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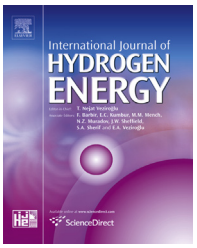

Facile synthesis and catalytic application of selenium doped graphene/$CoFe_2O_4$ for highly efficient and noble metal free dehydrogenation of formic acid

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ABSTRACT

The ongoing search for new noble metal free catalysts with excellent catalytic performance to replace homogeneous catalysts with difficult synthesis, separating and recycling and also expensive heterogeneous catalysts has been viewed as an important strategy to promote the development of hydrogen generation from formic acid. In this study, we reported the facile fabrication of selenium doped graphene/$CoFe_2O_4$ hybrid materials which exhibited excellent catalytic activity and magnetic recyclability for dehydrogenation of formic acid. Besides facilitating the catalyst isolation, $CoFe_2O_4$ nanoparticles have crucial role on the catalytic activity of the as-obtained material. Our results confirmed that combining $CoFe_2O_4$ with graphene is an effective strategy to inhibit metal oxide aggregation and synergistically improve the catalytic activity. Moreover, it is also demonstrated that selenium with large atomic size and high polarizability can enhance the catalytic activity of selenium doped graphene/$CoFe_2O_4$ hybrid materials.

Introduction

Formic acid (FA) has attracted considerable attention as a suitable liquid source for hydrogen (containing 4.4 wt.%, 53 g/L hydrogen) and hydrogen based green-energy applications because of the low toxicity, low cost, and high stability [1–5]. FA, which has been obtained in large quantities by the hydrogenation of waste carbon dioxide from industry, biomass processing, and artificial photosynthesis can undergo a catalytic dehydrogenation reaction, releasing H_2 that will be important for the generation of hydrogen in a more sustainable manner [6]. The main problem for practical applications of this approach is the development of efficient catalysts. Recently, the dehydrogenation of FA is catalyzed by homogeneous organometallic catalysts with high selectivity and efficiency [7,8]. The difficulties in synthesis, controlling, separating and recycling are the main drawbacks of homogeneous catalysts preventing them for practical applications [3]. So, the development of heterogeneous catalysts with high performance for hydrogen generation from FA has recently been a hot topic [9]. Most of the reported heterogeneous catalysts include high cost and rare noble metals such as Au, Pd, and Pt which impede their practical applications [10,11]. So, the development of high-performance heterogeneous

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catalysts without expensive noble metals for dehydrogenation of FA is urgently desired. Recently, bimetallic nanoparticles catalysts were shown to be more active than their single component counterparts for hydrogen generation from FA because of the charge redistribution between bimetals which reinforces the adsorption of formate through strong back donation [4].

From the point view of green chemistry, the practical approach to recover nanosized catalysts is a bottleneck for their applications. Compared with time-consuming procedures, such as filtration, centrifugation or gravitational separation, magnetic isolation leads to easier and better separation especially for small particles [12,13].

In the past two decades, magnetic cobalt ferrite ($CoFe_2O_4$), have attracted great attention in various fields such as electronics [14], catalysis [15–17], cancer therapy [18], and magnetic resonance imaging (MRI) [19] owing to its intrinsic nature of exhibiting magnetic hardness with high coercivity, high cubic magneto crystalline anisotropy, and moderate saturation magnetization [20]. However, due to the large surface area and strong dipole–dipole interactions, the pristine $CoFe_2O_4$ nanoparticles suffer from irreversible aggregation. Among the various methods to reduce aggregation and settling, introduction of graphene oxide is expected to overcome these problems because of the large surface area, unique planar structure, low density, flexibility, chemical stability, and very high electrical conductivity [21]. On the other hand, by the combination of inorganic nanocrystals and graphene, such systems could have rich chemical/physical properties and also a possible synergistic effect [22–24]. Several groups have reported the synthesis of the cobalt ferrite/graphene nanocomposites employing different methods and also investigation of their application in various fields [25–27]. In 2015, Li et al. prepared light-weight sandwich-structured $CoFe_2O_4$/graphene oxide hybrids by a facile one-pot polyol method followed by chemical conversion into FeCo/graphene hybrids for microwave absorber [28].

The introduction of foreign non-metallic atoms into graphene have been found to increase active sites, enhance the catalytic activity, and developing the electronic structure of graphene [29]. Recently, Se with similar electronegativity as carbon (selenium electronegativity: 2.55) was proposed as one of the attractive dopants for carbon materials because of its larger atomic size, inducing high strain at the edges of carbon materials and facilitating charge localization, as well as higher polarizability compared to S and facile interaction of lone Se pairs with the surrounding molecules [30,31]. In 2012, Yang et al. demonstrated that Se-graphene have better catalytic activity for the oxygen reduction reaction (ORR) than the commercial Pt/C in alkaline media which can potentially use for a substitute for Pt-based catalysts in fuel cells [32]. Jin et al. reported the fabrication and investigation of electrocatalytic performance of CNT/graphene doped with Se atoms, which shows excellent catalytic activity, long-term stability, and a high methanol tolerance [30].

