Synthesis of Monodispersed MFe_2O_4 (M = Fe, Co, Ni) Ferrite Nanoparticles: Effect of Reaction Temperature on Particle Size

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ABSTRACT

We have synthesized different classes of monodispersed MFe_2O_4 (M=Fe, Co, Ni) nanoparticles by decomposition of metal-organic precursors in organic solvent and explored the reaction temperature effect on the nanoparticles average dimension. We obtained particle sizes in the range of 2-6 nm at different reaction temperatures. Moreover, we have tested some of these nanoparticles as patterned catalyst for CVD synthesis of carbon nanotubes on silicon wafer.

Keywords: Synthesis, monodispersed nanoparticles, ferrites, temperature effect.

1 INTRODUCTION

The possibility of preparing monodispersed transition metal-oxides nanoparticles, covered by functionalized long chain organic molecules, in the sub size range of 20 nm, has recently open an entire field of research. In fact, inorganic core at the nanoscale provides unusual properties with respect to the corresponding bulk counterpart. Moreover, functionalization of the organic coating with different groups makes these systems building blocks for novel nanostructured materials. Today, ferrite nanoparticles find significant applications in high frequency devices, memories, heat transfer devices, drug delivery systems, medical diagnostics, cancer therapy, catalysis.

The synthesis of monodispersed magnetite nanoparticles by decomposition of metal-organic precursors in organic solvent was reported by Sun [1]. The authors obtained nanoparticles at reaction temperature of 265°C. By using the smallest nanoparticles as seeds, they obtained larger monodisperse nanoparticles up to 20 nm in diameter by seed-mediated growth.

In this work we have explored the temperature effect on the average size of the oxide nanoparticles in the range from 220°C to 265°C. The lowest value was the minimum temperature to obtain crystalline ferrite nanoparticles by decomposition of organic precursor in phenyl ether.

Moreover, we have also tested some of these nanoparticles as catalyst for CCVD synthesis of carbon nanotubes on silicon wafers.

2 EXPERIMENTAL

Phenyl ether (99%), 1,2-hexadecanediol (97%), oleic acid (90%), oleylamine (>70%), cobalt(II) acetylacetonate, Ni(II)acetylacetonate, Iron(III) acetylacetonate were purchased from Aldrich Chemical Co. Monocrystalline oriented silicon wafers (100) were kindly provided by ST Microelectronics of Catania (Italy).

2.1 Synthesis of MFe_2O_4 nanoparticles (M=Fe(II),Co(II),Ni(II))

$Fe(acac)_3$ (2 mmol), 1,2 hexadecanediol (10 mmol), oleic acid (6 mmol), oleylamine (6 mmol), and phenyl ether (20 mL) were mixed and magnetically stirred under nitrogen flow. The mixture was heated respectively to 220 °C or to 265°C for 30 min.

The two black-brown mixtures were cooled to room temperature. For each sample, under ambient condition, ethanol was added; the black material was precipitated and separated via centrifugation. The products were dispersed in hexane and stored in two vials named respectively Fe_3O_4-220°C and Fe_3O_4-265°C.

Under identical conditions, reaction of $Co(acac)_2$ (1 mmol) or $Ni(acac)_2$ with $Fe(acac)_3$ produced $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles.

The samples were analyzed by TEM Microscopy, EDX and Electron Diffraction.

2.2 Deposition of nanoparticles on silicon substrate.

Spin coating method was used to spread the colloidal nanoparticles on silicon wafer. We used hexane dispersion of cobalt ferrite and nichel ferrite nanoparticles, synthesized at 265°C. The rotational speed was fixed at 4000 rpm and the time of spinning was 10 min. Samples were analyzed by Field emission Scanning Electron Microscopy.

2.3 CCVD grown of Carbon Nanotubes

To synthesize CNTs the silicon substrates were mounted into a vertical quartz tube reactor and maintained at room temperature in N_2 flow (80(stp) cm^3/min) for 4 min. The reactor was then introduced in a pre-heated furnace at 800°C and after 10 min the pure N_2 flow was replaced by a gas mixture of C_2H_4 (99.998 pure) with a flow rate of 8 (stp) cm^3/min in N_2 (99.999 pure) (72 (stp) cm^3/min) and maintained at 800°C for 10min. After the reaction the quartz tube was cooled down to room temperature under N_2 flow.

3 RESULTS AND DISCUSSION

The morphological and structural properties of the as prepared particles were characterized by transmission electron microscopy (TEM) analyses. In Figure 1 are reported the TEM images and corresponding electron diffraction patterns of cobalt ferrite nanoparticles synthesized at 265°C and 220°C (a,b), and magnetite nanoparticles synthesized in the same condition (c,d).

TEM images revealed the formation, for each class of compounds, of highly uniform particles that, once deposited over a carbon coated copper grid, tend to self-organize in regular hexagonal lattices.

The size distributions obtained from a statistic analysis over 100 nanoparticles for each sample are reported in Table 1.

