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Production of Silica Coated Cobalt Nanoparticles Via A Synthetic Nanofabrication Method

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Abstract: In the periodic table, cobalt is the second-highest magnetic element at room temperature, which makes it a material of choice in many applications ranging from magnetic sensors and memory devices to catalysis and magnetic resonance imaging. Cobalt nanoparticles have been synthesized via chemical methods to further capitalize on their properties. However, the limited range of nanoparticle sizes and purity is the biggest challenge encountered when traditional synthesis approaches are considered. In order to fully realize the potential of cobalt nanoparticles, this research uses a non-chemistry-based, synthetic nanofabrication approach to produce ferromagnetic and surface passivated cobalt nanoparticles that are less than 100 nm in size.

Sentetik Nanofabrikasyon Yöntemiyle Silika Kaplı Kobalt Nanoparçacıklarının Üretimi

Anahtar Kelimeler
Nanoparçacık,
Kobalt,
Nanofabrikasyon,
Manyetizma

Öz: Kobalt, periyodik tablodaki elementler arasında, oda sıcaklığında en yüksek ikinci manyetik elementtir ve bu, onu manyetik sensörler ve hafıza cihazlarından kataliz ve manyetik rezonans görüntülemeye kadar birçok uygulamada tercih edilen bir malzeme haline getirmiştir. Kobalt nanoparçacıkları genel itibariyle kimyasal yöntemlerle sentezlenmiştir. Bununla birlikte, sınırlı nanoparçacık boyutları ve saflık limitleri, geleneksel kimyasal sentez yaklaşımları göz önüne alındığında karşılaşılan en büyük zorluklardır. Kobalt nanoparçacıklarının potansiyelini tam olarak gerçekleştirmek için, bu araştırma, ferromanyetik ve yüzeyi pasifleştirilmiş, 100 nm altı boyutlarda kobalt nanoparçacıkları üretmek için ıslak kimya temelli olmayan, sentetik bir nanofabrikasyon yaklaşımını rapor etmektedir.

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1. Introduction

Cobalt (Co) is one of the most promising metallic nanoparticles (NPs) and has been of significant interest to researchers from a variety of sectors for a long time. Co NPs often feature exceptional magnetic, electrical, and catalytic capabilities, which are of scientific and technological interest in a variety of domains, such as recording media, magnetic sensors, magnetic memory, and catalysis [1]. Cobalt powder, its oxides, salts, and complexes are used as catalysts in the petrochemical sector. Due to their high saturation magnetization and significant anisotropy, Co NPs are well-suited for high-density data storage and permanent magnet applications. Recently, it was shown that Co NPs are useful for absorption of electromagnetic waves, wireless communications, and high-frequency circuit devices [2, 3]. Besides, Co NPs have a natural advantage in biomedical applications, such as drug delivery and magnetic resonance imaging, where high quality and purity are demanded to minimize magnetization or response stability changes. As the metal center of vitamin B12, cobalt plays a significant role from the standpoint of biological function [4]. Despite this, excessive exposure has a number of negative health impacts. Consequently, it is essential to monitor the amount of cobalt in its many forms in the human body. However, great interest in cobalt remains due to its unique features and numerous applications. Notably, the discovery of the extraordinary physical and chemical characteristics of Co NPs, which are connected with the existence of quantum size effects, has made the already amazing features of cobalt much more intriguing. The continuous density of states typical of bulk matter is replaced with discrete levels that depend on the size and spacing of the particles. As the size of NPs decreases, the fraction of surface atoms increases compared to the total number of atoms [5]. There is a significant shift in the characteristics of surface atoms, and as a result, the interaction between surface atoms and atoms within the particle alters, which can result in a fundamental change in physical properties. Cobalt nanoclusters, for instance, have a higher magnetism than bulk cobalt due to the greater magnetization of surface atoms resulting from their tiny size. To produce Co with varying morphology and size distribution, numerous synthetic methods, such as solvothermal, microemulsion, sonification, reduction of Co salt, reduction in inverse micelles, and electrochemical synthesis, have been utilized in the past [6–9].

