

# Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C Composite with Magnetic Core and Au Enwrapped in Double-Shelled Carbon: An Excellent Catalyst in the Reduction of Nitroarenes and Suzuki–Miyaura Cross-Coupling

Minoo Dabiri<sup>1</sup> · Noushin Farajinia Lehi<sup>1</sup> · Siyavash Kazemi Movahed<sup>1</sup>

Received: 6 March 2016/Accepted: 12 June 2016 © Springer Science+Business Media New York 2016

Abstract Magnetic core double-shelled carbon with  $Fe_3O_4$  nanoparticles as the core, reduced graphene oxide (RGO) as the inner shell and carbon (C) layer as the outer shell, have been successfully designed and prepared. This tailor-making structure acts as an excellent capsule for encapsulating Au nanoparticles (Au NPs), which could effectively prevent Au NPs from aggregation and leaching. Because of its structural features, magnetic coredouble-shell  $Fe_3O_4@RGO@Au@C$  architecture exhibits

extremely high catalytic performance on two different kinds of organic reactions (1) reduction of nitroarenes, and (2) Suzuki–Miyaura cross coupling of phenyl boronic acid with aryl halides. Moreover, the synthesized catalyst can be easily recovered and reused for at least ten cycles due to its magnetically separable feature and good stability.

### **Graphical Abstract**



**Electronic supplementary material** The online version of this article (doi:10.1007/s10562-016-1792-8) contains supplementary material, which is available to authorized users.

Keywords Heterogeneous catalysis  $\cdot$  Suzuki reaction  $\cdot$  Nanostructure  $\cdot$  Reduction

Minoo Dabiri m-dabiri@sbu.ac.ir

<sup>&</sup>lt;sup>1</sup> Faculty of Chemistry, Shahid Beheshti University, Tehran 1983969411, Islamic Republic of Iran

#### 1 Introduction

In recent years, the design of magnetic nanoparticles (MNPs) has become important because of fundamental scientific interest in MNPs and in their various cutting-edge technological applications, including their use as magnetic fluids, magnetic storage media, biomedicine, magnetic recording devices, biosensors, targeted drug delivery, separation, contrast enhancement agents for magnetic resonance imaging (MRI), bioprobes, and catalysis [1, 2]. Among these, the application of magnetic NPs as a catalyst support has received increasing interest in recent decades because they can be easily prepared from inexpensive precursors, give the excellent dispersion in the reaction mediums owing to their nanosizes, and can be simply separated from the reaction mixture by employing an external magnetic field. As a result, the magnetic NP-based catalysts can potentially provide a unique, environmentally acceptable catalytic route for organic transformations by combining high activity with easy recyclability [3].

Recently, much attention has been paid on the synthesis of Fe<sub>3</sub>O<sub>4</sub> NPs/graphene as a new kind of hybrid material, owing to wide-ranging applications such as immobilizing bioactive substances, energy storage and environmental remediation [4-6]. The unique properties of Fe<sub>3</sub>O<sub>4</sub> NPs/graphene hybrids, combining characteristics of graphene as a polycyclic aromatic molecule, which has high conductivity, low price, high chemical inertness, and large specific surface area [7-9], and Fe<sub>3</sub>O<sub>4</sub> NPs, with high magnetism, low-cost, and environmentally benign nature [10–14], open a new window for fabricating most stable multifunctional nanomaterials using these hybrids as support materials. In addition, Fe<sub>3</sub>O<sub>4</sub> has already been introduced as a suitable support for preparing highly active metal catalysts, and immobilizing noble metal nanocatalysts on magnetic Fe<sub>3</sub>O<sub>4</sub> support prevents agglomeration of the catalyst particles during recovery and can be increasing catalyst durability [15, 16]. Therefore, a combination of Fe<sub>3</sub>O<sub>4</sub> NPs and graphene may optimize both dispersion and catalytic activity of metal NPs.

There have been many efforts toward synthesizing highly dispersed supported Au NPs. The catalytic performance of Au NPs-support strongly depends on the size and shape of Au NPs, the nature of the support, and the Au NPs-support interface interaction [17]. The  $\pi$ -interaction of aromatic rings of the supports with gold nanoparticles leads to nanoparticle stabilization and improve the catalyst performance in a variety of gold catalyzed reactions [18]. Graphene is an ideal candidate because of its a two-dimensional sheet of sp<sup>2</sup> bonded carbon atoms, which can be viewed as an extra-large polycyclic aromatic molecule and large specific surface area [18]. Therefore graphene as a polycyclic aromatic molecule is a potential candidate as both support and stabilizer of Au NPs for chemical transformations. For instance, Li et al. synthesized Au/graphene hydrogel under hydrothermal conditions through the selfassembly process. Exhibited excellent catalytic performance towards the reduction of 4-Nitrophenol (4-NP) to 4-Aminophenol (4-AP), which is arising from the synergistic effect of graphene with Au NPs [19]. Additionally, Wang and co-workers synthesized rGO/Fe<sub>3</sub>O<sub>4</sub>/Au nanocomposite with highly dispersed Au NPs and Fe<sub>3</sub>O<sub>4</sub> particles by a facile hydrothermal method. This graphene/ Au nanocomposite display good stability against agglomeration and show excellent catalytic activity in the reduction of 4-NP into 4-AP [20].

