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Abstract

In this research an efficient synthesis of a novel nanocomposite including $\text{SiO}_2@(\text{3-aminopropyl})\text{triethoxysilane-coated cobalt oxide (Co}_3\text{O}_4)$ nanocomposite has been reported by three step method. The structure and magnetic characterization of $\text{Co}_3\text{O}_4@\text{SiO}_2@\text{NH}_2$ have been done by using various spectroscopic analyses which include FT-IR, X-ray powder diffraction, scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy and vibrating sample magnetometry. Amino-functionalized SiO_2 coated Co_3O_4 nanocomposite exhibited superparamagnetic behavior and strong magnetization at room temperature. The average crystallite sizes of the Co_3O_4 are 23.7 nm. The obtained magnetic nanocomposite showed excellent catalytic activity as a new heterogeneous magnetic catalyst for the synthesis of some indazole derivatives under mild reaction conditions along with high level of reusability.

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Scientific paper

Preparation and Catalytic Study on a Novel Amino-functionalized Silica-coated Cobalt Oxide Nanocomposite for the Synthesis of Some Indazoles

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Abstract

In this research an efficient synthesis of a novel nanocomposite including SiO₂@(3-aminopropyl)triethoxysilane-coated cobalt oxide (Co₃O₄) nanocomposite has been reported by three step method. The structure and magnetic characterization of Co₃O₄@SiO₂@NH₂ have been done by using various spectroscopic analyses which include FT-IR, X-ray powder diffraction, scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy and vibrating sample magnetometry. Amino-functionalized SiO₂ coated Co₃O₄ nanocomposite exhibited superparamagnetic behavior and strong magnetization at room temperature. The average crystallite sizes of the Co₃O₄ are 23.7 nm. The obtained magnetic nanocomposite showed excellent catalytic activity as a new heterogeneous magnetic catalyst for the synthesis of some indazole derivatives under mild reaction conditions along with high level of reusability.

Keywords: Co₃O₄@SiO₂@NH₂, heterogeneous catalyst, spectroscopic analysis, indazole derivatives, nanocomposite

1. Introduction

Over the last decade, organic–inorganic magnetic nanocomposites have become interesting as magnetic catalysts in both academic and industrial fields.^{1–3} The spinel cobalt oxide Co₃O₄ is a magnetic semiconductor and widely used catalyst for a variety of reactions.^{4–5} The use of this magnetic nanoparticle catalyst can address the isolation and recycling problem encountered in many heterogeneous and homogenous catalytic reactions. Most importantly, the magnetic-supported catalysts show not only high catalytic activity but also high degree of chemical stability. The Co₃O₄ surface has a strong affinity for silica, and the cobalt-oxide NPs were easily coated with silica via the sol–gel process.⁶ It has been exhibited that the formation of silica coating on the surface of Co₃O₄ NPs can hinder their aggregation and keep their chemical stability.⁷ In addition, the silanol (Si–OH) groups, which have often located in the terminal of silica coating surface, SiO₂ is stab-

le under acidic conditions and inert to redox reactions, as compared with the organic coating materials, and hence functions like an ideal shell composite to protect the inner Co₃O₄ particles. Silica-coated Co₃O₄ nanocomposite, i.e., Co₃O₄@SiO₂, has recently been investigated for potential biomedical applications.^{8–10} Additionally, the SiO₂ coating shell has an abundance of surface hydroxyl groups which can be easily coupled with organosilanes by formation of Si–O–Si covalent bonds. The importance of this field is highlighted by the use of bio molecules which control the self-assembly of nanodevices.^{11–13} This led to the idea of preparing an active catalyst, Co₃O₄@SiO₂@NH₂, through morphology-controlled synthesis which ensure that faces which are active specifically are exposed predominantly at the surface. As well as, to the best of our knowledge, no attempt has been made to synthesis of Co₃O₄@SiO₂@NH₂ nanostructures. In this study, a novel Co₃O₄ magnetic nanocomposite was developed by grafting amino groups covalently onto the surfaces of Co₃O₄@SiO₂ nanocomposite.

The resulted nanocomposite was characterized by Fourier transform infrared (FTIR), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM). This study on the synthesis of $\text{Co}_3\text{O}_4@\text{SiO}_2@\text{NH}_2$ nanocomposite may open up new routes in the research for highly active catalysts.

In continuing our efforts towards the development of efficient and environmentally benign heterogeneous catalysts,^{14–18} herein, $\text{Co}_3\text{O}_4@\text{SiO}_2@\text{NH}_2$ nanocomposite was prepared as a highly efficient magnetic catalyst by a simple method. The main goal of this catalytic synthesis was to introduce a novel and effective magnetic nanocomposite to expand the use of these types of composites for organic reactions. In order to investigate the catalytic activity of this magnetic catalyst, synthesis of some indazole derivatives have been done via two-component reactions.

2. Experimental

2.1. Chemicals and Apparatus

Chemicals were purchased from the Sigma-Aldrich and Merck in high purity. All of the materials were of commercial reagent grade and have been used without further purification. The α,α' -bis (substituted-arylidene) cycloalkanones were synthesized via aldol condensation as described previously.^{19,20} All melting points are uncorrected and were determined in capillary tube on Boetius melting point microscope. The ultrasonic irradiation was used in reactions by a multi-wave ultrasonic generator (Sonicator 3200; Bandelin, MS 73, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 200 W. The ultrasonic generator automatically adjusted the power level. ^1H NMR and ^{13}C NMR spectra were obtained on Bruker 400 MHz spectrometer with CDCl_3 as solvent using TMS as an internal standard. FT-IR spectrum was recorded on Magna-IR, spectrometer 550. The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with mono chromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Microscopic morphology of products was visualized by SEM (LEO 1455VP). The mass spectra were recorded on a Joel D-30 instrument at an ionization potential of 70 eV. Transmission electron microscopy (TEM) was performed with a Jeol JEM-2100UHR, operated at 200 kV. Magnetic properties were obtained on a BHV-55 vibrating sample magnetometer (VSM) made by MDK-I.R.Iran. The compositional analysis was done by energy dispersive analysis of X-ray (EDX, Kevex, Delta Class I).