It is important to note that, in continuation of our interest in different catalysts [33–37], though the present study provides a simple approach to achieve Se doped graphene $CoFe_2O_4$ hybrid materials as a noble metal free heterogeneous catalyst for hydrogen generation from FA. The influence of $CoFe_2O_4$, graphene and Se dopant on the catalytic activity have been investigated.

Experimental

Materials

Graphite powder (325 mesh), sulfuric acid (H_2SO_4), potassium peroxodisulfate ($K_2S_2O_8$), di-phosphorus pentoxide (P_2O_5), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), ethylene glycol (EG), iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), sodium acetate (NaAc), and diphenyl diselenide (DDSe) were purchased from Merck Chem. All other chemicals were purchased from Aldrich or Merck companies and used as received without any further purification.

Instruments and characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. Transmission electron microscopy (TEM) was performed by LEO 912AB electron microscope. Ultrasonic bath (EUROSONIC® 4D ultrasound cleaner with a frequency of 50 kHz and an output power of 350 W) was used to disperse materials in solvents. Thermogravimetric analysis (TGA) was carried out using STA 1500 instrument at a heating rate of 10 °C min^{-1} in air. X-ray powder diffraction (XRD) data were collected on an XD-3A diffractometer using Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was performed using a VG multilab 2000 spectrometer (ThermoVG scientific) in an ultrahigh vacuum. Ultraviolet–Visible (UV–Vis) spectra were obtained using a Shimadzu UV-2100 spectrophotometer. Scanning electron microscope (SEM) was performed on a Zeiss Supra 55 VP SEM instrument. AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer (AAS) with a deuterium background corrector was used for determination of the metal. The magnetization of the samples in a variable magnetic field was measured using a vibrating sample magnetometer (VSM) with a sensitivity of 10^{-3} EMU and a magnetic field of up to 8 kOe. The magnetic field was changed uniformly at a rate of 66 Oe s^{-1}. The gas chromatography (GC) analysis was performed on Shimadzu GC-2014 gas chromatograph.

Synthesis of graphene oxide (GO)

Graphene oxide (GO) was prepared through a modified Hummers method [38,39]. Graphite powders were first oxidized by sulfuric acid. Then 2.5 g of the graphite powder was treated with a solution by mixing 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 using a hotplate. Subsequently, the mixture was cooled to room temperature and diluted with 500 mL de-ionized (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 pretreated graphite powder was put into cold (0 °C) concentrated H_2SO_4 (125 mL). Then $KMnO_4$ (15 g) was added gradually under stirring, and the temperature of the mixture was kept below

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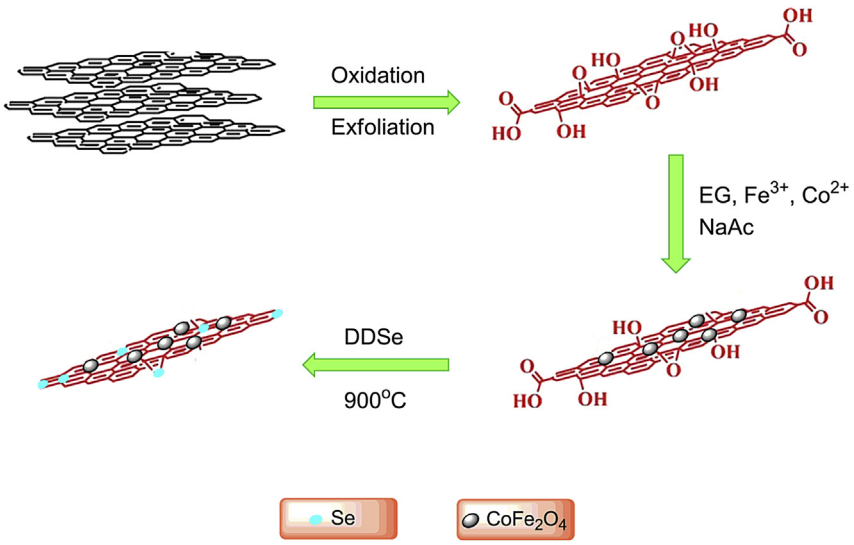

Scheme 1 – Schematic procedures to prepare selenium doped graphene/$CoFe_2O_4$.

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_2O_2 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 0.1 M HCl to remove metal ions, followed by 500 mL DI water to remove the acid. The resulting GO solid was dried in air.