Co NPs are prone to oxidation under ambient conditions; thus, preventing oxidation is one of the most essential issues during their production [10]. Chemical reduction of Co NPs is, in general, the simplest method for controlling the composition, size, and shape of NPs, as well as scaling up production, without the need for specialized lab equipment or conditions. Nonetheless, it has considerable limitations when it comes to the production of chemically pure NPs without reagent or byproduct contamination of the surface layer. However, heat degradation makes it difficult to regulate the chemical composition of the final NPs. Therefore, it is essential to develop novel manufacturing methods and synthesis approaches in order to create Co NPs that are clean and of a regulated size. A synthetic and nanofabrication-based methodology was used to produce surface-passivated, water-dispersed, and stable Co NPs, as described in this study.

2. Material and Method

2.1. Materials

Four-inch p-type (100) silicon wafers were purchased from UniversityWafer (USA). 150 nm diameter polystyrene nanospheres with no surface functionalization were obtained from Magsphere Inc. (USA). Electron beam evaporation sources and crucibles were supplied from Testbourne Ltd. (UK). The chemicals employed were received from Sigma-Aldrich (USA), and used without further purification.

2.2. Nanofabrication process

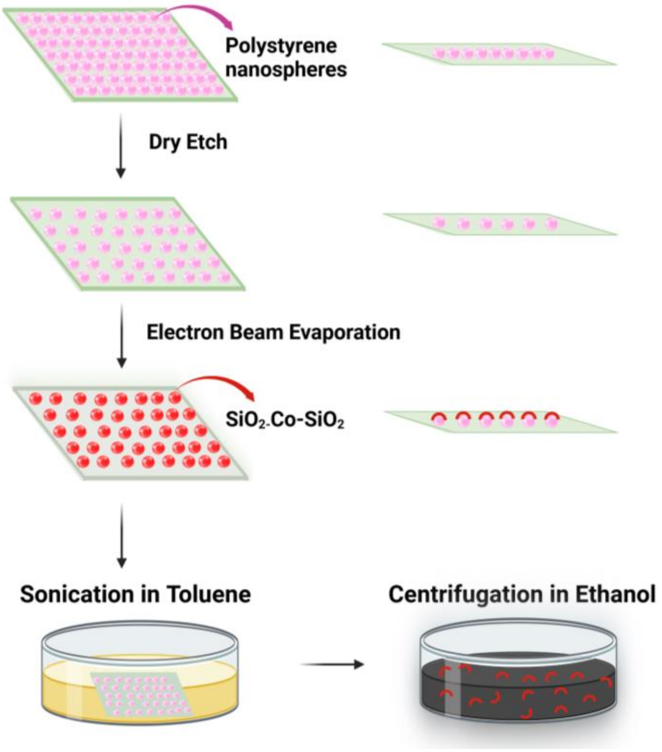

Figure 1. Schematics of the nanofabrication process. Polystyrene nanospheres are first coated onto silicon wafers, and then their sizes are reduced using a dry etch process utilizing oxygen gas. Later, silica and cobalt layers are deposited using the electron beam evaporation technique. The substrates are then immersed in a solution of toluene and sonicated for 12 hours to etch away the polsyrene nanospheres. The nanoparticles are centrifuged in an ethanol solution three times to remove the polystyrene residues and purified for further use.