Recently, Zhang et al. [21] have reported new doubleshelled hollow carbon spheres with reduced graphene oxide (RGO) as inner shell and carbon (C) layer as outer shell. This tailor-making structure acts as an excellent capsule for encapsulating with ultrafine Pd NPs, which could effectively prevent Pd NPs from aggregation and leaching. (Scheme 1a). The as-obtained RGO@Pd@C nanohybrid exhibits superior and stable catalytic performance on the reduction reaction of 4-NP to 4-AP.

Herein, we report for the first time the design and synthesis of magnetic core/double-shelled reduced graphene oxide@gold@carbon (Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C) with the RGO as the inner and amorphous C as the outer shells. Graphene is a two-dimensional sheet of sp<sup>2</sup> bonded carbon atoms, which can be viewed as an extra-large polycyclic aromatic molecule. Recently, graphene has been used as the support for metals and metal oxides, mainly because of its large surface area, excellent electrical and thermal conductivity, low price, high chemical inertness, ease of modification and strong interactions with metal clusters [22–24]. Au NPs grow well on the surface of inner shell by spontaneous redox reaction between graphene oxide (GO) and HAuCl<sub>4</sub> [25]. Moreover, the outer shell combined with the inner shell, confines Au NPs in itself, effectively prevents the aggregation and leaching of Au NPs and increases their catalytic active area, therefore, enhancing their stability and catalytic.

#### 2 Experimental

#### 2.1 Characterization

Diffraction data were collected on a STOE STADI P with scintillation detector, secondary monochromator and Cu-Ka1 radiation ( $\lambda = 1$ . 5406 Å). XPS analysis was performed using a Gammadata-scienta ESCA 200 hemispherical analyzer equipped with an Al Ka (1486.6 eV)



Scheme 1 Schematic diagram illustrating the synthesis of a RGO@Pd@C hollow sphere b magnetic core/double-shell  $Fe_3O_4@RGO@Au@C$  CDSNs architectures

X-ray source. Scanning electron microscope of nanocomposites were performed using an electron microscope Philips XL-30 ESEM. Transmission Electron Microscopy characterization of nanocomposites were performed using a transmission microscope Philips CM-30 with an accelerating voltage of 150 kV, Zeiss EM10C transmission electron microscope with an accelerating voltage of 80 kV and JEOL JEM-2100 transmission electron microscope with an accelerating voltage of 200 kV. The concentration of gold was estimated using Shimadzu AA-680 flame atomic absorption spectrophotometer and inductively coupled plasma optical emission spectrometer (ICP-OES) Varian Vista PRO Radial. The thermal stability of the Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C YSNs was determined using a thermogravimetric analyzer (TGA/DTA BAHR: STA 503) under air and a heating rate of 10 °C min<sup>-1</sup>. The magnetic

properties of the prepared nanocomposites were measured using a homemade vibrating sample magnetometer (Meghnatis Daghigh Kavir Company, Iran) at room temperature from -8000 to +8000 Oe. The nitrogen adsorption-desorption isotherm of Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C YSNs collected by using a Micrometrics PHSwas 2828(PHSCHINA) surface area analyzer with N2 at 77.3 K. UV/Vis spectra were recorded employing an Analytik Jena Specord S600 Diode Array spectrometer. Gas chromatography was performed on a Trace GC ultra from the Thermo Company equipped with FID detector and Rtx<sup>®</sup>-1 capillary column. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were recorded spectra on a BRUKERDRX-300AVANCEspectrometer at 300.13 and 75.03 MHz, respectively. <sup>1</sup>H-NMR spectra were obtained in DMSO- $d_6$ using TMS as internal standard. Melting points of products were measured on an Elecrtothermal 9100 apparatus and are uncorrected.

### **3** Materials

#### 3.1 Synthesis of Fe<sub>3</sub>O<sub>4</sub> Microsphere

The magnetic particles were synthesized through a solvothermal reaction according to the method reported by Zhao et al. [26] with some modification. In a typical procedure, 1.08 g of FeCl<sub>3</sub>·6H<sub>2</sub>O was first dissolved in 20 mL of ethylene glycol under magnetic stirring until the solution became clear. Then 2.99 g of sodium acetate.3H<sub>2</sub>O was added to this solution and stirred for another 1 h. Afterwards, 0.29 g trisodium citrate.2H<sub>2</sub>O was added. When the mixed solution was stirred for 5 h to form a homogeneous dispersion, the resulting solution was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 50 mL. The autoclave was sealed and heated at 200 C for 12 h and naturally cooled to 25 °C. The black particles were collected with the help of a magnet, followed by washing with ethanol and deionized water several times, and then dried under vacuum at 60 °C overnight [27].

# 3.2 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> Core–Shell Nanoparticle

Firstly,  $Fe_3O_4$  microspheres (500 mg) were added to a mixture of de-ionized (DI) water (150 mL), NH<sub>3</sub>.H<sub>2</sub>O (50 mL) and ethanol (1500 mL), and sonicated for 4 h at 25 °C. Secondly, tetraethylorthosilicate (TEOS) (0.75 mL) was dissolved in ethanol (250 mL). Thirdly, TEOS/ethanol mixture (50 mL) was injected into Fe<sub>3</sub>O<sub>4</sub> suspension at every 10 min interval under sonication, and the same procedures repeated for five times. After that, the mixture was further sonicated for 70 min. The obtained products were separated by a magnet and washed several times with ethanol [28].

