Structural and Morphological Characteristics of Cobalt Oxide Nanoparticles Incorporated in Porous Silicon Structures

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Abstract

This letter explores the preparation of porous silicon (PSi) layer by electrochemical etching, followed by the Co_3O_4 nanoparticles deposition using a sol-gel method to incorporate these nanoparticles inside the porous network, to fabricate multilayer Co_3O_4NPs/PSi structures as hybrid nanocomposite systems. The structural and morphological characteristics of these hybrid systems were studied. The structures of the components of the hybrid systems (Co_3O_4 and PSi) were not affected by the incorporation process and no new structural phases or materials were formed. As well, the morphological characteristics were enhanced as the high surface area resulted from high porosity, in addition to the crystalline morphology of the silicon walls, make these structures ideal for various practical applications such as photonics, catalysts, biosensing, drug delivery, and solar cells.

Keywords*:* Porous silicon; Cobalt oxide; Nanoparticles; Morphology
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1. Introduction

Recently, the interest in design and fabrication of hybrid nanocomposites has increased to achieve superior functional characteristics when compared to those of individual materials. Such hybrid system are increasingly employed in energy catalysis, sensing, electrochemical storage, optoelectronics and nanoelectronics [1-5]. In this context, the incorporation of metal oxide nanoparticles – especially those of multiple equivalence and catalysis activity like cobalt oxide (Co_3O_4) – inside porous structures, such porous silicon, of high surface area, chemical and structural stability, became a promising strategy to combine the features of each component as synergetic effects [6-9].

Co_3O_4 shows spinel crystalline structure with reasonable electrochemical and catalysis activities due to the multiple oxidation states of cobalt (Co^{2+} and Co^{3+}), good electrical conductivity, and chemical stability [10]. When prepared at the nanoscale, these properties are drastically enhanced due to the quantum confinement phenomenon as well as the drastic increase in the surface active atoms [11]. On the other hand, porous silicon usually prepared by electrochemical etching represents a unique substrate containing a complex network of uniform nanopores, high internal surface area, biocompatibility, and ability to integrate with dominant silicon fabrication techniques [12,13]. Also, the optical and electronic properties of porous silicon are precisely controllable by the pore morphology (diameter, depth, and uniformity). Therefore, the incorporation of Co_3O_4 nanoparticles into such porous network leads to maintain these particles and prevent their agglomeration, which is a common challenge in most applications of nanomaterials. Such incorporation also generate wide and multiple interfaces between the two solid materials [14,15]. The final properties of this hybrid system depend on the structural and morphological characteristics of both the host (porous structure) and the guest (nanoparticles), and the interaction nature at the interface. Consequently, the accurate analysis of these characteristics is pivotal to optimize such hybrid systems [16-18].

Several and various methods and techniques were used to fabricate hybrid nanocomposite systems from metal oxide nanomaterials and porous structures. They include sol-gel, pulsed-laser deposition (PLD), dc and rf reactive sputtering, hydrothermal deposition, and chemical vapor deposition (CVD) [19-22]. The optimum preparation method should produce homogeneous thin films with high adhesion to the substrate, precisely controllable thickness, and efficient coverage of 3D and complex surfaces, such as internal walls of pores [23-25].

In this letter, hybrid nanocomposite systems were fabricated by deposition of nanostructured Co_3O_4 thin films on porous silicon structure and their structural and morphological characteristics were studied.

2. Experimental Part

Figure (1) shows a schematic explanation for the experimental procedure used to fabricate Co_3O_4NPs/PSi multilayer structure. The integration of metal oxide semiconductors with silicon nanostructures represents a powerful strategy for developing advanced optoelectronic and sensing devices. One particularly promising hybrid nanocomposite system is formed by depositing Co_3O_4 nanoparticles onto a PSi layer (substrate). This hybrid system combines the unique structural, morphological and surface properties of PSi with the excellent optical, electronic, and catalytic characteristics of Co_3O_4, leading to enhanced overall performance. The fabrication of this sophisticated structure is a multi-step process, beginning with the formation of the PSi template and culminating in the deposition of the metal oxide.

