Research Article

Preparation of N-Doped Composite Shell Encapsulated Iron Nanoparticles and Their Magnetic, Adsorptive, and Photocatalytic Properties

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The N-doped composite shell encapsulated iron nanoparticles (CSEINPs) were prepared by DC arc discharge under nitrogen at 800°C, using the anode with high Fe content and good homogeneity. The morphology, microstructure, composition, and some properties of the N-doped CSEINPs were characterized by various characterization techniques. The results revealed that the shells of the N-doped CSEINPs were composed of homogeneously amorphous structure containing C, Fe, O, and N elements; the saturation magnetization (M_s) and coercivity (H_c) of them at room temperature were 130 emu/g and 194 Oe, respectively. Due to the surface structure and the electrostatic interaction, the N-doped CSEINPs are employed to remove methylene blue (MB) from the waste solution, and they exhibited high adsorption properties and photocatalytic activity under irradiation of visible light (IVL). The kinetics of adsorption of MB on the N-doped CSEINPs was investigated and the recycling test was carried out. The formation mechanism of the N-doped CSEINPs is discussed briefly.

1. Introduction

Magnetic nanoparticles exhibit some important properties and have many applications, like magnetic recording materials [1], microwave absorber [2], magnetic hyperthermia treatment [3], drug delivery [4], catalyst supports [5], organic dye adsorbent [6], lithium-ion battery anode [7], and so forth. The magnetic nanoparticles, however, usually have high chemical activity and are easily aggregated or oxidized in the air, leading to the loss of magnetism and some unique properties. Carbon encapsulated magnetic nanoparticles (CEMNPs) have attracted increasing interests, as carbon layers can not only protect the magnetic nanoparticles from oxidation and magnetic degradation, but also inhibit their aggregation and promote phase formation by weakening the magnetic coupling [8]. Various methods, such as hydrothermal reaction [9], chemical vapor deposition [10], laser ablation [11],

sol-gel [12], spray pyrolysis [13], and arc discharge [14], have been used to prepare CEMNPs.

The carbon shell usually consists of graphite structure, amorphous carbon, or turbostratic structure. But, sometimes, the shell may be a composite one containing several different substances. Zhang et al. prepared the carbon encapsulated iron nanoparticles by DC arc discharge and found that the shell contained C, Fe, and O elements and its structure consisted of three parts; that is, the inside part was nongraphite, the middle one was incomplete graphite, and the outside one was amorphous carbon [15]. Kim et al. employed the process of chemical vapor condensation to prepare the carbon-coated Fe nanocapsules, and the shell was a double layer structure, that is, Fe_3C and graphite layers [16]. Zhang et al. synthesised the core-shell-shell composite submicrospheres ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MnO}_2$) by homogeneous precipitation of MnO_2 on $\text{Fe}_3\text{O}_4@\text{SiO}_2$ spheres, which were

prepared by a modified sol-gel method in the presence of Fe_3O_4 particles, and the submicrospheres showed superparamagnetic property (M_s value 29.41 emu/g), high activity of chemical adsorption, and good stability for the decolouration of organic dye [17].

Organic dyes with complex aromatic structures and xenobiotic properties seriously induce water pollution and are difficult to be degraded, leading to very harmful effects on aquatic lives and human beings [18]. For example, MB can cause eye burns of humans and animals and also gives rise to dyspnea, tachycardia, and mental confusion [19]. Therefore, it is necessary to remove MB from waste solution before discharge. To date, the processes of adsorption and photodegradation, in which the magnetic materials are used, are the most well-developed methods to remove organic dyes from waste water. Qu et al. used B- Fe_3O_4 @C composites as adsorbent for the removal of MB. The adsorption capacity at equilibrium increases from 26.1 to 40.88 mg/g, with an increase in the initial dye concentration from 14 to 52 mg/L [20]. Wang et al. employed the graphite carbon encapsulated Fe_3C nanoparticles (Fe_3C @GC NPs) to remove MB. The Fe_3C @GC NPs exhibited ferrimagnetic behavior at room temperature, with a value of M_s of 61.5 emu/g. The adsorption capacity of MB on Fe_3C @GC NPs was 33.1 mg/g [21]. Bai et al. fabricated the ferrite hybrids (MFe_2O_4 , $\text{M}=\text{Mn}$, Zn , Co , and Ni) supported on the reduced graphene oxide (RGO). The maximum adsorption capacities of RhB and MB on RGO- MFe_2O_4 were 22.52 mg/g and 34.72 mg/g, with the initial dyes concentration of 10 mg/L. The different RGO- MFe_2O_4 hybrids decomposed over 85% of RhB and MB after 180 min under tungsten lamp of 500 W [22]. Mansour used the prepared $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles as catalyst and hydrogen peroxide as oxidant to degrade MB under UV light, and about 98% of MB was degraded within about 100 min [23]. Rashid et al. reported that the magnetic core-shell-shell nanoparticles $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ showed high photocatalytic activity toward 2-chlorophenol in wastewater. They also carried out the leaching test to check the robustness of the nanoparticles in aqueous medium [24].