2.2. Preparation of Co_3O_4 Nanoparticles

Co_3O_4 MNPs were prepared according to previously

reported procedure by Vela et. al with some modifications.²¹ Firstly, cobalt nitrate hexahydrate (8.60 g) was dissolved in 100 ml of ethanol and the resulting mixture was stirred vigorously. Then, the mixture was heated up to 50 °C and kept for 30 min. Finally oxalic acid (2.14 g) was added quickly to the solution and the reaction mixture was stirred for 2 h at 50 °C. The formed precipitate which includes cobalt (II) oxalate was collected by centrifuges and then the prepared cobalt (II) oxalate powder was calcined at 400 °C for 2 h to produce Co_3O_4 nanoparticles.

2.3. Preparation of $\text{Co}_3\text{O}_4@\text{SiO}_2$ Nanoparticles

$\text{Co}_3\text{O}_4@\text{SiO}_2$ MNPs were prepared according to the slightly modified previously reported method by Vela et. al.²¹ Briefly, CTAB (2.2 g) was added to a solution of 0.5 g of Co_3O_4 nanoparticles in EtOH (350 mL), and then concentrated ammonia aqueous solution (40 mL, 28 wt %) was added dropwise to the reaction mixture under sonication. After the treatment for 20 min which followed by the addition of tetraethylorthosilicate (TEOS) (0.4 mL in 10 mL of EtOH) to the mixture under ultrasound irradiation, then solution was stirred for 20 h at room temperature. Co_3O_4 nanoparticles coated with porous SiO_2 shell were collected by centrifugation and washed three times with deionised water and then were calcined at 600 °C for 6 h.

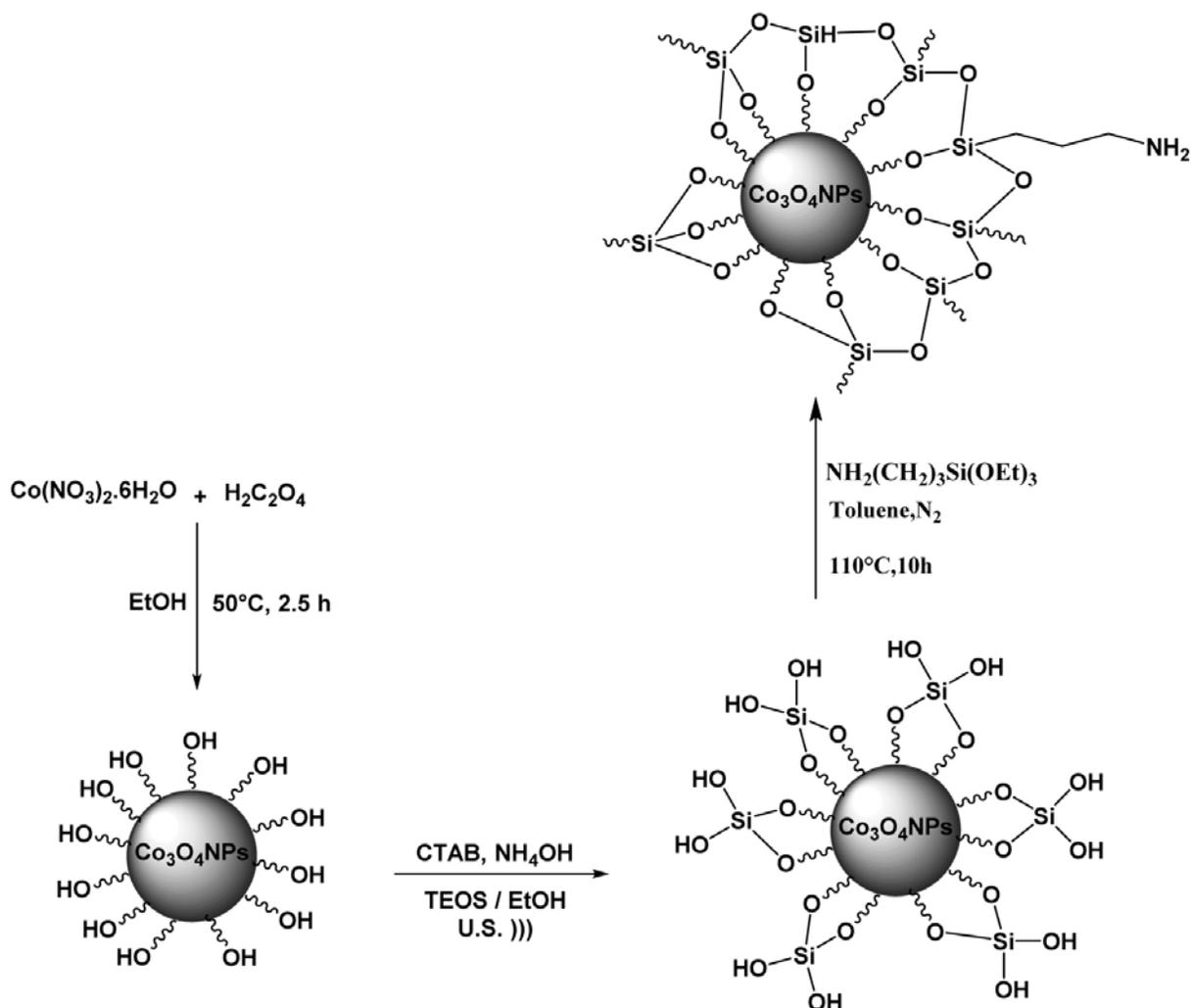
2.4. Preparation of $\text{Co}_3\text{O}_4@\text{SiO}_2@\text{NH}_2$ Nanocomposite