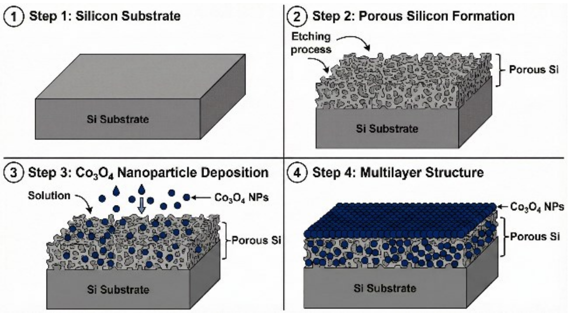


Fig. (1) Schematic explanation of the experimental procedure to fabricate Co_3O_4NPs/PSi structure

The foundation of the hybrid system is a PSi layer, typically fabricated using the electrochemical etching (ECE) method. This process offers superior control over the porosity and morphology compared to standard anodic etching. A p-type or n-type silicon wafer acts as the substrate and anode in a Teflon cell equipped with a platinum cathode. The electrolyte is a hydrofluoric acid (HF)-based solution, often mixed with ethanol to improve wettability and prevent hydrogen bubble accumulation.

The structural characteristics of the prepared samples were introduced by the X-ray diffraction (XRD) while the morphological characteristics were introduced by the field-emission scanning electron microscopy (FE-SEM).

3. Results and Discussion

Figure (2) shows the XRD patterns of the Co_3O_4 nanoparticles, porous silicon (PSi) structure, and Co_3O_4/PSi structure. The XRD pattern of the Co_3O_4 sample prepared by sol-gel method shows an intense distinct diffraction peak at 37.04°, which corresponds to the crystal plane of (311). Other peaks seen at 31.68°, 45.08°, 59.76°, and 65.48° are corresponding to the crystal planes of (220), (400), (511), and (440), respectively. This pattern reveals the polycrystalline structure of the prepared Co_3O_4 sample with an initial indication for nanostructure formation. The average crystallite size was determined for the (311) diffraction peak by Scherrer's formula to be 19 nm.

The XRD pattern of the porous silicon (PSi) layer formed on the surface of the silicon substrate shows typical peaks at 28.17°, 47.05°, and 68.87°, corresponding to the crystal planes of (111), (220), and (400), respectively, with the preferred orientation at (400), which is dominantly expected for porous silicon structures formed by electrochemical etching of silicon surface.

The XRD pattern of the multilayer Co_3O_4/PSi structure typically shows that all peaks assigned in the former patterns are seen, which may be attributed to the small thickness of the Co_3O_4 layer deposited on the PSi structure that could not prevent the diffraction from the PSi layer. With the assumption of filling the pores of the PSi layer with the Co_3O_4 nanoparticles, no chemical reaction was induced even though a change in the surface morphology is highly expected. Therefore, the diffraction peaks of both materials were observed with not new peaks belonging to new materials or structural phases. Such result encourages to employ the prepared structure in the applications requiring a combination of two materials, such as photonics and sensing devices, to invest their properties individually and collectively.

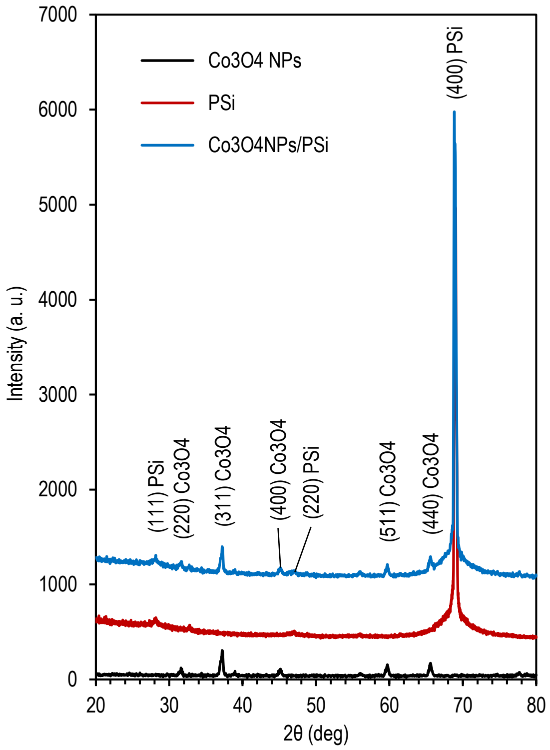


Fig. (2) The XRD patterns of Co_3O_4 NPs, PSi layer, and Co_3O_4/PSi structure prepared in this work