The results confirm that the temperature of nanoparticles synthesis is a critical parameter for the formation of nanocrystals and for their growth.

Sample	Temp (C°)	Size (nm)	Sd(nm)
Fe_3O_4	265°C	4.0	±0.5
Fe_3O_4	220°C	3.0	±0.4
$NiFe_2O_4$	265°C	2.6	±0.5
$NiFe_2O_4$	220°C	2.0	±0.3
$CoFe_2O_4$	265°C	6.0	±0.8
$CoFe_2O_4$	220°C	2.8	±0.6

Table 1: Reaction temperature effect on nanoparticles averagesize

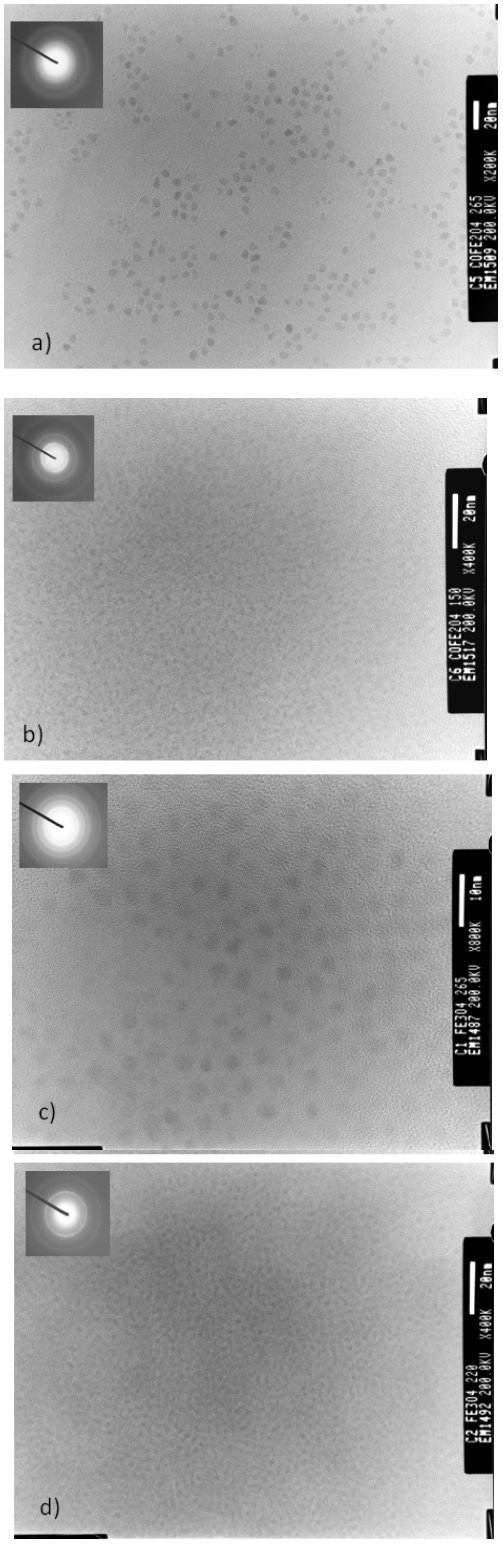

Figure 1:TEM images and corresponding electron diffraction patterns of cobalt ferrite nanoparticles synthesized at a) 265°C and b) 220°C, and magnetite nanoparticles synthesized at c) 265°C and d) 220°

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The minimum temperature necessary to obtain nanoparticles of ferrites through the reaction investigated is ≈ 210°C. In fact, the magnetic properties depend of the inverse spinel structure of ferrites and at less than 210°C there isn't any formation of a magnetic precipitate. In a previous work we synthesized magnetite nanoparticles at 265°C with a reaction time of 60 min. We obtained nanoparticles with an average size of ≈ 7 nm. Reaction time is another crucial parameter to control the growth of particles [4].

The chemical compositions of nanoparticles were evaluated with EDX analysis. The EDX spectra are reported in Figure 2.