Synthesis of graphene oxide/$CoFe_2O_4$ hybrid material

The graphene oxide/$CoFe_2O_4$ hybrid material was synthesized by a one-pot polyol method [28]. In a typical procedure, 40 mg GO was dispersed into 100 mL of ethylene glycol (EG) and ultrasounded for 3 h. 8 mmol $FeCl_3 \cdot 6H_2O$ and 4 mmol $CoCl_2 \cdot 6H_2O$ were added into the above suspension of GO and ultrasounded for another 3 h. 60 mmol NaAc was dissolved into the above solution. The solution was stirred and refluxed for 10 h. The black products were washed by water and ethanol for several times, and then dried in the atmospheric environment. For comparison purposes, pure $CoFe_2O_4$ nanocrystals were fabricated in the same approach without GO.

Synthesis of Se-doped graphene/$CoFe_2O_4$

Selenium doped graphene/$CoFe_2O_4$ was prepared by directly annealing GO/$CoFe_2O_4$ hybrid material and DDSe in argon [30]. In a typical procedure, GO/$CoFe_2O_4$ hybrid material (4 mg) was firstly ultrasonically dispersed in ethanol for about 90 min, and subsequently DDSe (4 mg) were added into the suspension under ultrasonic conditions. The resulting suspension was spread onto an evaporating dish and dried at 40 °C, forming a uniform solid mixture. The mixtures were placed into a quartz tube with an argon atmosphere and annealed at 900 °C for 3 h. After that, the sample was cooled to room temperature under Ar ambient and collected from the quartz tube.

To investigate the effect of $CoFe_2O_4$ on the catalytic activity of the as-obtained material, selenium doped graphene was synthesized by a similar procedure and using GO instead of $CoFe_2O_4$ hybrid material.

Hydrogen generation from formic acid aqueous solution

An aqueous suspension containing the as-prepared catalyst was placed in a two-neck round-bottom flask, which was placed in a water bath under ambient atmosphere. A gas burette filled with water was connected to the reaction flask to measure the volume of released gas. The reaction was started when the mixed aqueous solution of FA was injected into the sealed flask to form a 4.5 mL of suspension. The molar ratio of CoFe/FA was fixed at 0.034 for all the catalytic reactions. The volume of the evolved gas was monitored by recording the displacement of water in the gas burette.

Results and discussion

Synthesis and recognition of the catalyst

The experimental scheme for preparation of selenium doped graphene/$CoFe_2O_4$ is illustrated in Scheme 1. In a typical procedure, the graphene oxide/$CoFe_2O_4$ hybrid material was synthesized by thermal decomposition of metal salts in the presence of GO with NaAc as a stabilizer and EG as the solvent through a facile one-pot polyol method. Owing to the abundant oxygen-containing functional groups on the surface of GO comprising carboxyl, hydroxyl and epoxy groups, GO is negatively charged. After adding Co and Fe salts to GO suspension, the electrostatic interaction between negative charge on GO and cobalt and iron cations lead to the in situ formation of $CoFe_2O_4$ magnetic nanoparticles on GO sheets. To prepare selenium doped graphene/$CoFe_2O_4$, GO and DDSe were first ultrasonically dispersed in ethanol. The resulting suspension

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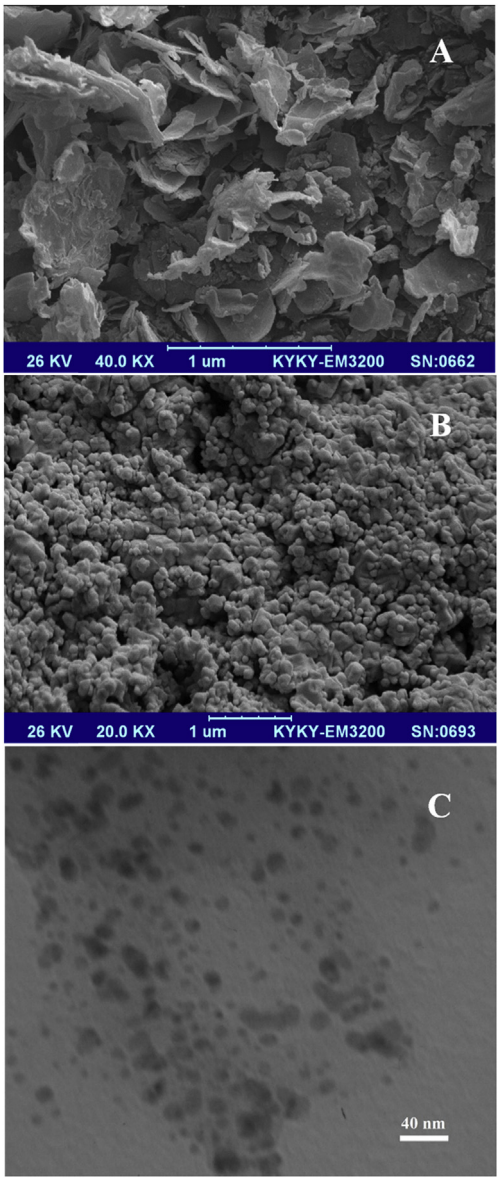

Fig. 1 – SEM images of GO (A) and Se-doped graphene/$CoFe_2O_4$, and TEM image of Se-doped graphene/$CoFe_2O_4$ (B and C).

was dried to form a uniform solid mixture and then placed in a quartz tube under an argon atmosphere and annealed at 900 °C. The amount of Co and Fe metals in the as-obtained catalyst were determined by AAS to be 1.5 and 3.7 mmol/g, respectively.