# 3.3 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@GO Core-Shell Nanoparticle

In a typical synthesis, 0.2 g of  $Fe_3O_4@SiO_2$  core-shell nanoparticle were firstly dispersed in 100 mL ethanol by sonication for 20 min. Next, 1 mL of 3-aminopropyltrimethoxysilane was added and refluxed for 5 h to get amine-functionalized  $Fe_3O_4@SiO_2$  core-shell nanoparticle. Then the products were separated by a magnet and rinsed with ethanol to wash away the unreacted 3-aminopropyltrimethoxysilane. After that, the 30 mL of 0.2 mg/ mL GO aqueous solution was added and the mixture was stirred vigorously for 1 h. Finally, the products were collected by centrifugation, washed with DI water for several times, and then dried at 60  $^{\circ}$ C overnight.

# 3.4 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@GO@Au Nanocompiste

150 mg of as-synthesized  $Fe_3O_4@SiO_2@GO$  core-shell nanoparticle were dispersed in 60 mL of DI water, then 3 mL of 20 mM HAuCl<sub>4</sub> aqueous solution was added and the mixture was kept in a vial under vigorous stirring for 3 h in an ice bath (0 °C). The products were centrifuged and washed with DI water to remove the remaining reagents followed by drying at 60 °C overnight.

# 3.5 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@RGO@Au@C Nanocompiste

150 mg of as-prepared  $F_{e3}O_4@SiO_2@GO@Au$  nanocompiste were dispersed in 16 mL water/ethanol (volume ratio = 3/1) mixture by ultrasonication, then 4 mL of 0.5 M aqueous glucose solution was added under vigorous stirring for 30 min. After that, the suspension was transferred to a 25 mL Teflon-lined autoclave, and heated in an oven at 180 °C for 16 h. The dark gray products were collected by a magnet and washed with ethanol and DI water for six times, respectively. After drying at 60 °C overnight, the resulting dark brown powder was carbonized at 500 °C for 4 h under N<sub>2</sub> atmosphere.

# 3.6 Synthesis of Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C Core-Shell Nanoparticle

150 mg of as-prepared Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@RGO@Au@C nanocompiste were dispersed in 500 mL of 0.5 M NaOH by ultrasonication and stirred for 24 h at 25 °C. Finally, the products were collected by a magnet and washed with DI water for several times, and then dried at 60 °C overnight. Additionally, the loading level of the immobilized gold was measured to be 0.092 mmol  $g^{-1}$  by inductively coupled plasma-optical emission spectrometry (ICP-OES).

#### 3.7 Preparation of GO

The graphite powder (2.5 g) was first treated with a mixture of 12.5 mL of concentrated  $H_2SO_4$  with 2.5 g  $K_2S_2O_8$ and 2.5 g  $P_2O_5$ . The mixture was kept at 80 °C for 6 h. Subsequently, the mixture was cooled to 25 °C and diluted with 500 mL DI water and left overnight. The mixture was then filtered and washed with DI water to remove the residual acid. The product was dried under ambient conditions overnight. The pre-oxidized graphite was then subjected to oxidation by Hummers's method. The pretreated graphite powder was put into cold (0 °C) concentrated H<sub>2</sub>SO<sub>4</sub> (125 mL). Then KMnO<sub>4</sub> (15 g) was added gradually under stirring, and the temperature of the mixture was kept below 20 °C by cooling. The mixture was then stirred at 35 °C for 4 h and then diluted with DI water (250 mL). Because adding water to concentrated sulfuric acid medium releases a large amount of heat, the dilution was carried out in an ice bath to keep the temperature below 50 °C. After adding all of the 250 mL DI water, the mixture was stirred for 2 h, and then an additional 750 mL DI water was added. Shortly thereafter, 20 ml 30 % H<sub>2</sub>O<sub>2</sub> was added to the mixture and the color of the mixture changed into brilliant yellow and began bubbling. The mixture was filtered and washed with 0.5 M HCl to remove metal ions, followed by 500 mL DI water to remove the acid, and then was dialyzed against DI water. The resulting GO solid was dried in air [29, 30].

#### 3.8 General Procedure for the Reduction of 4-NP

The reduction of 4-NP by NaBH<sub>4</sub> was chosen as a model reaction to investigate the catalytic performance of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@GO@Au Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@RGO@Au@C and Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C nanostructures. In short 30 mL of 4-NP (0.12 mM) were mixed with 30 mL of a freshly prepared aqueous NaBH<sub>4</sub> solution (0.17 M). Then nanocomposite (2 mol% of Au) was added to the resulting solution and the reaction was allowed to proceed until the solution became colorless. The reaction conversion was determined by ultraviolet visible spectroscopy (UV-Vis). After completion of the reaction the heterogeneous mixture was cooled to room temperature and the catalyst was separated. Then the reaction mixture was extracted by ethylacetate  $(15 \times 3 \text{ ml})$  and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>.

# 3.9 General Procedure for Suzuki-Miyaura Cross-Coupling

A mixture of nanocomposite  $(2 \text{ mol}\% \text{ of Au}) \text{ K}_3\text{PO}_4$ (3 mmol) aryl halide (1.0 mmol) phenyl boronic acid (1.3 mmol) and H<sub>2</sub>O (3 mL) under air was stirred for 12 h at 100 °C. The reaction progress was monitored by gas chromatography (GC). After completion of the reaction the heterogeneous mixture was cooled to 25 °C and the catalyst was separated from the reaction medium by using an external magnet. Then the reaction mixture was concentrated and then the residue was purified by thin layer chromatography (SiO<sub>2</sub> *n*-Hexane) to yield pure product. The catalysts were recovered by using an external magnet and washed extensively with acetone and deionized water and drying in the air.