$\text{Co}_3\text{O}_4@\text{SiO}_2$ nanoparticles (0.5 g) were added to the three-necked flask and ultrasonically dispersed for 15 min in dry toluene (25 mL). Afterwards, 1 milliliter (4.27 mmol) of 3-aminopropyltriethoxysilane (APTES) was added into the flask, and the reaction mixture was refluxed at 110 °C with continuous stirring for 10 h under nitrogen atmosphere. After completion of the reaction, the resulting amine-functionalized $\text{Co}_3\text{O}_4@\text{SiO}_2$ was gathered by centrifugation and washed with water and ethanol for several times. Finally, it was dried at 50 °C under vacuum conditions for 10 h (Scheme1).

Nitrogen content of the amine-grafted sample was estimated by back titration using NaOH (0.1 mol/L).^{22–24} First, the known amount of the catalyst was stirred in HCl (0.5 mol/L) for 30 min. Then, the mixture was filtrated and titrated with NaOH (0.1 mol/L). Nitrogen content of the catalyst was 5.86 mmol/g using 8.54 mmol/g trimethoxysilylpropylamine.

2.5. General Procedure for Synthesis of Some Indazole Derivatives

In a typical procedure, a mixture of α,α' -bis (substituted-arylidene) cycloalkanone (1 mmol), phenyl hydra-



Scheme 1. Preparation steps for fabricating $\text{Co}_3\text{O}_4@\text{SiO}_2@\text{NH}_2$ nanocomposite

zinc (2 mmol), and $\text{Co}_3\text{O}_4@\text{SiO}_2@\text{NH}_2$ (0.003 g) were placed in a round-bottom flask. The suspension was stirred under solvent-free conditions at 80 °C. Completion of the reaction was monitored by Thin Layer Chromatography (TLC). After termination of the reaction, the catalyst was separated from the solid crude product by using an external magnet. The precipitated solid was then collected and recrystallized from ethanol to afford the pure product.

The products were identified with ^1H NMR, ^{13}C NMR and FT-IR spectroscopic techniques.

3. Results and Discussion

3. 1. Catalyst Characterization

The synthesis strategy of $\text{Co}_3\text{O}_4/\text{SiO}_2/\text{NH}_2$ MNPs involves three steps. Figure 1 shows the XRD patterns of prepared Co_3O_4 , $\text{Co}_3\text{O}_4@\text{SiO}_2$ and $\text{Co}_3\text{O}_4@\text{SiO}_2@\text{NH}_2$. All the XRD patterns show raising background which is

attributed to X-ray fluorescence since $\text{Cu-K}\alpha$ has been used as the X-ray source during the measurements.²⁵

The reflections of XRD pattern of Co_3O_4 in Fig. 1a confirm the synthesis of cubic normal spinel Co_3O_4 (JCPDS file no. 42–1467). Fig. 1b shows the SiO_2 coating of Co_3O_4 by the presence of the new broad peak at 2θ approximately 22–25°. As shown in Figure 1, the characteristic peaks of Co_3O_4 are also observed for $\text{Co}_3\text{O}_4@\text{SiO}_2$ and $\text{Co}_3\text{O}_4@\text{SiO}_2@\text{NH}_2$, which represent the stability of the crystalline phase of Co_3O_4 nanoparticles during silica coating and surface amino-functionalization. Although these characteristic diffraction peaks are weakened in $\text{Co}_3\text{O}_4@\text{SiO}_2$ and $\text{Co}_3\text{O}_4@\text{SiO}_2@\text{NH}_2$, because of the silica coating and surface amino-functionalization. The average crystallite sizes of the Co_3O_4 in Figure 1 (a, b and c) which have been estimated by using the Scherrer equation were 23.5, 24.2 and 26.0 nm respectively.

Further information about the chemical structure of Co_3O_4 , $\text{Co}_3\text{O}_4@\text{SiO}_2$ and $\text{Co}_3\text{O}_4@\text{SiO}_2@\text{NH}_2$ nanocomposites have been obtained from FT-IR spectroscopy