To investigate the morphology and structure of the materials, SEM and TEM images were provided. SEM image of GO clearly shows a crumpled flaky structure with a very low thickness (Fig. 1A). According to the SEM image of Se-doped graphene/$CoFe_2O_4$, after the introduction of $CoFe_2O_4$ nanoparticles, the GO sheets were homogeneously decorated by the nanoparticles (Fig. 1B). As shown in Fig. 1C, the thin and wrinkled GO nanosheets appears in TEM image of Se-doped graphene/$CoFe_2O_4$. Moreover, it can be observed that two-dimensional GO nanosheets are fully exfoliated and uniformly covered by a large number of spherical $CoFe_2O_4$ nanoparticles. From Fig. 1C the average particle size of $CoFe_2O_4$ was determined to be 14 nm. It is worth mentioning that almost no free $CoFe_2O_4$ nanoparticles are seen outside of GO nanosheets suggesting the strong interaction between $CoFe_2O_4$ and GO. So, SEM and TEM results confirm that $CoFe_2O_4$ nanoparticles are well wrapped by the graphene which lead to prevent the aggregation of $CoFe_2O_4$ NPs to a certain extent, which provides a great advantage for catalytic reactions.

XRD measurements were accomplished to investigate the phase and structure of the synthesized products (Fig. 2A). The XRD pattern of GO shows a diffraction peak at 2θ of 10.3°, related to (002) of GO, demonstrating the introduction of oxygen-based functional groups on the surface of the graphite. All the diffraction peaks of GO/$CoFe_2O_4$ can be assigned to a single phase of $CoFe_2O_4$ with a face-centered cubic spinel structure (JCPDS card No. 22-1086). The diffraction peaks at 2θ of 18.2°, 29.8°, 35.4°, 42.8°, 56.9° and 62.4° are related to (111), (220), (311), (400), (511) and (440) crystal planes of $CoFe_2O_4$, respectively. Moreover, because of destroying the regular layer stacking of GO by the crystal growth of $CoFe_2O_4$ between the interlayers and consequently the exfoliation of GO, the characteristic peak of GO is not observed in XRD pattern of GO/$CoFe_2O_4$. The average size of the $CoFe_2O_4$ nanoparticles were calculated to be 12.9 according to the Scherrer's formula which is consistent with TEM observations. In the XRD pattern of Se-doped graphene/$CoFe_2O_4$, all the diffraction peaks of $CoFe_2O_4$ are clearly observed which confirmed the retained morphology of nanoparticles after selenium doping.

FT-IR spectra of GO/$CoFe_2O_4$ and Se-doped graphene/$CoFe_2O_4$ samples are shown in Fig. 2B. For GO/$CoFe_2O_4$, the peaks at 3453, 1377 and 1070 cm^{-1} are assigned to the –OH, C=O in carboxylic acid, and C–O stretching vibrations, respectively which confirm the existence of oxygen-containing functional groups on the surface of the nanosheets. Moreover, the peaks at 2921 and 2848 cm^{-1} are ascribed to the asymmetric and symmetric stretching vibration of $-CH_2$, respectively. A prominent absorption band appeared at about 594 cm^{-1} corresponds to the stretching mode of Fe(Co)–O [40]. The peak at 1631 cm^{-1} is associated with the vibration of adsorbed water. In FT-IR spectrum of Se-doped graphene/$CoFe_2O_4$, most of the bands related with the oxygen-containing functional groups disappeared. It is revealed that the bulk of the oxygen-containing functional groups were removed from GO in the process of selenium doping thus the GO was effectively transformed into graphene in the synthesis. But the peak of Fe(Co)–O is still observed proving the successful synthesis of Se-doped graphene/$CoFe_2O_4$.

The magnetic properties of GO/$CoFe_2O_4$ and Se-doped graphene/$CoFe_2O_4$ were investigated by VSM at room temperature. The hysteresis loops are shown in Fig. 2C. The saturation magnetization (Ms) of GO/$CoFe_2O_4$ is about 45.4 emu/g [41]. The negligible remanence and coercivity in the magnetic hysteresis loops suggests the superparamagnetic behavior of GO/$CoFe_2O_4$. The magnetization curve of Se-doped graphene/$CoFe_2O_4$ indicate the ferromagnetic characteristics of as-prepared material and the coercivity is estimated to be ~500 Oe, proposing that the as obtained catalyst might be