#### **4** Results and Discussion

The synthetic procedure of Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C CDSNs is illustrated in scheme 1b. The magnetite particles were synthesized via a modified solvothermal reaction of FeCl<sub>3</sub> in the presence of sodium acetate and trisodium citrate [27]. Then, magnetite nanoparticles were coated with silica through classical Stober method using tetraethyl orthosilicate (TEOS) as a precursor [28]. The  $Fe_3O_4@SiO_2$  coreshell nanoparticles were modified by 3-aminopropyltrimethoxysilane (APTMS) in order to introduce amine groups on their surface. Subsequently, the amino-functionalized  $Fe_3O_4@SiO_2$  is wrapped by the GO layer through the electrostatic reaction and hydrogen bonds between the amino group and the oxygen-containing groups on GO sheets. Next, the Au NPs were deposited on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@GO nanocomposite by a facile and green method via a spontaneous redox reaction between HAuCl<sub>4</sub> and GO. Then, the C precursor layers were coated on the surface of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@GO@Au nanocomposite by the pyrolysis of glucose under hydrothermal conditions [21]. The as-obtained product is then dried and heated at 500 °C under inert atmosphere to carbonize the C precursor shell. During this process, the GO layer is partially converted to the reduced graphene oxide by thermal reduction [21, 31]. Finally, the SiO<sub>2</sub> layers were etched by NaOH solution and the magnetic core/double shelled Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C CDSNs were obtained.

The morphologies of the intermediate and final products were characterized by the transmission electron microscope (TEM). From Fig. 1a, b, it is seen that  $Fe_3O_4@SiO_2$ core-shell nanoparticles are tightly coated with the GO sheet. Figure 1c, d shows TEM micrographs of Fe<sub>3</sub>O<sub>4</sub> @SiO<sub>2</sub>@GO@Au nanocomposite. The surfaces of Fe<sub>3</sub>O<sub>4</sub> @SiO<sub>2</sub>@GO nanocomposite are covered with good dispersion of Au NPs. The mechanism of the spontaneous reductive deposition process that generates Au NPs on the GO sheets likely involves a galvanic displacement and redox reaction because of the relative potential difference between the reduction potential of  $AuCl_4^{-1}$  (0.76 V vs. SCE) and the oxidation potential of GO (0.48 V vs. SCE) [25]. After the pyrolysis of glucose under hydrothermal conditions and following calcination, the C shell covered around Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@GO@Au nanocomposite (Fig. 1e, f). The size of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@GO@Au nanocomposites are about 120-140 nm. Additionally, the thickness of carbon layer is about 4-5 nm.

After the removal of the sacrificial silica layer by NaOH solution,  $Fe_3O_4@RGO@Au@C$  CDSNs were. The high resolution-transmission electron microscope (HR-TEM) micrograph  $Fe_3O_4@RGO@Au@C$  CDSNs is shown in Fig. 2c. The chemical composition of the  $Fe_3O_4@RGO@Au@C$ 



Fig. 1 TEM micrographs of a, b Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@GO, c, d Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@GO@Au, e, f Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@RGO@Au@C nanostructures

CDSNs is determined using energy dispersive spectroscopy (EDS) analysis. We predict that the final nanostructure is the yolk-double shell structure, and the estimated nanostructure size will be about 120–140 nm. But the size of the final structures is smaller than the predicted size that is 70–90 nm. The Fe<sub>3</sub>O<sub>4</sub> core is wrapped by RGO layer due to the decreasing size of the final structures [32–34]. The EDS analysis in Fig. 2e clearly shows the sample consists mainly of Fe and the presence of C and Au in the CDSNs.

Additionally, the morphologies of the intermediate and final products were characterized by the scanning electron microscope (SEM) and shown in Fig. 3. From Fig. 3a, it is seen that  $Fe_3O_4@SiO_2$  core-shell nanoparticles are wrapped with the GO sheets.

The porous nature of  $Fe_3O_4@RGO@Au@C$  CDSNs is evaluated by nitrogen physisorption measurements. The specific surface area is calculated from the adsorption isotherms based on the Brunauer–Emmett–Teller (BET) analysis. It is found that the isotherm of  $Fe_3O_4@$ RGO@Au@C CDSNs is the type IV according to the IUPAC classification with a distinct hysteresis loop of the H3 type (Fig. 4a). The distinct H3 hysteresis loop indicates that the pores in the carbon shell directly open into the hollow interior of double shell, supporting the idea that a guest molecule could quickly diffuse into the hollow space without any obstacle [35]. The BET total surface area of  $Fe_3O_4@RGO@Au@C$  CDSNs is found to be 221 m<sup>2</sup> g<sup>-1</sup>. The average pore size diameter of  $Fe_3O_4@RGO@Au@C$  CDSNs is calculated to be 2.57 nm using Barrett–Joyner–Halenda (BJH) analysis (Fig. 4b).

As the magnetic  $Fe_3O_4$  core is residing inside the double-shell RGO and C CDSNs, the magnetic property of the obtained CDSNs is characterized (Fig. 5). The saturation magnetization values were measured to be 20.39 and

Fig. 2 TEM micrographs of a, b Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C CDSNs, c HR-TEM micrographs of Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C CDSNs, d SAED pattern and e EDS spectrum of Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C CDSNs



56.25 emu g<sup>-1</sup> for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@RGO@Au@C and Fe<sub>3</sub>. O<sub>4</sub>@RGO@Au@C nanostructures, respectively. The obvious increase in the Ms value of the Fe<sub>3</sub>O<sub>4</sub>@ RGO@Au@C CDSNs is attributed to the removal of the SiO<sub>2</sub> template [36].