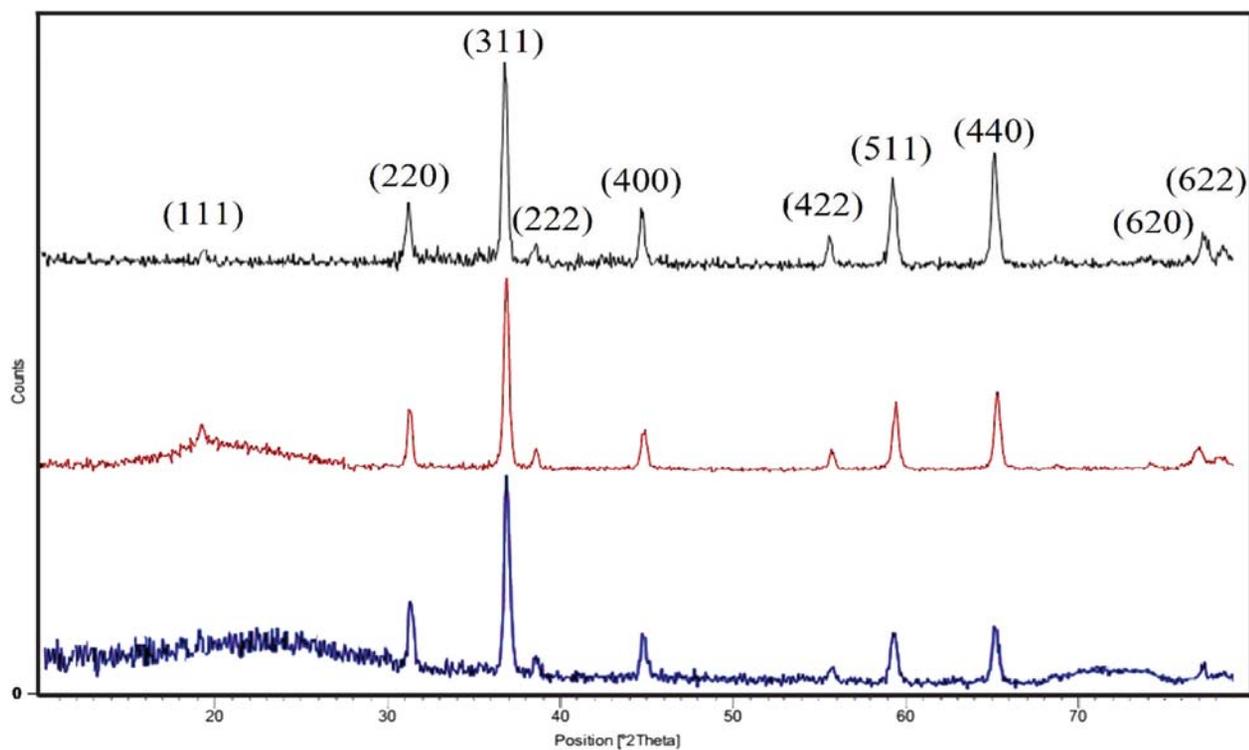


Figure 1. X-ray diffraction of Co_3O_4 (a), $\text{Co}_3\text{O}_4@ \text{SiO}_2$ (b) and $\text{Co}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2$ (c) MNPs.

shown in Figure 2. For all three nanoparticles, the analyses indicated two strong absorption bands at 565 and 662 cm^{-1} which correspond to the vibrations of Co-O in Co_3O_4 .

The peaks at 460 and 1070 cm^{-1} are attributed to the Si-O-Si bond stretching of $\text{Co}_3\text{O}_4@ \text{SiO}_2$ and $\text{Co}_3\text{O}_4@ \text{SiO}_2@ \text{NH}_2$. The weak intensity band at 830 cm^{-1} can be

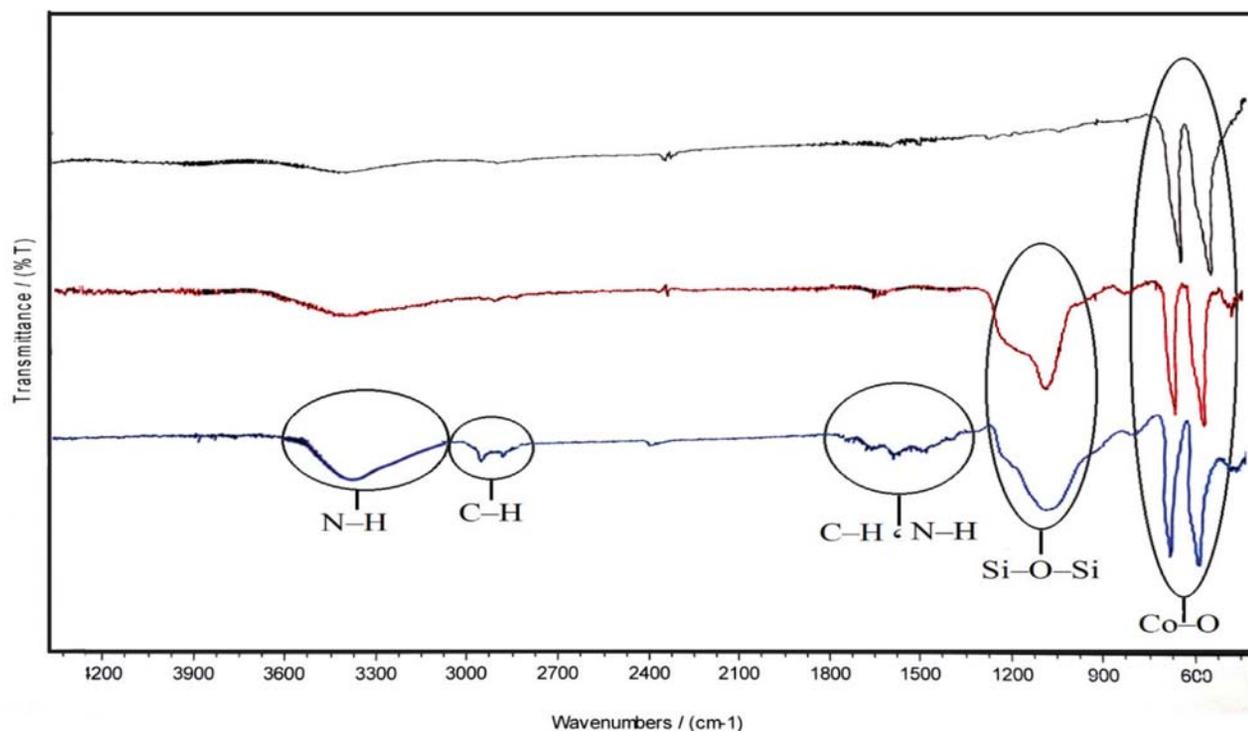


Figure 2. Comparative FT-IR spectra of Co_3O_4 (a), $\text{Co}_3\text{O}_4@ \text{SiO}_2$ (b) and $\text{Co}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2$ (c) MNPs.