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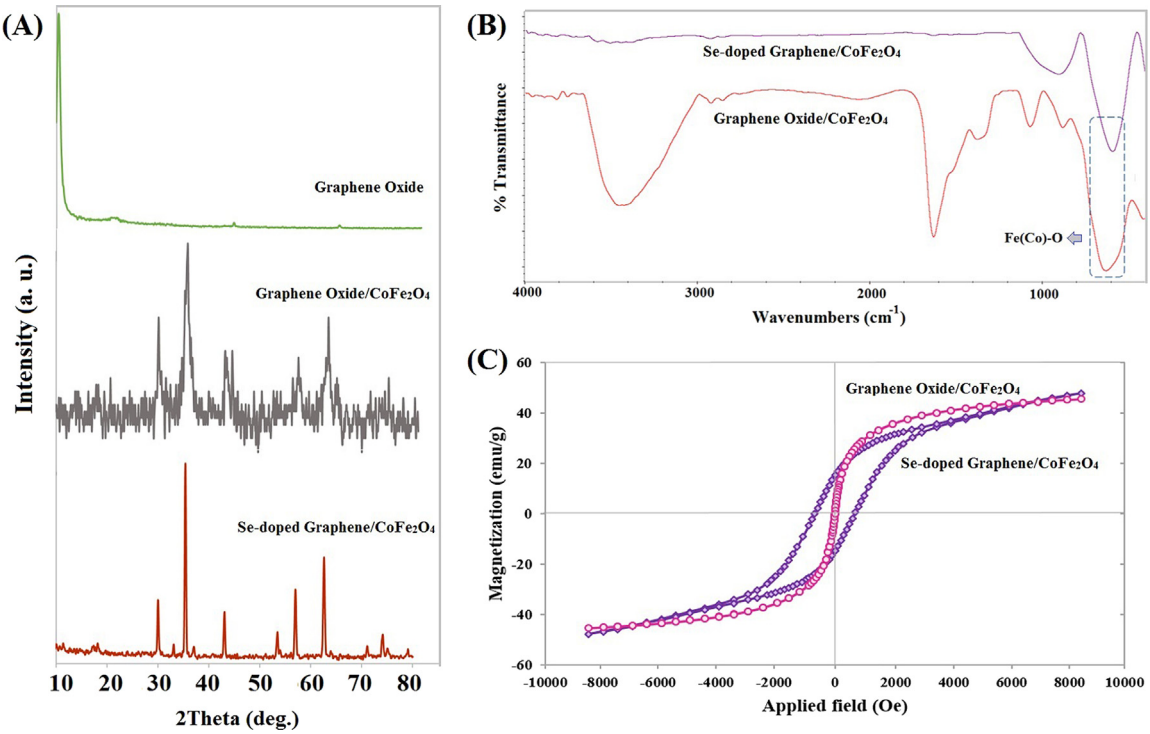

Fig. 2 – XRD patterns of GO, GO/$CoFe_2O_4$, and Se-doped graphene/$CoFe_2O_4$ (A), FT-IR spectra of GO/$CoFe_2O_4$ and Se-doped graphene/$CoFe_2O_4$ (B), and the field-dependent magnetization of GO/$CoFe_2O_4$ and Se-doped graphene/$CoFe_2O_4$ (C).

easily separated from solution phase through inducing an external magnetic field [42].

TGA and DTA curves of GO, GO/$CoFe_2O_4$ and Se-doped graphene/$CoFe_2O_4$ were obtained and presented in Fig. 3. In this experiment, the samples are heated to 780 °C under air atmosphere at a heating rate of 10 °C/min and a change in mass loss was recorded. TG analysis allows us to investigate thermal decomposition pattern and thermal stability of the as obtained materials. Three samples showed a slight weight loss below 120 °C, related to the evaporation of adsorbed water molecules. Thermogram of GO shows the weight losses between 120 and 205 °C due to the decomposition of labile oxygen-containing functional groups (such as C–O, C=O, etc.) [43], and another weight loss between 530 and 600 °C due to the thermal decomposition of the carbon skeleton [44]. After the introduction of $CoFe_2O_4$ nanoparticles to GO sheets, besides the weight loss due to the destruction of oxygenated functional groups of GO and removal of physically adsorbed water on $CoFe_2O_4$ nanoparticles at about 200 °C, a slight weight loss at 400 °C probably corresponds to the decomposition of surface adsorbed ethylene glycol is observed. In TGA curve of Se-doped graphene/$CoFe_2O_4$, almost no weight loss occurred because of the elimination of oxygen containing groups of GO after Se-doping.