Thermogravimetric analysis (TGA) is further used to study the thermal behaviour and stability of the Fe<sub>3</sub>O<sub>4</sub>@ RGO@Au@C CDSNs. This CDSNs showed high thermal stability (Fig. 6). The total weight lost for Fe<sub>3</sub>O<sub>4</sub>@ RGO@Au@C CDSNs is only 9.86 % at temperatures 600 °C.

The electronic properties of Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C CDSNs is probed by XPS analysis. As shown in Fig. 7a, the peaks corresponding to Au 4d and 4f, C 1 s, Fe 2p & 2 s, and O 1 s, are clearly observed in the XPS full spectrum. The XPS spectrum of Au 4f core for Fe<sub>3</sub>O<sub>4</sub>@ RGO@Au@C CDSNs level displays main peaks at 82.02 and 86.50 eV which correspond to the binding energy of Au<sup>0</sup> 4f<sub>7/2</sub> and Au<sup>0</sup> 4f<sub>5/2</sub>, respectively (Fig. 7b). From the Fe 2p XPS scan shown in Fig. 7c, the two peaks at 724.38 and

710.52 eV, are assigned to Fe  $2p_{1/2}$  and Fe  $2p_{3/2}$  for Fe<sub>3</sub>O<sub>4</sub>, respectively. Additionally, the absence of Si in XPS analysis of Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C CDSNs corroborates the removal of SiO<sub>2</sub> layer by NaOH.

X-ray diffraction (XRD) patterns of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@GO, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@GO@Au, Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>@GO@Au@C, and Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C nanostructures are illustrated in Fig. S1. XRD pattern of Fe<sub>3</sub> O<sub>4</sub>@RGO@Au@C CDSNs, the diffraction peak positions at  $2\theta = 30.11$ , 35.64, 43.35, 53.77, 57.33, 62.95, and 74.39 can be attributed to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (5 3 3) planes of Fe<sub>3</sub>O<sub>4</sub>, respectively. Additionally, the diffraction peak positions at  $2\theta = 38.25$ , 44.48, 64.62, and 77.75, can be attributed to (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes of Au, respectively.

After careful investigation of the  $Fe_3O_4@RGO@Au@C$ CDSNs prepared, it is tested for catalyzing two different kinds of organic reactions (*i*) reduction of nitroarenes, and (*ii*) Suzuki cross coupling of phenyl boronic acid with aryl halides.



Fig. 3 SEM micrographs of a  $Fe_3O_4@SiO_2@GO$ , b  $Fe_3O_4@SiO_2@GO@Au$ , c  $Fe_3O_4@SiO_2@RGO@Au@C$  and d, e  $Fe_3O_4@RGO@Au@C$  nanostructure

As shown in Fig. 8a, the pure of 4-NP solution exhibited a distinct absorption maximum at 317 nm, which shifts to 400 nm in the presence of an alkali because of the formation of 4-nitrophenolate ion. It is found that the intensity of the characteristic absorption peak of 4-nitrophenolate ion at 400 nm quickly decreases, and the characteristic absorption of 4-AP at around 300 nm also appears rapidly (Fig. 8b-d). The reaction kinetics could be analyzed and confirmed from the timedependent absorption spectra, which showed the gradually decrease of 4-nitrophenolate ion. Linear relationships between  $\ln(C_t/C_0)$  and reaction time is obtained in the reduction reaction catalyzed by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@GO@Au, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@RGO@Au@C, and Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C catalysts, which match well with the first-order reaction kinetics (Fig. 8e).

The rate constant k is calculated to be 0.033, 0.170 and 0.496 min<sup>-1</sup> for the reactions catalyzed by  $Fe_3O_4@$  SiO<sub>2</sub>@GO@Au, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@RGO@Au@C, and Fe<sub>3</sub>O<sub>4</sub>

@RGO@Au@C catalysts, respectively (Table 1). In case of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@GO@Au catalyst, during the reaction time GO reduced to RGO with NaBH<sub>4</sub> [37] so the actual catalyst is Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@RGO@Au. Therefore, the increase in the rate constant of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@RGO@ Au@C rather than Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@GO@Au (in actual state Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@RGO@Au) is related to addition of the outer carbon shell. Additionally, Ji et al. reported the carbon species have no influence on the structure of catalyst but enhance the stability and the activity of Au catalysts and also increase the organic reactants adsorptive ability [38]. Furthermore, the increase in the rate constant of Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C rather Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@ than RGO@Au@C can be related to the nanorattle structure characteristics, such as the large free reaction voids inside the CDSNs [39] and the catalytic activity of iron species. To prove the latter case, we have synthesized RGO@Au@C hollow spheres [40] and used for the reduction of 4-NP. The rate constant k is calculated to be



Fig. 4 a Nitrogen adsorption–desorption isotherm and b the corresponding pore size distribution curve of  $Fe_3O_4@RGO@Au@CCDSNs$ 

0.412 min<sup>-1</sup> for the reactions catalyzed by RGO@Au@C hollow spheres that show the magnetic core lead to the increase in the rate constant in Fe<sub>3</sub>O<sub>4</sub>@RGO@

Au@C CDSNs. This enhancement is similar to that reported by Lin et al. [41] using Au-Fe<sub>3</sub>O<sub>4</sub> heterostructures. The recyclability of the Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C CDSNs is also examined by the reduction of 4-nitrophenol. It is found that the recovery can be successfully achieved in twenty successive reaction runs (Fig. 8f). ICP-OES result of the used Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C CDSNs catalyst indicates the leaching of 0.5 % of gold in the reduction of 4-NP after twenty cycles.

