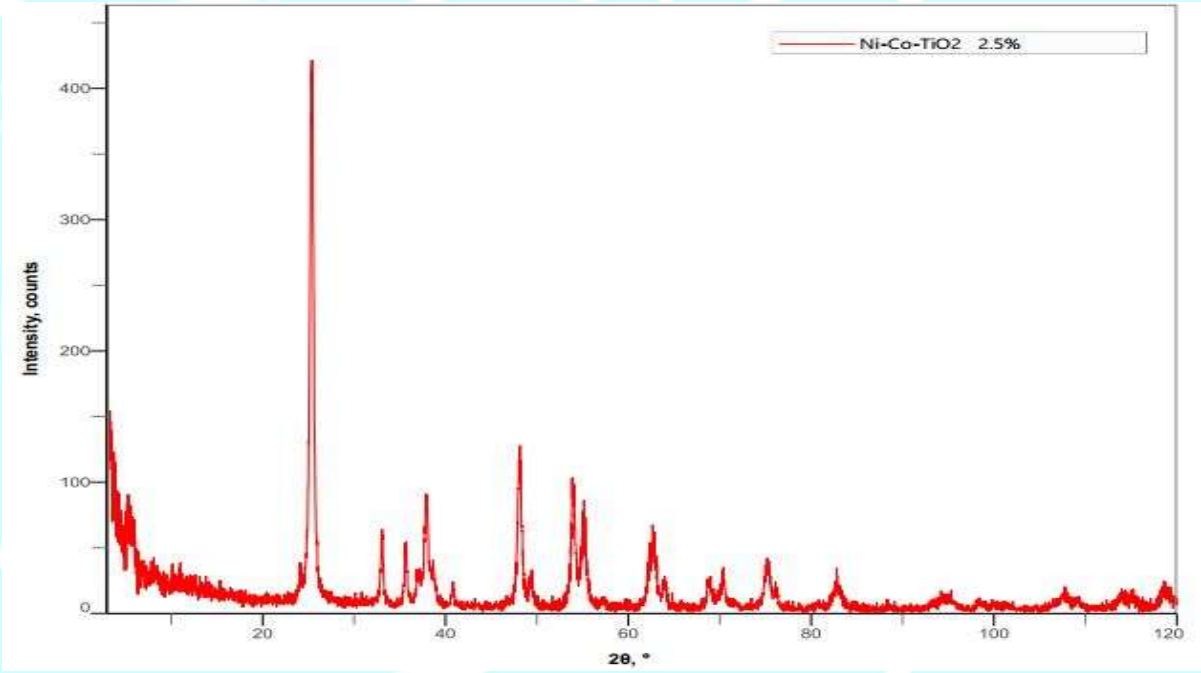


Fig. 4. Results of X-ray analysis of Co-Ni-TiO_2 nanocrystals calcined at 500 °C for 5 hours

The positions of the diffraction peaks would be used to calculate the lattice parameters of the TiO_2 phase. If both Ni and Co ions are incorporated into the TiO_2 lattice by substituting for Ti^{4+} ions, the changes in lattice parameters might reflect the combined effect of their ionic radii and concentrations.

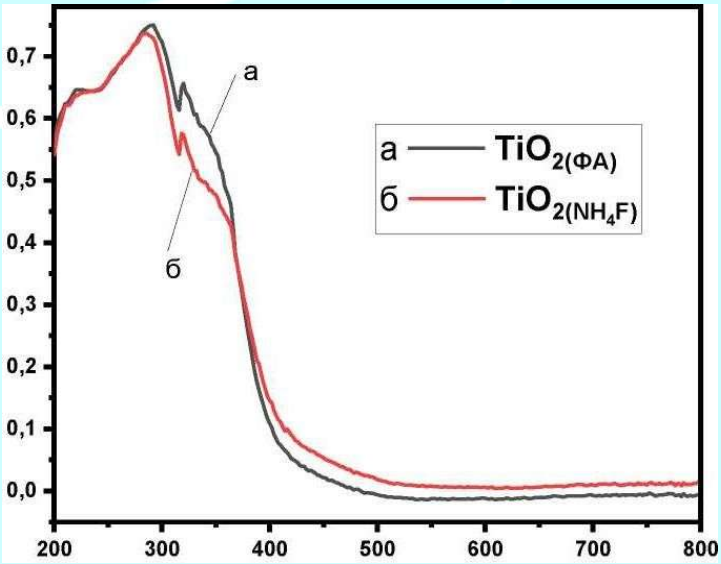


Fig. 5. UV spectra of titanium dioxide samples synthesized in the presence of formamide (a) and ammonium fluoride (b) hydrolytic agents

The ultraviolet (UV) absorption spectra of titanium dioxide synthesized in the presence of formamide (FA) and ammonium fluoride (NH_4F) as hydrolytic agents are shown in Fig. 5. These spectra were analyzed comparatively. The TiO_2 sample synthesized in the presence of FA exhibits an absorption peak at

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approximately 380 nm, whereas the sample obtained in the presence of NH_4F shows a peak near 390 nm.

CONCLUSION

In this study, Ni-TiO_2, Co-TiO_2, and Co-Ni-TiO_2 nanomaterials were synthesized via the sol-gel method, and their photocatalytic degradation efficiency was evaluated against phenol under visible light irradiation. Characterization results confirmed the successful incorporation of dopants into the TiO_2 lattice, improving light absorption and charge separation. This research highlights the importance of optimizing synthesis parameters and dopant concentrations to achieve desired properties in co-doped TiO_2 nanomaterials, with potential for future applications in energy conversion and storage, advancing sustainable solutions for environmental challenges.

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