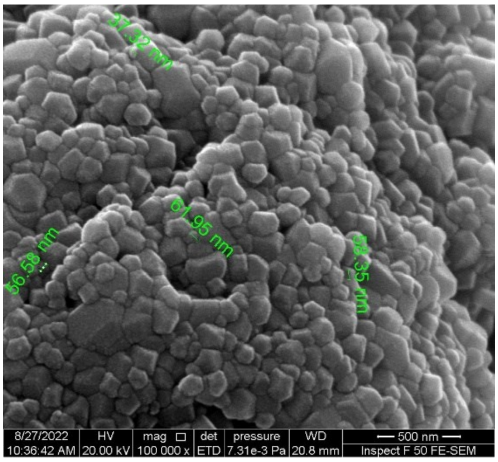
Figure (3) shows the FE-SEM images of the Co_3O_4 nanoparticles, porous silicon (PSi) structure, and multilayer Co_3O_4NPs/PSi structure fabricated in this work. In Fig. (3a), the Co_3O_4 sample shows an apparent and distinguished nanostructure with semi-spherical particles and homogeneous distribution in particle sizes within 37-62 nm. This is attributed to the capability of the dc reactive sputtering technique to control growth process. Slight agglomeration can be seen, which is common in nanomaterials due to the high surface tension. Such homogeneous morphology and narrow range of particle size variation are crucial parameters in supporting the catalyst and electrochemical characteristics of Co_3O_4 to serve various practical applications such as energy storage and photocatalysis.

Figure (3b) of PSi structure indicates porous structure with high uniformity and purity as a complex and homogeneous network of approximately cylindrical pores is seen. The pore diameters are ranging in 300-675 nm and pore walls show homogenous thickness and high surface roughness, which can be ascribed to the selective and uniform etching process. The high surface area resulted from high porosity, in addition to the crystalline morphology of the silicon walls, make this structure ideal for biosensing, drug delivery, and solar cells. As well, such porous structure can be successfully used as efficient substrates for nanostructured photonic-active layers to fabricate advanced photonic and optoelectronic devices.

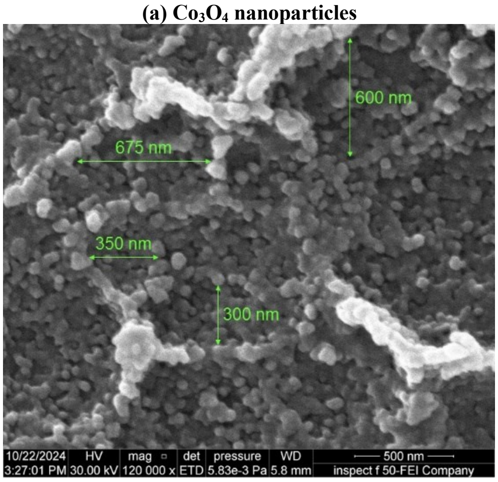
In Fig. (3c), the successful deposition and formation of nanoparticle layer on the porous silicon structure can be revealed. The original porous structure can be clearly seen in the background and the agglomerations of Co_3O_4 nanoparticles are also observed. These nanoparticles are distributed over the surface with high density around the pore crater. They efficiently cover the 3D complex surface to form reasonably homogeneous multilayer Co_3O_4NPs/PSi structure. This result reveals the feasibility and reliability of the sol-gel technique in the preparation of such multilayer hybrid structures from metal oxide nanostructured thin films deposited on complex porous structures to fabricate integrated photonic and optoelectronic devices.

4. Conclusions

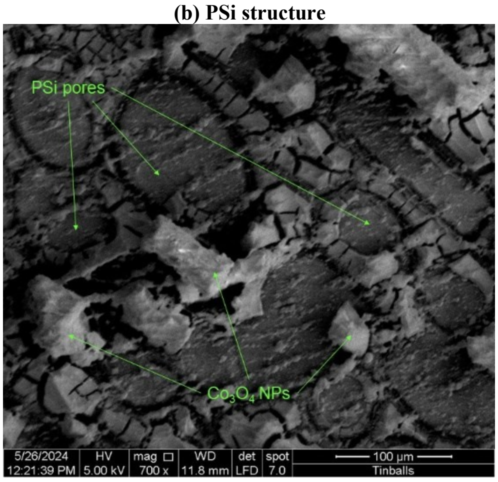
In concluding remarks, the preparation of porous silicon (PSi) layer by electrochemical etching, followed by the Co_3O_4 nanoparticles deposition using a sol-gel method to incorporate these nanoparticles inside the porous network, to fabricate multilayer Co_3O_4NPs/PSi structures as hybrid nanocomposite systems was presented. The structures of the structures of the components of the hybrid systems (Co_3O_4 and PSi) were not affected by the incorporation process and no new structural phases or materials were formed. As well, the morphological characteristics were enhanced as the high surface area resulted from high porosity, in addition to the crystalline morphology of the silicon walls, make these structures ideal for various practical applications such as photonics, catalysts, biosensing, drug delivery, and solar cells.



(a) Co_3O_4 nanoparticles



(b) PSi structure



(c) Co_3O_4NPs/PSi structure

Fig. (3) The FE-SEM images of (a) Co_3O_4 nanoparticles, (b) PSi structure, and (c) Co_3O_4NPs/PSi structure

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