In this work, we present the preparation of N-doped CSEINPs by DC arc discharge. Their morphology, structure, composition, and magnetic properties were investigated. The N-doped CSEINPs were used as adsorbent to remove MB from its aqueous solution and their photocatalytic activity was also investigated. They exhibited high adsorptive capacity and photocatalytic activity for the removal and photodegradation of MB, respectively, and may be the highly efficient and environmentally friendly candidate for the treatment of waste water. The possible mechanism for the process of formation of N-doped CSEINPs is briefly discussed.

2. Experimental

2.1. Preparation of Anode. Iron (III) oxide (purity > 99 wt.%) and graphite (purity > 99.99 wt.%) powders were mixed at the weight ratio of 9:1. The equal amount (50 wt.%) of binder (syrup, mainly consisting of glucose) was mixed with the above mixture and then dried at ca. 150°C. After cooling to room temperature, the dried product was ground into

powders and then filled in a mold, and subsequently the filler was compressed under ~3 MPa to form a composite rod. Finally, the rod was carbonized at 800°C under argon atmosphere for one hour and a cylindrical anode (~6.6 mm diameter and ~50 mm length) was obtained. The phase composition of the as-prepared anode mainly includes Fe, graphite carbon, FeO, and a small amount of Fe_3O_4 (see Figure S1 in Supplementary Material available online at <https://doi.org/10.1155/2017/7868121>). The content of Fe in the anode was ca. 75.5 wt.% (see Figure S2 and the calculations in Supplementary Material).

2.2. DC Arc Discharge. The arc discharge apparatus is similar to that reported in [25], but some modifications were made [26]. The cathode was a pure graphite rod (15 mm diameter and 10 mm length). The intake temperature of nitrogen was chosen as 800°C because of the considerations of the decrease of temperature gradient in the environment around arc discharge zone, the possible decomposition of nitrogen, and the lifetime of the heating apparatus. The arc discharge voltage and current between anode and cathode were about 30–40 V and 30–40 A, respectively. The gap between two electrodes was kept at a distance of 1–2 mm by manually advancing the anode, while keeping the cathode fixed. The duration of arc discharge was 50 s. The products A–E were collected from the different parts inside the arc discharge chamber (ADC), as described previously [25]. The main morphologies of the products A, B, D, and E are similar and all of them mainly consist of the nanoparticles, as shown in Figure 1. The insets in Figure 1 show the core-shell structure of nanoparticles in the products A, B, D, and E. The product C deposited on the top of cathode mainly consists of the nanosheets (see Figure S3 in Supplementary Material) and may be presented in another paper. As the research emphasis of this work is the nanoparticles and the amount of the product B is the most among products A, B, D, and E, all of the characterizations were focused on product B. The schematic diagram for the preparation of product B is shown in Figure 2.

2.3. Characterizations. Product B was characterized by using high-resolution transmission electron microscope (HRTEM, TECNAI G²F20, Philips), energy dispersive X-ray (EDX) spectroscopy, and electron energy loss spectroscopy (EELS, GIF 863 Tridiem, detectable limit 0.05–0.1 at.%) both of which were equipped with HRTEM, X-ray diffractometer (XRD, Pert PRO, Panalytical), Fourier Transform Infrared Spectrometer (FTIR, Perkin-Elmer Spectrum GX), and thermogravimetry-differential scanning calorimeter (TG-DSC, STA409PC, Netzsch). The magnetic properties were measured by using Physical Property Measurement System (QUANYUM DESIGE PPMS-9, Quantum Design) at room temperature. The adsorptive properties of the N-doped CSEINPs were measured by using UV-vis spectrophotometer (TU-1901, Phenix) and their photocatalytic activity was evaluated by the degradation of MB under IVL.

2.4. Adsorption Experiment of MB. 25 mg N-doped CSEINPs was added to 50 mL MB aqueous solution (10–60 mg/L) and the mixture was shaken under natural light for some time.

FIGURE 1: TEM images of products (a) A, (b) B, (c) D, and (d) E. The inserts are the images at higher magnification and show the core-shell structure of the nanoparticles.

FIGURE 2: Schematic illustration of preparation process of product B [27].