Furthermore, the composition of Se-doped graphene/$CoFe_2O_4$ is also confirmed by XPS analysis (Fig. 4), which reveals the presence of C, O, Se, Fe, and Co on the surface of as-obtained material. The C 1s high resolution spectrum shows the peaks corresponding to sp^2 carbon atoms up-shifted to a higher binding energy (284.7 eV) than that of pristine graphene (284.5 eV) with Se introduction. The C1s XPS spectrum can be divided into two different peaks, which correspond to the signals of C–C/C=C (284.7 eV), and C–O (285.5 eV). The O 1s XPS spectrum can be deconvoluted into two different peaks, chemical bindings which ascribed to the signals of C–OH or C–O–C (533.4 eV) and the lattice oxygen in the Co/Fe–O framework.32–36 (531.5 eV) [45,46]. It can be observed that the high-resolution Se3d peak for Se-doped graphene/$CoFe_2O_4$ has an evidently binding energy at 56.5 eV due to C–Se–C bond in the Se-doped carbon similar to other literature for Se-doped carbon materials [30]. These results demonstrate that the bonds of Ph–Se–Se–Ph in DDSe were broken during the pyrolysis step, and the Se atoms were doped into the GO/$CoFe_2O_4$. According to the XPS results, selenium content in Se-doped graphene/$CoFe_2O_4$ is 1.59 at.%.

Catalytic activity

A sustainable and cost-effective approach for the release of H_2 from water solution of FA as a hydrogen source for practical applications (e.g. fuel cells) needs dehydrogenation reactions under the mild conditions without any additives and noble metals-based catalysts. So, we tested the activity of the Se-doped graphene/$CoFe_2O_4$ catalyst for the decomposition of FA in water (Fig. 5). The gas generation volume and rate over Se-doped graphene/$CoFe_2O_4$ catalyst are considerably influence by the temperature and catalyst amount. To optimize the reaction conditions, we tested different temperatures and catalyst amounts as the results are summarized in Fig. 5. The dehydrogenation of FA at 60 °C with 0.007 g catalyst which released 110 mL of gas within 13 min was chosen as the optimized condition for further investigations.

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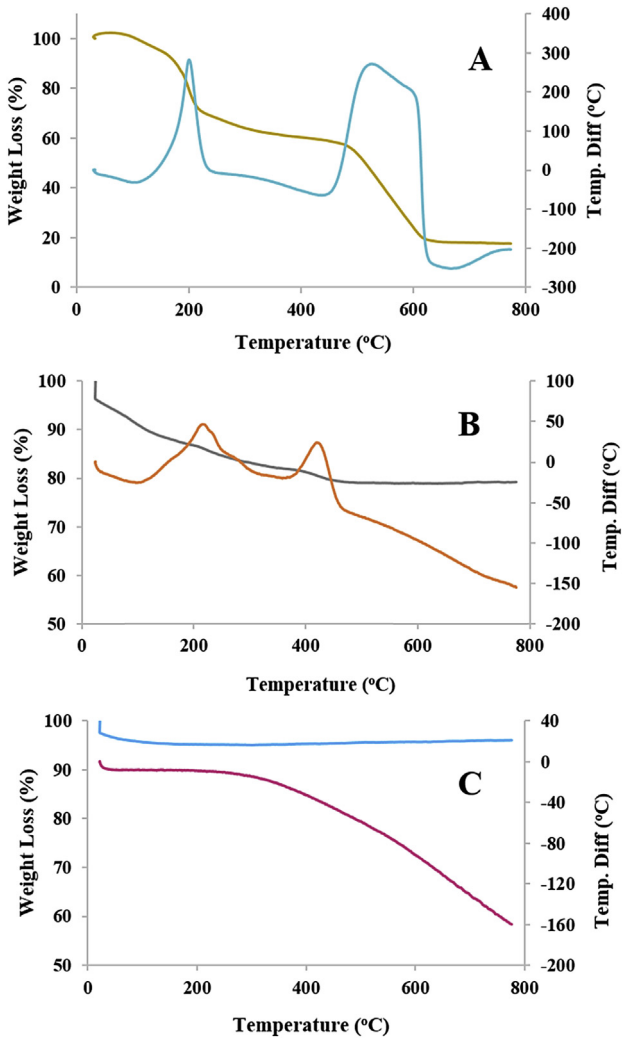

Fig. 3 – TGA and DTA curves of GO (A), GO/$CoFe_2O_4$ (B) and Se-doped graphene/$CoFe_2O_4$ (C).

It is noteworthy that the Se-doped graphene/$CoFe_2O_4$ gave a turnover frequency (TOF) of 306 h^{-1}, comparable to the most heterogeneous catalysts (Table S1), but without any additive and noble metals which make it unique among all previously reported catalysts.

To examine if graphene, Se dopants and $CoFe_2O_4$ have a dramatic effect on the catalytic performance, the as-synthesized GO, $CoFe_2O_4$, GO/$CoFe_2O_4$, Se-doped graphene together with the as-synthesized Se-doped graphene/$CoFe_2O_4$ were evaluated as catalysts for H_2 generation from FA decomposition. The results are given in Fig. 5. Se-doped graphene/$CoFe_2O_4$ clearly exhibits a much better activity than GO and GO/$CoFe_2O_4$ catalysts. That is, Se-doped graphene/$CoFe_2O_4$ exhibits much higher gas volume toward FA, which is more than two times compared to GO. From Fig. 6, it can be seen that the catalytic activity of GO/$CoFe_2O_4$ is much more than that of $CoFe_2O_4$, suggesting that the graphene plays a key role on the as-obtained hybrids. In a word, graphene was used as the support and the suspended bonds on the graphene oxide play an important role for the uniform distribution of $CoFe_2O_4$ nanoparticles during the synthesis. Besides, GO with high migration efficiency of electrons has unique electronic structure which plays a vital role in improving the catalytic activity for hydrogen generation. Moreover, graphene can also prevent the aggregation and loss of activity of nanoparticles.