We have further investigated the catalytic activity of Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C CDSNs for the reduction of a series of nitroarenes with structurally divergent functional groups (Table 2). Nitrobenzene yielded the desired aniline product in 120 min in 79 % yield (Table 2, entry1). 2-, 3- and 4-nitrophenols gave excellent yields of the corresponding anilines in a very short span of time (Table 2, entries 2-4). 3-NP is found to be the most reactive among all the three nitrophenols. One can conclude that as the reaction proceeds through the formation of nitrophenolate ion, the 4-nitrophenolate ion will be the most stable ion due to the delocalization of the oxygen's negative charge throughout the benzene ring making the system resonance stabilized. 2-NP is somewhat less stable than 4-NP because of less effective resonance coupled with the certain degree of steric effect. On the other hand, in 3-NP, the resonance effect is entirely absent other than through conjugation. So it is the least stable and the most reactive among all the three nitrophenols [39, 42]. Nitroarenes possessing electron-donating groups such as *p*-toluidine and *p*-anisidine also afforded excellent yield of the corresponding product (Table 2, entries 5–6).

In order to evaluate the catalytic results, we use the turnover frequency (TOF) to determine the efficiency of our structure catalyst for reduction of 4-NP and compared





Fig. 7 a Full range XPS spectrum of  $Fe_3O_4@RGO@Au@C$  CDSNs, b Au 4f and c Fe 2p, core level regions XPS spectra of  $Fe_3O_4@RGO@Au@C$  CDSNs, respectively



**Fig. 8** UV–Vis spectra of **a** 4-nitrophenol and 4-nitrophenolate, the reduction of 4-NP to 4-AP over **b**  $Fe_3O_4@SiO_2@GO@Au$ , **c**  $Fe_3$ - $O_4@SiO_2@RGO@Au@C$  and **d**  $Fe_3O_4@RGO@Au@C$ ; **e** plot of  $\ln(C_t/C_0)$  against the reaction time of the reduction of 4-NP over

Nanostrucutre	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @GO@Au	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @RGO@Au@C	Fe <sub>3</sub> O <sub>4</sub> @RGO@Au@C	RGO@Au@C
Rate constant k (min <sup>-1</sup> )	0.033	0.170	0.496	0.412

with previously reported gold based heterogeneous catalysts. The TOF of  $Fe_3O_4@RGO@Au@C$  CDSNs catalyst is 3.77 min<sup>-1</sup>, calculated by the moles of 4-NP reduced per mole of gold complex per consumed time under the present

reaction conditions. Table 3 compares efficiency of  $Fe_{3-}O_4@RGO@Au@C CDSNs$  (TOF and mol% of catalysts) with efficiency of other reported gold based catalysts in reduction of 4-NP.

Inspired by the high activity and stability of  $Fe_3O_4@$ -RGO@Au@C CDSNs the Suzuki coupling reaction is further employed as another model reaction to test further the performance of  $Fe_3O_4@RGO@Au@C$  nanocatalyst. We chose the Suzuki coupling reaction of phenyl boronic acid with phenyl iodide as an optimum reaction in H<sub>2</sub>O as solvent at 100 °C in the presence of K<sub>3</sub>PO<sub>4</sub> as base and with a catalyst loading of 2 mol% of Au for 12 h (Table 4, entry 4). Under this condition, we found that the cross coupling reaction proceeds well, affording the excellent yield (97 %) of the corresponding biphenyl. Additionally,  $Fe_3O_4@SiO_2@GO@Au$  and  $Fe_3O_4@SiO_2@RGO@Au@C$ were tested in the model reaction and yields of biphenyl in both cases were remarkably lower (Table 4, entries 5 and 6).

We next managed to examine the scope and limitation of Suzuki–Miyaura reaction with various types of aryl haides derivatives and phenyl boronic acid. (Table 5). It can be seen from Table 5 that the Suzuki–Miyaura crosscoupling reaction with most substrates preceded in good yields. The hindered substrate such as 2-iodotoluene converted into the corresponding products with a moderate yield (Table 5, entry 4).

Table 2  $Fe_3O_4@RGO@Au@C CDSNs$  catalysed Reduction of various nitroarene

Entry	Substrate	Time (min)	Yield (%) <sup>a</sup>
1	Nitrobenzene	120	79
2	2-nitrophenol	7	99
3	3-nitrophenol	4	99
4	4-nitrophenol	13	98
5	1-methyl-4-nitrobenzene	140	79
6	1-methoxy-4-nitrobenzene	150	74

30 mL of  $1.20 \times 10^{-4}$  M nitroarene, 30 mL of 0.17 M NaBH<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C CDSNs (2 mol% with respect to the gold concentration) <sup>a</sup> Isolated yields after column chromatography

The heterogeneous nature of the catalysis is proved using a hot filtration test and atomic absorption spectroscopy (AAS) analysis. To determine whether the catalyst is actually functioning in a heterogeneous manner or whether it is merely a reservoir for more active soluble gold species, we performed a hot filtration test in the Suzuki cross coupling reaction of phenyl boronic acid with phenyl iodide after  $\sim 50 \%$  of the coupling reaction is completed. The hot filtrates were then transferred to another flask containing K<sub>3</sub>PO<sub>4</sub> (3 equiv.) in H<sub>2</sub>O (3 mL) at 100 °C. Upon the further heating of catalyst-free solution for 24 h, no considerable progress ( $\sim 1$  % by GC analysis) is observed. Moreover, using AAS of the same reaction solution at the midpoint of completion indicated that no significant quantities of gold were lost to the reaction liquors during the process. The reusability of the  $Fe_{3-}$ O4@RGO@Au@C CDSNs is examined in the Suzuki-Miyaura cross-coupling reaction of phenylboronic acid with phenyl iodide. It is found that the recovery can be successfully achieved in six successive reaction runs (Table 5, entry 1).