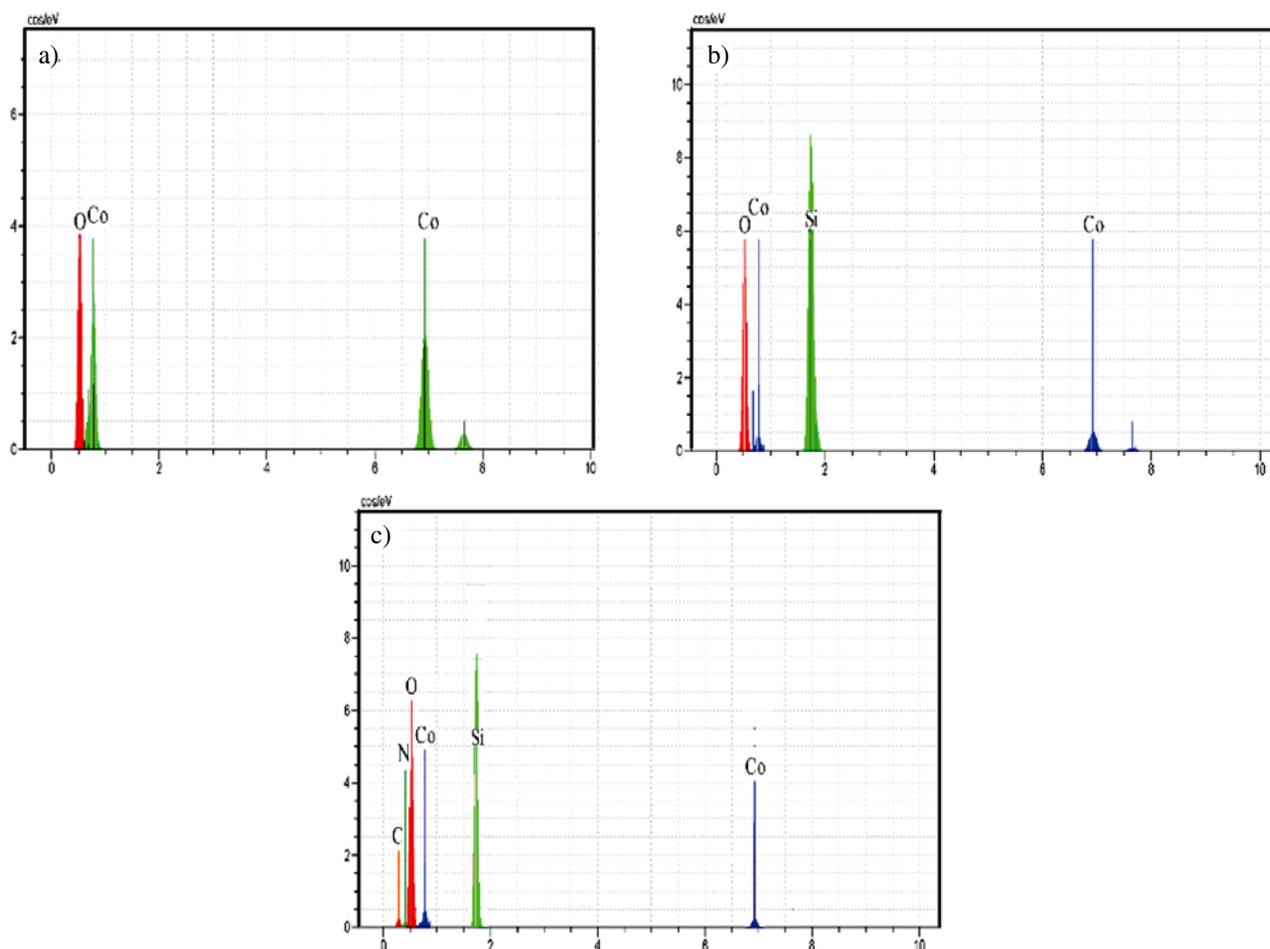


Figure 3. EDX spectra of Co_3O_4 (a), $\text{Co}_3\text{O}_4@SiO_2$ (b) and $\text{Co}_3\text{O}_4@SiO_2-NH_2$ (c) MNPs.

ascribed to the stretching of non-bridging oxygen atom in Si–OH bond. Therefore the silica coating on the surface of Co_3O_4 nanoparticles were confirmed by these absorption bands (Figure 2b and 2c). As indicated in Figure 2c, the peaks of $\text{Co}_3\text{O}_4@SiO_2@NH_2$ are located at 1480 cm^{-1} (C–H bending), 2880 cm^{-1} (C–H stretching), 1645 cm^{-1} (N–H bending), and 3360 cm^{-1} (N–H stretching). These peaks indicated that APTES has been bonded with the surface of $\text{Co}_3\text{O}_4@SiO_2$. The characteristic peaks of C–H stretching and N–H bending for the synthesized $\text{Co}_3\text{O}_4@SiO_2@NH_2$ are too weak to be observed clearly. Therefore, another analytical method, EDX, was employed to prove that the amine group has been bonded on the surface of $\text{Co}_3\text{O}_4@SiO_2$.^{26–28}

Figure 3 shows the EDX data for Co_3O_4 , $\text{Co}_3\text{O}_4@SiO_2$, $\text{Co}_3\text{O}_4@SiO_2@NH_2$ MNPs. In Figure 3 c, the weight ratio for C : N : O : Si : Co was calculated to be 12 : 3.5 : 36 : 6.5 : 42. These data demonstrate formation of $\text{Co}_3\text{O}_4@SiO_2@NH_2$ nanocomposite.