The nanoparticles were produced using a nanofabrication process in which monolayers of polystyrene nanospheres serve as templates for material deposition [11]. Polystyrene nanobeads were spin-coated onto silicon wafers to form a monolayer. As the nanospheres had no surface ligands, they displayed hydrophicility; therefore, the nanosphere solution was diluted with a 1:1 (v/v) ethanol solution to allow the nanospheres to spread over the wafer substrates to ensure the coating is uniform and surface coverage is high. Prior to the nanobead coating process, wafers were treated with O_2 plasma for 30 seconds at 125 W plasma power and 60 sccm O_2 flow to render the wafer surface hydrophilic and improve the dispersion of the nanosphere solution on the surface. The spin coating process was applied for 60 seconds at a speed of 6,000 rpm with a ramp rate of 500 rpm per second. The coating technique revealed that untreated wafers had low nanobead coverage in multilayer areas. In order to minimize the size of the polymer nanospheres, reactive ion etching (RIE) was conducted [12]. Specific nanosphere diameters might be obtained by altering the length and/or plasma power of this stage. However, extended etching should be avoided since it leads to the loss of spherical form. Adjustments were made to the process parameters in order to achieve nanospheres of 100 nm in diameter, as confirmed by scanning electron microscopy (SEM). Silica was chosen as the capping layer due to its biocompatible nature and ease of chemical functionalization in future applications. Layers of 10 nm of SiO_2, 20 nm of Co of 99.95% purity, and 10 nm of SiO_2 were deposited by electron-beam evaporation onto the 10° tilted substrates under a vacuum level of 10^{-6} mTorr to form Co@SiO_2 layers on the etched nanospheres. To guarantee layer consistency, the wafer holder was continually rotated at 20 rpm during the coating process. Deposition rates and film thicknesses for each coating were monitored in real time using quartz crystals. Transmission electron microscopy (TEM) was utilized to evaluate the film thicknesses. In order to minimize the oxidation of the Co layer, the oxygen concentration in the vacuum chamber needs to be reduced, which was achieved by pre-depositing the Co metal with the shutter closed. This process lowers the pressure of the vacuum chamber through the absorption of remaining oxygen by the Co metal. Following the deposition of silica and Co layers, the polymer beads on the wafer substrates were removed by sonicating them in a toluene suspension, leaving the Co@SiO_2 nanostructures freely floating in solution. Multiple centrifugation processes were then applied to collect the nanostructures, which were subsequently suspended in ethanol for future usage. The experimental schematics and process flow are given in Figure 1.

2.3. Characterization

The nanoparticles' morphology was visualized using SEM (JEOL JSM 7500F) and TEM (FEI CM120). Coulter Beckman Dynamic Light Scattering Analyzer – N4 Plus was utilized for size distribution measurements. Using a superconducting quantum interference device (SQUID, Quantum Design MPMS® XL, USA) with applied field strengths up to 1 T, magnetizations were performed. The diamagnetic contribution of the sample holder and background was removed from the magnetization measurements.

3. Results

Monolayer coating of polystyrene nanospheres on the surface of silicon wafers is an important step to achieve nanoparticles in the desired shape and size, because if monolayer is not ensured, the metal deposition step will produce aggregates and thin film formation where the end nanoparticles will be large and in irregular shapes. A large-area SEM view of the substrates with nanospheres is shown in Figure 2a, where monolayer formation was observed. After this critical step, via a dry etch process utilizing oxygen gas, the dimensions of the nanospheres were reduced as oxygen reacts with the organic nature of polystyrene and carbon dioxide, and water vapors were generated, which were pumped out of the reaction chamber. Following, silica and cobalt thin layers were electron beam evaporated with a controlled thickness. Figure 2b shows the SEM image of the substrate template after the deposition step, where the nanospheres are coated with silica and cobalt layers and the gaps between the nanospheres are visible. In order to remove the coated layers on the nanosphere template via a wet etch process utilizing toluene, these gaps are crucial; otherwise, the organic solvent cannot attach the polystyrene and remove the nanospheres from the surface in the ultrasonication step. The substrates were immersed in a glass beaker containing toluene solution, and ultrasonication was applied for 12 hours. In this step, toluene gradually etches away the polystyrene, leaving the Co@SiO_2 nanoparticle freely suspended in the solution. To purify the dissolved poltsyrene residues, samples were centrifuged three times at 15,000 rpm for 20 minutes in ethanol and collected for further use and characterization.