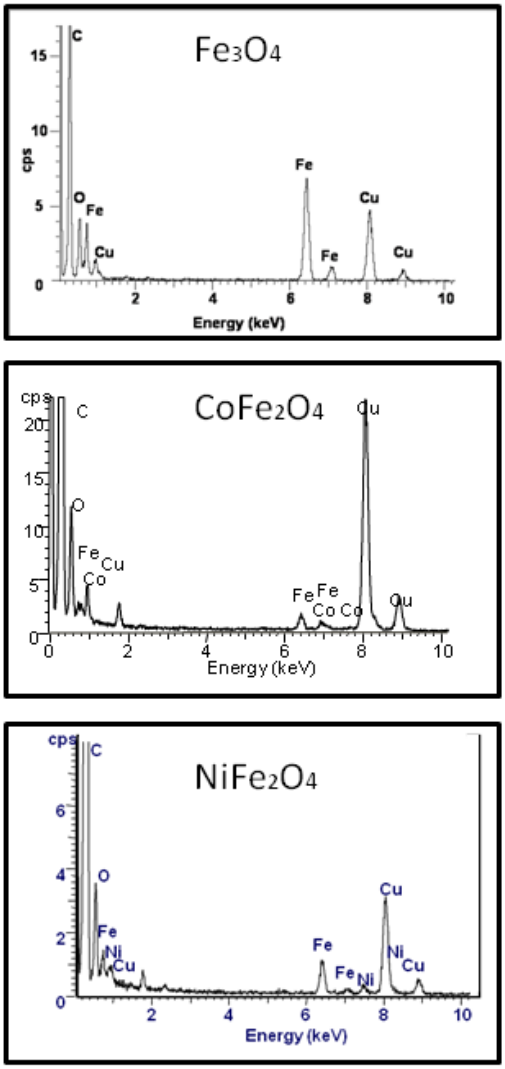

Figure 2: EDX spectra of ferrite nanoparticles

The CVD synthesis of multiwalled carbon nanotubes involves the use of nanoparticles of iron, cobalt, nickel or of their oxides as catalyst for the decomposition of carbon precursor molecules [2]. For these reasons we tested cobalt and nickel ferrite nanoparticles synthesized at 265°C as catalysts for the CVD growth of CNTs on silicon substrate.

In Figure 3 a FESEM image of cobalt ferrite nanoparticles spin coated on silicon substrate before CVD synthesis of CNT is reported.

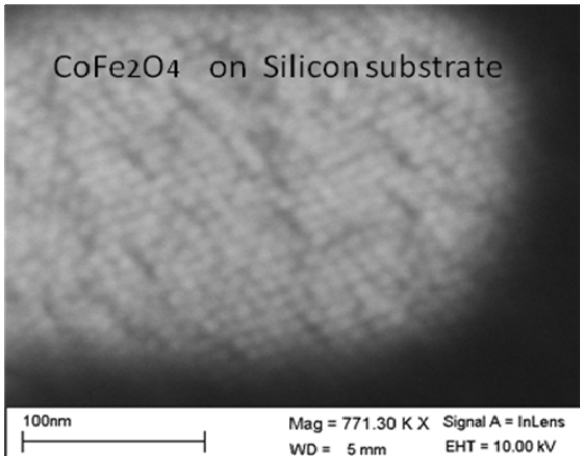

Figure 2: FESEM images of cobalt ferrite nanoparticles spin coated on silicon substrate before CVD growth of CNT.

In Figure 3 the cross section of a silicon wafer after CVD synthesis is shown. The formation of vertically aligned CNT forest on substrate is clearly observed. The thickness of CNT film is ≈12 µm. Similar results were obtained using nickel ferrite nanoparticles as catalyst [3].

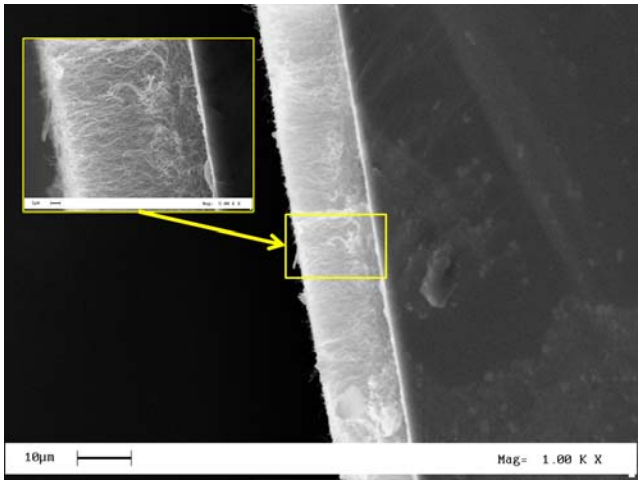

Figure 3: SEM image of CNT film grown on cobalt ferrite nanoparticles covered silicon wafer by CVD synthesis.

4 CONCLUSIONS

In summary, monodispersed Fe_3O_4,$CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles were prepared by thermal decomposition, in organic solvent, of iron and cobalt or (nickel) acetylcetonate using a mixture of protective agents. The sizes of the nanoparticles can be adjusted by changing the reaction temperature time. The process could be applied inexpensively for practical uses. A temperature of 220° generates crystalline nanoparticles of only 2 - 3nm. On the contrary, at higher temperature nanoparticles of larger size (4 - 6 nm) form. Nanoparticles were characterized by transmission electron microscopy, electron diffraction and Energy Dispersive X-ray analysiss. Moreover, thanks to the high surface area to volume ratio and to the presence of transition metals in the stoichiometry of these materials, nanoparticles were capable to promote the CVD growth of CNT on silicon substrate. Thin films of ferrite nanoparticles were deposited on silicon by spin coating and used as substrate for CVD synthesis. An homogeneous forest of CNTs vertically aligned in a large area on silicon wafer was obtained for each class of particles.

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