With Se introduction, the activity of Se-doped graphene/$CoFe_2O_4$ has been enhanced obviously compared to GO and GO/$CoFe_2O_4$. The enhanced catalytic activity with Se introduction can be attributed to several parameters. Firstly, the increased electron transfer due to restoring defects at carbon edges and formation of p conjugation system, secondly the induction of more strain in carbon materials owing to introduction of functional groups or doping atoms [47], as well as higher strain at the carbon edges due to the larger atomic size of Se than carbon, and thirdly higher polarizability of Se and interaction of lone selenium pairs with molecules in the surrounding media as compared with other heteroatoms such as N, P, or S. In addition, recent reports suggests that doping of graphite materials with large size atoms may be a promising approach to gain new metal free catalysts with high activity.

From Fig. 5, it is also obvious that $CoFe_2O_4$ nanoparticles are the crucial sites in the prepared catalyst. Namely, without $CoFe_2O_4$, Se-doped graphene shows much lower gas volume. The surface redox properties and Lewis acidity of $CoFe_2O_4$ due to the stabilizing effect of Co on the distribution of iron sites probably cause the enhanced ability of FA adsorption and O–H bond polarization on the binary spinel [48,49], which leads to its catalytic behavior in FA decomposition.

Another pathway for the decomposition of FA is a dehydration reaction which lead to release of CO. To investigate the possibility of this undesired reaction, a trap containing limewater was used to remove CO_2 from the as formed gas of the catalytic reaction. A loss of around 50% in volume was observed suggesting a volume ratio of CO_2 and H_2 to be 1:1 in the as-formed gas. Moreover, analysis by GC further confirmed that the gas treated with the limewater was pure hydrogen with no CO (Fig. S1).

Being highly stable, easily separable, and readily recyclable are very important for practical application of catalysts. We tested the durability of the Se-doped graphene/$CoFe_2O_4$ catalyst in the decomposition of FA at 60 °C (Fig. S2). The results showed a slight decrease in the productivity of hydrogen after six runs mainly ascribed to the slightly increased particle size of the $CoFe_2O_4$ NPs. Moreover, XRD measurement of the recovered catalyst show no significant change in the structure of the catalyst, exhibiting high durability and stability of the catalyst (Fig. S3). Moreover, the catalyst could easily be isolated from the reaction mixture by simply using magnet removing the need for filtration/centrifugation which the complete catalyst recovery is usually not possible. According to the results, the presented catalyst has a great potential for practical large scale and sustainable applications.

Conclusion

In summary, we have developed a noble metal free magnetic catalyst for dehydrogenation of formic acid that exhibits high efficiency in aqueous solution under the mild conditions. $CoFe_2O_4$ NPs were synthesized onto graphene oxide sheets and then selenium doping was accomplished to obtain the Se-

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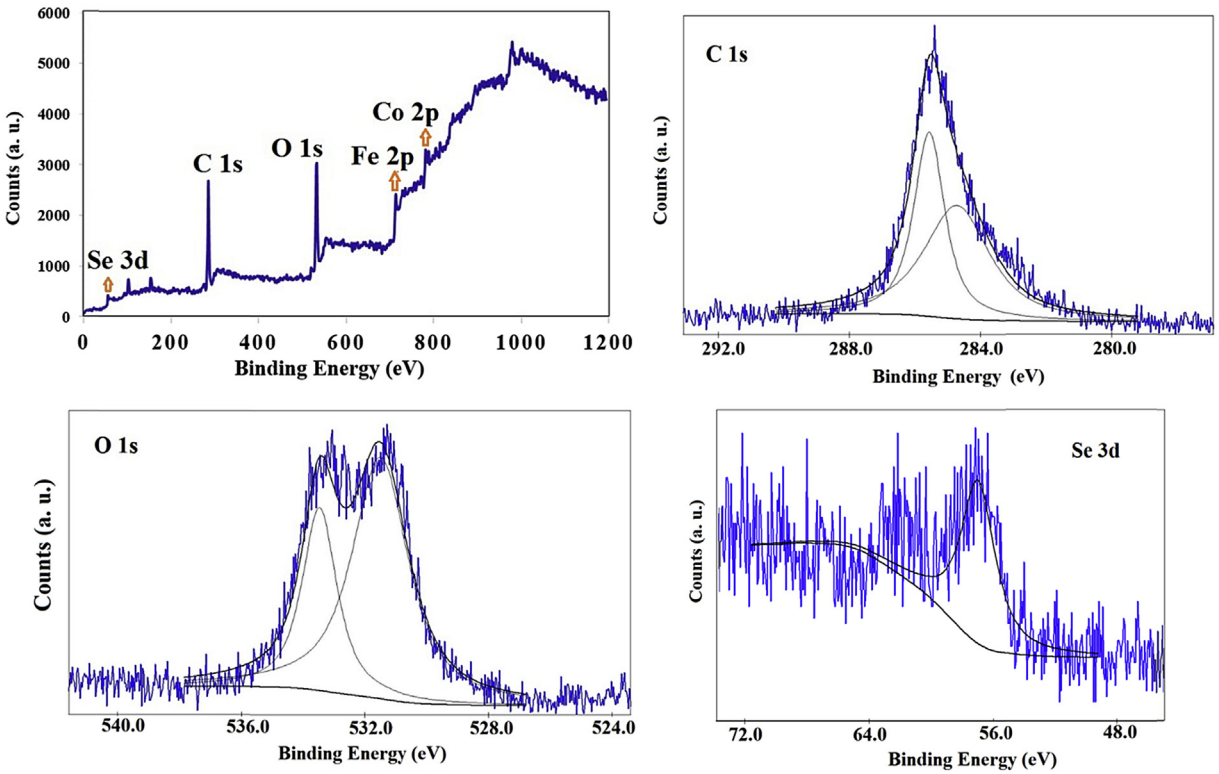