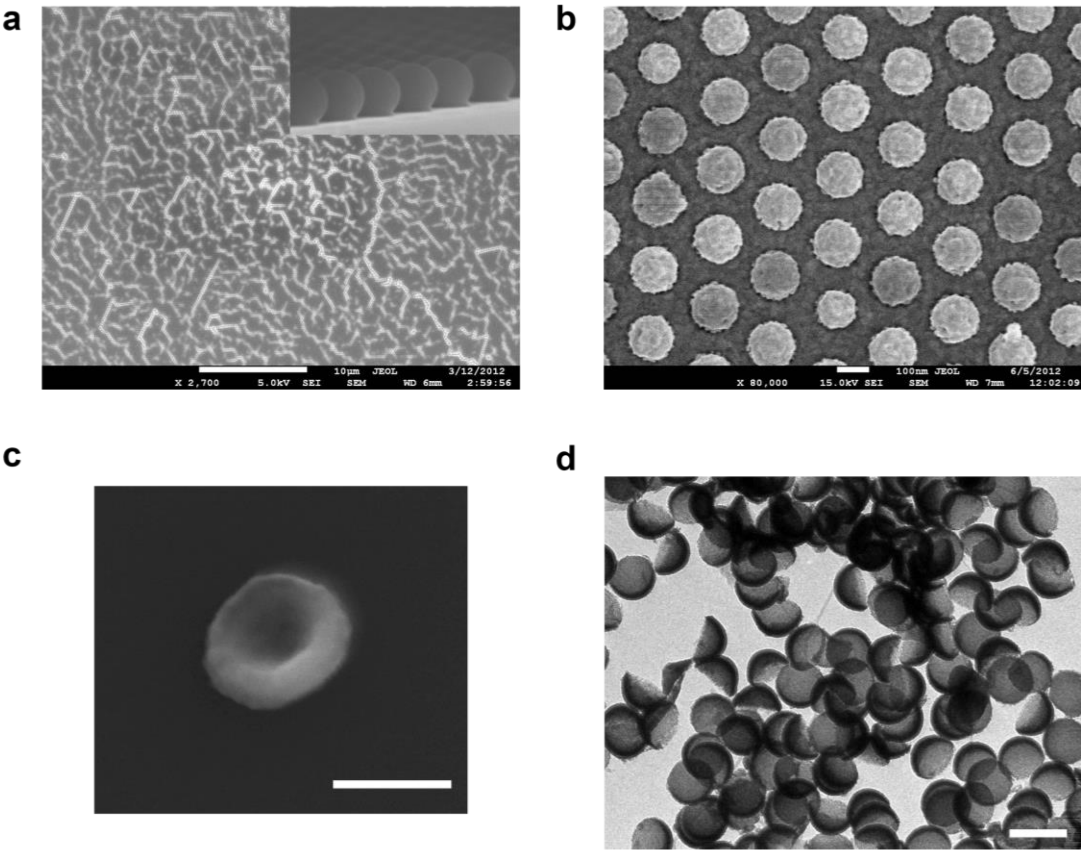

Figure 2. a) A large area scanning electron microscope (SEM) image of the wafer substrate coated with polsytyrene nanospheres in a monolayer fashion. Inset shows the angled side view of the coated nanospheres, b) SEM image of the polystyrene nanospheres after size reduction and coating with silica and metal layers using electron beam evaporation technique, c) SEM image of a single Co@SiO_2 nanoparticle after the removal of nanosphere templates, d) Tranmission electron microscope (TEM) image of the Co@SiO_2 core-shell nanoparticles, where ligher and darker areas clearly indicate silica and cobalt layers. Scale bars are 100 nm in (c) and (d).

Figure 2c shows the SEM image of a single Co@SiO_2 nanoparticle with a nanocrescent moon shape. TEM observation is provided in Figure 2d, where a clearly homogeneous size distribution and shape uniformity over a large sample of nanoparticles are ensured. Here, the dark contrast originates from the existence of cobalt, which has a higher atomic number compared to silica, whereas the lighter areas correspond to silica layers. After verifying the desired shape and size of the nanoparticles, the DLS technique was used to assess the size distribution and existence of aggregates, if any. Figure 3a shows DLS results where a single peak was observed, indicating no aggregation and similar size information obtained from SEM and TEM data. Here, it should be stressed that the nanoparticles are ligand-free; therefore, as opposed to regular DLS results where the mean hydrodynamic size is generally larger than the physical size observed from TEM, similar results were obtained from these different measurements. However, DLS is a technique that is most appropriate when measuring the size of spherical objects, whereas the produced nanoparticles are not symmetrical, where the largest dimension is around 100 nm and the thickness is 40 nm at the center and gradually decreases towards the edges of the nanocrescent moon structures, which also explains why the peak in DLS is less than 100 nm. In order to reveal the elemental compositions and presence of silica and cobalt, SEM-EDX analysis was conducted. Figure 3b shows the elemental spectrum, which includes the characteristic peaks for Si, O and Co atoms along with C. The background of the measurement setup provides this carbon contribution. Nevertheless, the compositional analysis proved the presence of silica and cobalt layers. The magnetic properties of the Co@SiO_2 nanoparticles were investigated by SQUID magnetometry using external fields up to 1 T (10 kOe) at room temperature (Figure 3c). The M–H curve displayed a hysteresis effect, indicating the ferromagnetic behavior of cobalt. The saturation magnetization was observed at 49 emu/g, which is attributable to the nanofabrication technique because, as opposed to the wet synthesis method, evaporation in a vacuum environment minimizes the formation of cobalt oxides, which display poor magnetism compared to pure cobalt.