Figure 4 represents the room-temperature magnetization curves of the Co_3O_4 , $\text{Co}_3\text{O}_4@SiO_2$ and $\text{Co}_3\text{O}_4@SiO_2-NH_2$ MNPs which have been obtained using a VSM. As it can be observed, there are no hysteresis, coercivity

and remanence in the three synthesized nanoparticles which indicate their typical superparamagnetic property. The plots which have been shown in Figure 4 exhibited a change in saturation magnetization (M_s) of the particles

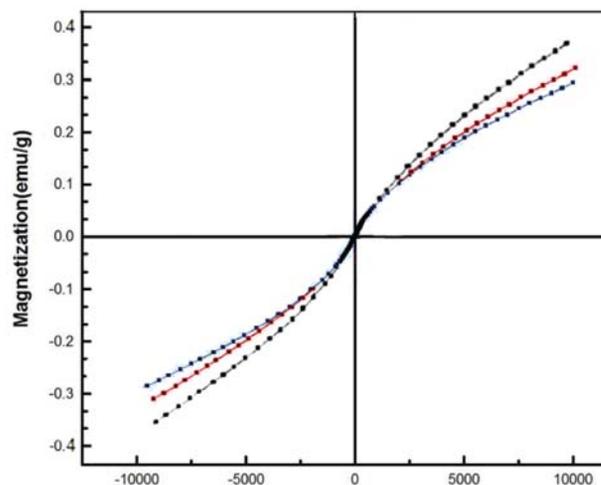


Figure 4. VSM magnetization curves of the Co_3O_4 (a), $\text{Co}_3\text{O}_4@SiO_2$ (b) and $\text{Co}_3\text{O}_4@SiO_2-NH_2$ (c) MNPs.

after incorporation of a NH_2/SiO_2 shell. The M_s values were measured to be 47.1, 36.9 and 33.8 emu/g respectively. It is clear that saturation magnetization of silica-coated Co_3O_4 nanoparticles is lower than that of pristine Co_3O_4 nanoparticles, and saturation magnetization of $\text{Co}_3\text{O}_4@/\text{SiO}_2-\text{NH}_2$ is lower than $\text{Co}_3\text{O}_4@/\text{SiO}_2$. This reduction in saturation magnetization can be attributed to the surface effects such as magnetically inactive layer which contains spins that are not collinear with the magnetic field.²⁹ Because the silica coating is a nonmagnetic mass, and this decrease was ascribed to the contribution of the nonmagnetic NH_2/SiO_2 shell to the total mass of the particles.

Figure 5 shows TEM image of amino-functionalized SiO_2 coated Co_3O_4 nanoparticles. Typical size of the

structure has been measured about 50 nm, and the aggregation of the nanoparticles can be observed clearly. Therefore, the TEM observation confirmed the formation of an amino-functionalized SiO_2 around the Co_3O_4 nanoparticles with typical nanostructure.

The scanning electron microscopy (FE-SEM) of the $\text{Co}_3\text{O}_4@/\text{SiO}_2@/\text{NH}_2$ MNPs shows the morphology and structure of the as-prepared samples (Figure 6). The Co_3O_4 nanoparticles are irregular sheets (non-spherical) in shape and hard aggregated powders with diameters ranging from 35 to 80 nm as seen in Figure 6a. The irregular Bullet-shaped $\text{Co}_3\text{O}_4@/\text{SiO}_2$ nanoparticles with diameters ranging from 95 to 220 nm are shown in Figure 6b. This illustrated that SiO_2 has been successfully coated on the Co_3O_4 nanoparticles. The micrograph of