Fig. 4 – XPS spectrum of Se-doped graphene/$CoFe_2O_4$, and high resolution XPS spectra of C 1s, O 1s and Se 3d.

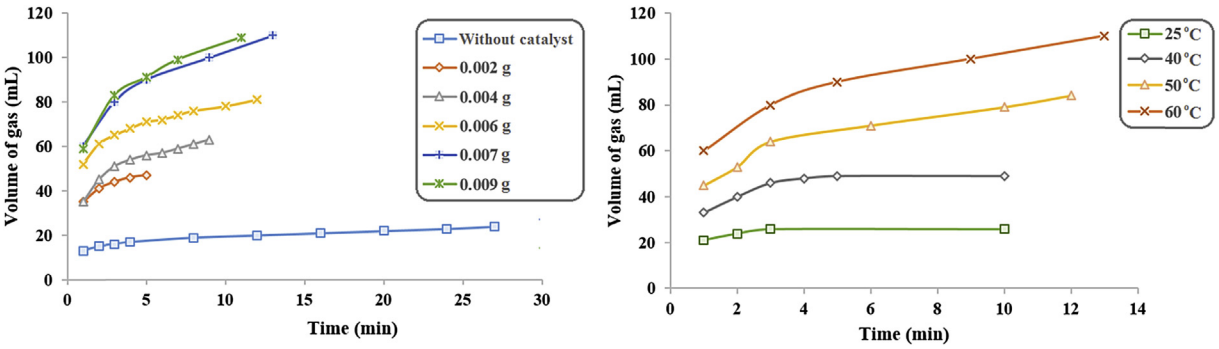

Fig. 5 – The effect of temperature and catalyst amount on gas generation (60 °C for optimization of catalyst amount, and 0.007 g catalyst for optimization of temperature).

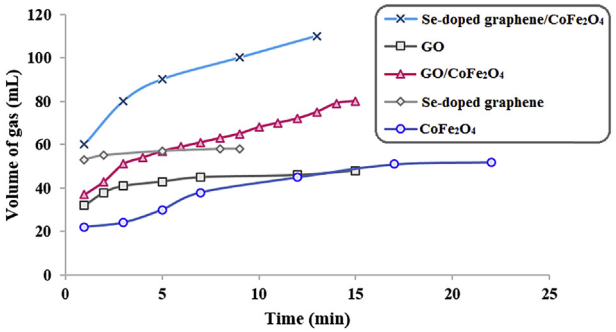

Fig. 6 – Volume of the generated gas versus time for the dehydrogenation of FA over GO, $CoFe_2O_4$, GO/$CoFe_2O_4$, Se-doped graphene and Se-doped graphene/$CoFe_2O_4$ (0.007 g catalyst, 60 °C).

doped graphene/$CoFe_2O_4$. Various characterization techniques such as SEM, TEM, FT-IR, XRD, TGA, XPS and VSM were performed to confirm the formation of as-obtained materials. According to the results, Se-doped graphene/$CoFe_2O_4$ exhibited better catalytic activity than pure $CoFe_2O_4$, GO, Se-doped graphene and GO/$CoFe_2O_4$ hybrid materials which the possible explanations were presented. The suggested catalyst provides a cost-effective, environmentally friendly and noble metal free catalyst with relatively good activity compared to most of reported heterogeneous catalysts for dehydrogenation of formic acid. In addition, the catalyst showed very good durability, stability and also fast and complete recovery by magnetic extraction representing new potentials for the development of more sustainable catalysts for green energy systems.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2016.08.108.

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