**Table 4** Screening of the Suzuki–Miyaura cross-coupling reactionconditions

Entry	Catalyst	Base	Time (h)	Yield <sup>a</sup>
1	Fe <sub>3</sub> O <sub>4</sub> @RGO@Au@C	K <sub>2</sub> CO <sub>3</sub>	12	49 %
2	Fe <sub>3</sub> O <sub>4</sub> @RGO@Au@C	NaOH	12	66 %
3	Fe <sub>3</sub> O <sub>4</sub> @RGO@Au@C	KOH	12	78 %
4	Fe <sub>3</sub> O <sub>4</sub> @RGO@Au@C	$K_3PO_4$	12	97 %
5	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @GO@Au	$K_3PO_4$	12	71 %
6	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @RGO@Au@C	$K_3PO_4$	12	86 %

Phenyl iodide (1.0 mmol), phenyl boronic acid (1.3 mmol), Base (3.0 mmol), catalyst (2 mol% of Au), 100 °C, and H<sub>2</sub>O (3 mL).<sup>a</sup> GC yield, *n*-dodecane is used as an internal standard

Table 3Comparison of<br/>catalytic activity by gold based<br/>catalysts for the reduction of<br/>4-NP

Entry	Catalyst	TOF $(\min^{-1})$	Catalysts (mol%)	Ref.
1	Fe <sub>3</sub> O <sub>4</sub> @RGO@Au@C	3.77	2	This work
2	HAuCl <sub>4</sub> .3H <sub>2</sub> O	0.11	46	43
3	Au-PMMA	1.23	7	44
4	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Au@mSiO <sub>2</sub>	0.73	9	45
5	Fe <sub>3</sub> O <sub>4</sub> @P(EGDMA-co-MAA)/Au	1.6	2.5	46
6	Au@SiO <sub>2</sub>	0.45	7	47
7	Au NPs/SNTs	0.77	28	48
8	Au/graphene hydrogel	0.19	43	19
9	rGO/Fe <sub>3</sub> O <sub>4</sub> /Au	11.93		20
10	GO-Fe <sub>3</sub> O <sub>4</sub> -Au NPs(G).	8.06	7.3	49

 Table 5
 Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C
 CDSNs
 catalyzed
 Suzuki–Miyaura

 cross-coupling
 reaction

 </t

$$Ar-X + Ph-B(OH)_2 \longrightarrow Ar-Ph$$

Entry	Ar	Х	Time (h)	Yield <sup>a</sup>
1	Ph	Ι	12	97 %, 95 % <sup>b</sup>
2	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	Ι	12	99 %
3	4-MeCO-C <sub>6</sub> H <sub>4</sub>	Ι	12	97 %
4	2-Me-C <sub>6</sub> H <sub>4</sub>	Ι	12	82 %
5	Ph	Br	18	88 %
6	4-Me-C <sub>6</sub> H <sub>4</sub>	Br	18	82 %
7	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	Br	18	93 %

Aryl halide (1 mmol), phenyl boronic acid (1.2 mmol), Fe<sub>3</sub>O<sub>4</sub>@-RGO@Au@C (2 mol% of Au), K<sub>3</sub>PO<sub>4</sub> (3 mmol), 100 °C. <sup>a</sup> Isolated yield. <sup>b</sup> Yield after sixth cycle

# **5** Conclusion

In this study, a novel magnetic core double-shelled carbon with Fe<sub>3</sub>O<sub>4</sub> nanoparticles as core, reduced graphene oxide (RGO) as the inner shell and carbon (C) layer as the outer shell have been successfully designed and prepared. This tailor-making structure acts as an excellent capsule for encapsulating Au nanoparticles (Au NPs), which could effectively prevent Au NPs from aggregation and leaching. The catalyst could be easily recovered by applying an external magnetic field, and reused for next catalytic run. The Fe<sub>3</sub>O<sub>4</sub>@RGO@Au@C nanocatalyst showed excellent catalytic activity for the reduction of nitrophenols and the Suzuki–Miyaura cross-coupling reaction. The  $Fe_3O_4@$ RGO@Au@C nanocatalyst acts as a relatively green catalyst with superparamagnetism, eco-friendly nature and convenient recovery, and is a promising candidate for Au NPs based catalytic applications in industrial synthesis.

Acknowledgments We gratefully acknowledge financial support from the Research Council of Shahid Beheshti University.