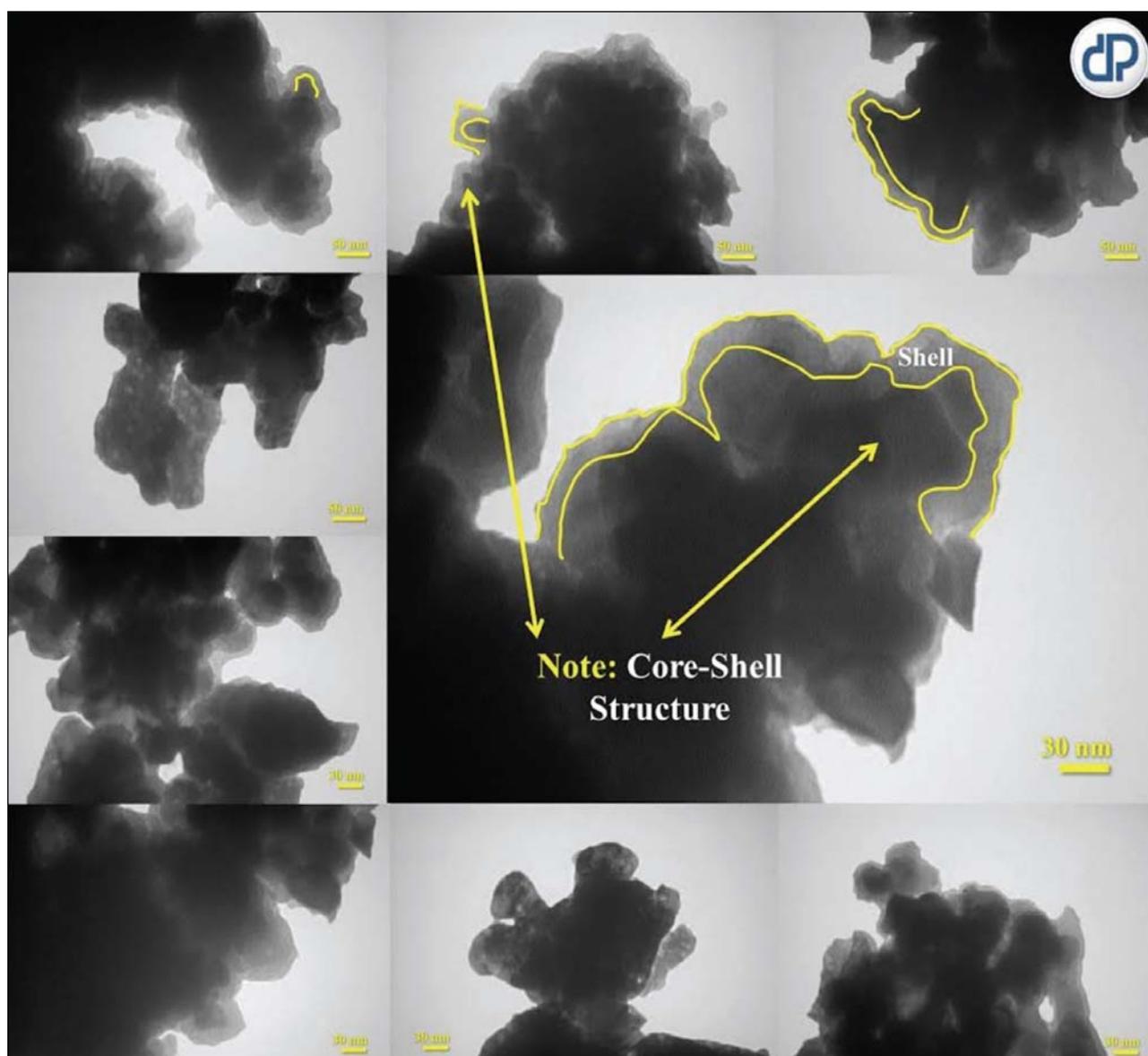


Figure 5. TEM images of $\text{Co}_3\text{O}_4@/\text{SiO}_2@/\text{NH}_2$ MNPs

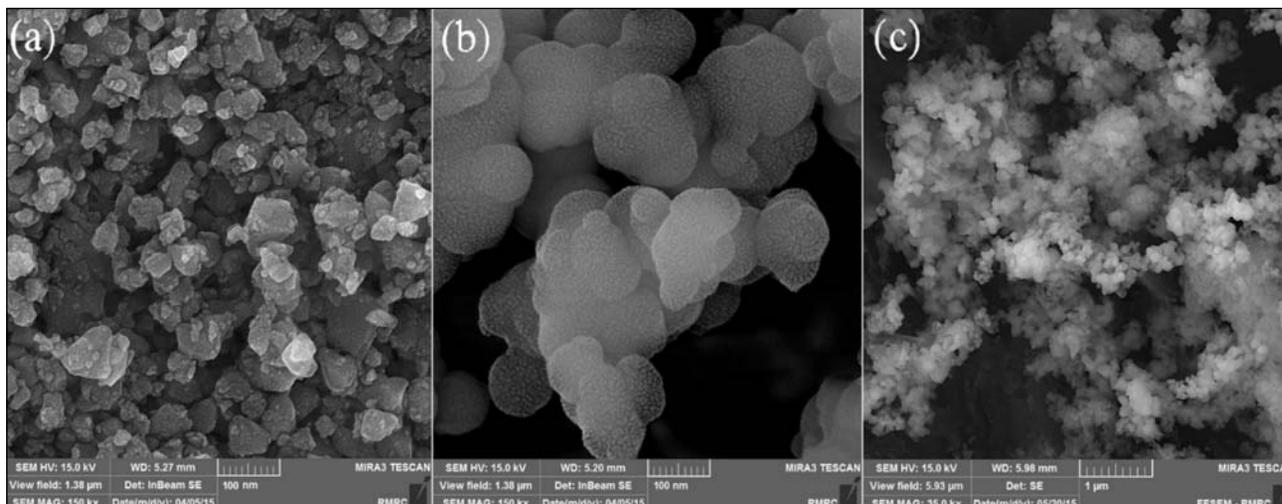


Figure 6. SEM images of Co_3O_4 (a), $\text{Co}_3\text{O}_4@SiO_2$ (b) and $\text{Co}_3\text{O}_4@SiO_2-NH_2$ (c) MNPs.

$\text{Co}_3\text{O}_4@SiO_2@NH_2$ MNPs represents a cloudy network of particles with spherical shape, as indicated in TEM image. This network is the result of self-poly condensation of aminopropylsilane groups.

3. 2. Catalyst Testing for the Synthesis of Some 7-benzylidene-2,3-diphenyl-3,3a,4,5,6,7-hexahydro-2H-indazole Derivatives

In order to optimize the reaction conditions and to obtain the best catalytic activity, the synthesis of 7-benzylidene-2,3-diphenyl-3,3a,4,5,6,7-hexahydro-2H-indazole derivatives was chosen as a model reaction. The reactions were conducted under solvent-free conditions at 80 °C (Scheme 2).

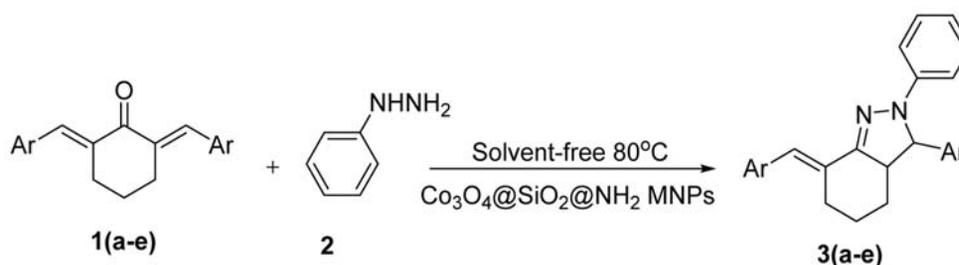
The synthesis of 7-benzylidene-2,3-diphenyl-3,3a,4,5,6,7-hexahydro-2H-indazoles with different amounts of the $\text{Co}_3\text{O}_4@SiO_2@NH_2$ MNPs has been considered. It was observed that while the amount of catalyst increased from 0 to 0.003 g, the product yield raised from 0% to 98% significantly. No reaction yield without using the catalyst corroborates that the $\text{Co}_3\text{O}_4@SiO_2@NH_2$ MNP catalyst plays a pivotal role in the synthesis of 7-benzylidene-2,3-diphenyl-3,3a,4,5,6,7-hexahydro-2H-indazole derivatives.