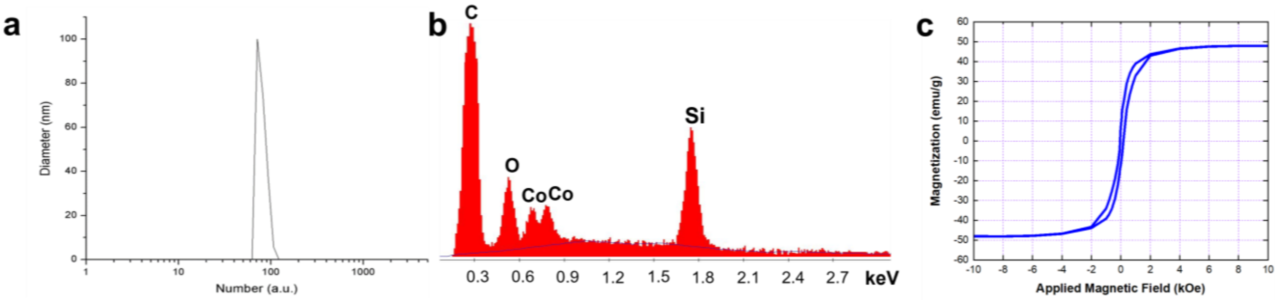

Figure 3. a) Dynamic light scattering measurement of the Co@SiO_2 core-shell nanoparticles, b) Elemental spectrum of the Co@SiO_2 nanoparticles, indicating the existence of Si, O and Co elemental compositions. The carbon peak comes from the bakground, c) Superconducting quantum interference device (SQUID) magnetometer measurement of the powder form nanoparticles. The hysteresis refers to the ferromagnetic nature of the sample.

4. Discussion and Conclusion

The production of surface-passivated nanoparticles with desirable magnetic properties is an important area of research. Cobalt is one of the elements in the periodic table with the highest magnetic moment, and the synthesis of cobalt nanoparticles is traditionally realized through standard chemical methods. Although wet chemistry enables size and shape control and functionalization of nanoparticle surfaces, its main limitation lies in the production of highly pure nanoparticles. Besides, there is a certain size above which cobalt nanoparticles cannot be produced. This research offers an alternative way of manufacturing cobalt nanoparticles with high magnetism and large sizes. Specifically, a vacuum environment was utilized to minimize the oxidation of cobalt, and silica shell layers were covered onto the cobalt core to produce surface passivated nanoparticles. To achieve this, polystyrene nanospheres were utilized as sacrificial templates on a silicon wafer. Through several nanofabrication steps such as dry etch and electron beam evaporation, crescent-moon-shaped Co@SiO_2 nanoparticles were obtained. Electron microscopy characterization confirmed the size, shape, and elemental composition of the end product. The dynamic light scattering technique was used to analyze possible aggregations, and it was verified that the nanoparticles were highly dispersed. Magnetic measurements were conducted at room temperature, and high saturation magnetism for cobalt was reported along with ferromagnetic behavior. A possible explanation for this is due to the formation of a cobalt layer without or with minimal oxidation, which is the main advantage of the developed production technique. This technology, unlike conventional methods, may be adapted to generate nanoparticles of various metals, making them suitable for technological applications.

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