#### References

- 1. Reddy LH, Arias JL, Nicolas J, Couvreur P (2012) Chem Rev 112:5818
- Polshettiwar V, Luque R, Fihri A, Zhu H, Bouhrara M, Basset JM (2011) Chem Rev 111:3036
- 3. Karimi B, Mansouri F, Vali H (2015) ChemPlusChem 80:1750
- 4. Zeng T, Zhang X, Ma Y, Niu H, Cai Y (2012) J Mater Chem 22:18658
- 5. Bai S, Shen X (2012) RSC Adv 2:64
- 6. Dabiri M, Shariatipour M, Movahed SK, Bashiribod S (2014) RSC Adv 4:39428
- 7. Pumera M (2010) Chem Soc Rev 39:4146
- 8. Huang X, Qi X, Boey F, Zhang H (2012) Chem Soc Rev 41:666

- 9. Yao J, Sun Y, Yang M, Duan Y (2012) J Mater Chem 22:14313
- 10. Latham AH, Williams ME (2008) Acc Chem Res 41:411
- 11. Frey NA, Peng S, Cheng K, Sun SH (2009) Chem Soc Rev 38:2532
- Roca AG, Costo R, Rebolledo AF, Veintemillas-Verdaguer S, Tartaj P, González-Carreño T, Morales MP, Serna CJ (2009) J Phys D Appl Phys 42:224002
- 13. Gijs MAM, Lacharme F, Lehmann U (2010) Chem Rev 110:1518
- 14. Kumar CSSR, Mohammad F (2011) Adv Drug Deliv Rev 63:789
- 15. Guo S, Dong S, Wang E (2009) Chem Eur J 15:2416
- 16. Guo S, Dong S, Wang E (2008) J Phys Chem C 112:2389
- 17. Guo S, Li J, Wang E (2008) Chem Asian J 3:1544
- 18. Corma A, Garcia H (2008) Chem Soc Rev 37:2096
- 19. Li J, Liu CY, Liu Y (2012) J Mater Chem 22:8426
- 20. Wang Y, Li H, Zhang J, Yan X, Chen Z (2016) Phys Chem Chem Phys 18:615
- Zhang Z, Xiao F, Xi J, Sun T, Xiao S, Wang H, Wang S, Liu Y (2013) Sci Rep 4:4053
- 22. Pumera M (2010) Chem Soc Rev 39:4146
- 23. Huang X, Qi X, Boey F, Zhang H (2012) Chem Soc Rev 41:666
- 24. Movahed SK, Fakharian M, Dabiri M, Bazgir A (2014) RSC Adv 4:5243
- 25. Zhang N, Qiu H, Liu Y, Wang W, Li Y, Wang X, Gao JF (2011) J Mater Chem 21:11080
- Liu J, Sun ZK, Deng YH, Zou Y, Li CY, Guo XH, Xiong LQ, Gao Y, Li FY, Zhao DY (2009) Angew Chem Int Ed 48:5875
- Yuan Q, Li N, Chi Y, Geng W, Yan W, Zhao Y, Li X, Dong B (2013) J Hazard Mater 254–255:157
- Zhang X, Jiang W, Zhou Y, Xuan S, Peng C, Zong L, Gong X (2011) Nanotechnology 22:375701
- 29. Hummers WS, Offeman RE (1958) J Am Chem Soc 80:1339
- Kovtyukhova NI, Olliver PJ, Martin BR, Mallouk TE, Chizhik SA, Buzaneva EV, Gorchinsky AD (1999) Chem Mater 11:771
- Akhavan O (2010) Carbon 48:509
  Xiao M, Huang M, Zeng S, Han D, Wang S, Sun L, Meng Y (2013) RSC Adv 3:4914
- 33. Bai S, Chen S, Shen X, Zhu G, Wang G (2012) RSC Adv 2:10977
- Wang Z, Lv X, Chen Y, Liu D, Xu X, Palmore GTR, Hurt RH (2015) Nanoscale 7:10267
- Zou H, Wang R, Li X, Wang X, Zeng S, Ding S, Li L, Zhang Z, Qiu S (2014) J Mater Chem A 2:12403
- Hu W, Liu B, Wang Q, Liu Y, Liu Y, Jing P, Yu S, Liu L, Zhang J (2013) Chem Commun 49:7596
- Choi Y, Bae HS, Seo E, Jang S, Park KH, Kim B-S (2011) J Mater Chem 21:15431
- 38. Ji T, Li L, Wang M, Yang Z, Lu X (2014) RSC Adv 4:29591
- Liu R, Qu F, Guo Y, Yao N, Priestley RD (2014) Chem Commun 50:478
- 40. The RGO@Au@C hollow sphere is synthesized with similar method in ref. 18
- 41. F-h Lin, R-a Doong (2014) Appl Catal A General 486:32
- Layek K, Kantam ML, Shirai M, Nishio-Hamane D, Sasaki T, Maheswaran H (2012) Green Chem 14:3164
- 43. Pachfule P, Kandambeth S, Diaz DD, Banerjee R (2014) Chem Commun 50:3169
- 44. Kuroda K, Ishida T, Haruta M (2009) J Mol Catal A Chem 298:7
- 45. Deng Y, Cai Y, Sun Z, Liu J, Liu C, Wei J, Li W, Liu C, Wang Y, Zhao D (2010) J Am Chem Soc 132:8466
- 46. Woo H, Park KH (2014) Catal Commun 46:133
- 47. Wang Z, Fu H, Han D, Gu F (2014) J Mater Chem A 2:20374
- Zhang Z, Shao C, Zou P, Zhang P, Zhang M, Mu J, Guo Z, Li X, Wang C, Liu Y (2011) Chem Commun 47:3906
- Hua J, Dong Y-L, Chen X-J, Zhang H-J, Zheng J-M, Wang Q, Chen X-G (2014) Chem Eng J 236:1