In the respect of industrial aims, reusability of the catalyst was examined by repeating the model reaction under the optimized reaction conditions (Table 1). In order to reuse the catalyst after each cycle, it was separated by a magnet, washed several times with deionized water and chloroform. Then, it was dried in oven at 60 °C and reused in the next run. According to the results, the $\text{Co}_3\text{O}_4@SiO_2@NH_2$ MNPs can be reused six times without any significant loss of activity in this organic reaction. Moreover, nitrogen content of the catalyst was estimated by back titration after sixth cycle (5.72 mmol/g), which indicates low NH_2 leaching during the reaction.

Table 1. Reusability of the $\text{Co}_3\text{O}_4@SiO_2-NH_2$ nanocomposite

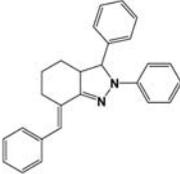
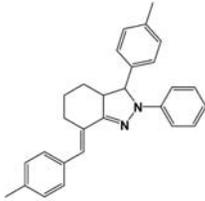
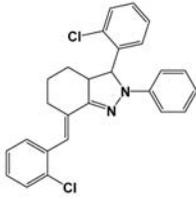
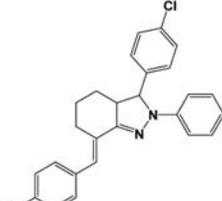
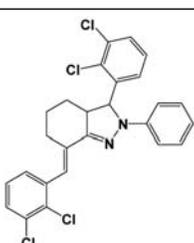
Yield (%)					
First	Second	Third	Fourth	Fifth	Sixth
98	96	95	92	91	87

In order to evaluate scope of this research, we tried to prepare a range of 7-benzylidene-2,3-diphenyl-3,3a,4,5,6,7-hexahydro-2H-indazole derivatives under the same reaction conditions. The results are presented in (Table 2).³⁰



Scheme 2. The model reaction for the synthesis of 7-benzylidene-2,3-diphenyl-3,3a,4,5,6,7-hexahydro-2H-indazole

Table 2. $\text{Co}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2$ catalyzed synthesis of some indazoles^a

Entry	Product ^b	Time (min)	Yield (%) ^c	Lit. M.p. ^{°C}	M.p. ^{°C}
1	 3a	17	94	136–138 ³⁰	136–136
2	 3b	20	91	141–143 ³⁰	142–144
3	 3c	15	93	156–158 ³⁰	155–157
4	 3d	12	96	174–176 ³⁰	174–176
5	 3e	10	98	202–204 ³⁰	200–202

^a Reaction conditions: phenyl hydrazine (1 mmol), α, α' -bis (substituted-arylidene) cycloalkanone (1 mmol), catalyst (0.003 g, $\text{Co}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2$), under solvent-free conditions at 80 °C ^b Products were characterized by FT-IR, ¹H NMR and ¹³C NMR analysis ^c Isolated yield.

4. Conclusions

In this research, Co_3O_4 nanoparticles were coated with amino-functionalized SiO_2 as organic shell via three step method. The average crystallite size of the Co_3O_4 was calculated 23.7 nm, by using the Scherrer equation. The synthesized nanocomposite exhibited super paramagnetic behaviour at room temperature because of the magneti-

cally inactive layer of $\text{SiO}_2@ \text{NH}_2$. The saturation magnetization of $\text{Co}_3\text{O}_4@ \text{SiO}_2@ \text{NH}_2$ MNPs is less than that of pure Co_3O_4 nanoparticles. This new magnetic nanocomposite showed the following advantages: (a) simple preparation; (b) recoverability and easy separation by an external magnet, c) highly effective for chemical transformations as a heterogeneous catalyst. These unique results open new perspectives for application of these types of

magnetic nanocomposites in many reactions. Moreover, we have developed a facile, convenient and environmentally benign synthesis of some 7-benzylidene-2,3-diphenyl-3,3a,4,5,6,7-hexahydro-2H-indazole derivatives by utilizing novel nano-scale materials including $\text{Co}_3\text{O}_4 @ \text{SiO}_2 @ \text{NH}_2$ nanocomposite.

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Povzetek

V tej raziskavi poročamo o učinkoviti sintezni poti v treh stopnjah s katero smo pripravili nov nanokompozit kobaltovega oksida (Co_3O_4) prevlečen s $\text{SiO}_2 @ (3\text{-aminopropil})\text{-trietoksisilanom}$. Strukturne in magnetne lastnosti kompozita $\text{Co}_3\text{O}_4 @ \text{SiO}_2 @ \text{NH}_2$ smo določili s pomočjo različnih metod: infrardečo spektroskopijo (FT-IR), rentgensko praškovo difrakcijo, vrstično elektronsko mikroskopijo (SEM), presevno elektronsko mikroskopijo (TEM), energijsko disperzijsko spektroskopijo (EDX) in magnetometrijo z vibrirajočim vzorcem (VSM). V nanokompozitu Co_3O_4 , ki je prevlečen z amino funkcionaliziranim SiO_2 je opaziti superparamagnetne lastnosti in močno magnetizacijo pri sobni temperaturi. Povprečne velikosti kristalitov Co_3O_4 so 23,7 nm. Dobljeni magnetni nanokompozit je pokazal odlično katalitsko aktivnost kot novi heterogeni magnetni katalizator za sintezo nekaterih derivatov indazola pri blagih reakcijskih pogojih in visoko stopnjo ponovne uporabe.