Subsequently, the suspension was handled with a magnet and then the MB concentrations were measured with UV-vis spectrophotometer. The amounts of MB adsorbed on the N-doped CSEINPs were calculated from its concentrations before and after adsorption at room temperature.

The removal (%) of MB was calculated based on the following equation [6]:

$$\text{Removal (\%)} = \left(1 - \frac{C_t}{C_0}\right) \times 100\%, \quad (1)$$

where C_0 and C_t are the concentrations (mg/L) of the beginning and time t of MB, respectively.

The adsorbed amount (q) of MB was calculated using the following equation [6]:

$$q = (C_0 - C_t) \frac{V}{m}, \quad (2)$$

where m is the mass of adsorbent (g) and V is the volume of solution (L).

2.5. Photocatalytic Degradation Experiment of MB. The visible light was obtained by a 500 W xenon lamp (Institute of Electric Light Source, Beijing) with a 420 nm cutoff filter. 18 mg N-doped CSEINPs was dispersed in 50 mL MB aqueous solution (10 mg/L). The suspension was magnetically stirred in the dark for 60 min to reach the adsorption-desorption equilibrium. After the light was turned on, 4 mL suspension was sampled at certain intervals and then centrifuged to remove the nanoparticles. The filtrates were analyzed by recording the variations at the absorption band of 664 nm in the UV-vis spectra of MB.

3. Results and Discussion

Figure 3(a) shows the HRTEM image of product B at low magnification, in which many relatively dispersed and approximately spherical nanoparticles can be observed. It can be clearly seen that the nanoparticles have typical core-shell structure (Figure 3(b)), that is, the light black core and gray shell. The diameter of nanoparticle A is about 91 nm and the thickness of its shell is about 6 nm. The result of EDX measurement shows that the atomic percent contents of the elements C, Fe, O, and N at the region inside the white circle in Figure 3(b) are 15.05%, 68.87%, 5.63%, and 10.46%, respectively (see Figure S4 in Supplementary Material). Figures 3(c) and 3(d) are the enlarged images of the upper and lower shells of nanoparticle A in Figure 3(b), respectively. Both of the shells are composed of disordered structure and there is no layered structure of graphite. The histogram of size distribution of the nanoparticles is shown in Figure 3(e). The diameters of approximately 95.6% nanoparticles are in the range of 3–44 nm and the average diameter is about 20.8 nm.

As the temperature at the center of arc discharge zone may reach 3500–5000 K [28], it is impossible to take the samples in situ or monitor the process of reactions during arc discharge with any present technique, so there is little direct experimental evidence for the mechanisms of formation of graphene and carbon nanotubes [29]. By analyzing the results of EELS line scanning measurement in detail, however, it may be possible to get helpful information or indirect evidence for one to understand the mechanism of formation of the as-prepared core-shell nanoparticles, like the investigation on fossil. As far as we know, no such analyzing work has been reported until now.

Figure 4(a) shows the image of the morphology corresponding to the EELS line scanning measurement of nanoparticle A in Figure 3(b). It is shown in Figure 4(b) that, in the region of the upper shell (3.7–9.7 nm), along the radial direction of nanoparticle A, C signal gradually increases to

the maximum and then reduces gradually; Fe signal gradually reduces to zero; O signal gradually increases to a maximum and then gradually decreases to zero; N signal is very weak. In the region of the lower shell (87.5–94.2 nm), also along the radial direction of nanoparticle A, the C, Fe, O, and N signals show the similar changes as those observed in the region of the upper shell. The above results indicate that the elemental compositions in the upper and lower shells are not uniform and the trends of their changes are basically the same.

It is also shown in Figure 4(b) that in the core region (9.7–87.5 nm) of nanoparticle A, C signal is gradually weakened in the region of 9.7–20 nm at first and then slightly remains unchanged; it gradually increases in the region of 83–87.5 nm; that is, it gradually increases on both sides of the center, along the radial direction of nanoparticle A; Fe signal gradually increases in the region of 9.7–14 nm and gradually decreases in the region of 82–87.5 nm; that is, there is a slight concave on the curve between 14 and 82 nm. The slight concave may be caused by the comparatively large diameter of nanoparticle A, as the electron beam of EELS line scanning measurement could not penetrate it completely, leading to the decrease of Fe signal collected; the maximum of O signal appears in both the upper and lower shells, near the position of interface between shell and core, and it gradually increases in both regions of 9.7–20 nm and 80–87.5 nm along the radial direction of nanoparticle A but is very weak in the region 20–80 nm, though there are some fluctuations; N signal is very weak almost in the whole region. The above results indicate that the elemental compositions of two regions with lengths of about 10 nm at the inner sides of the interfaces between shell and core are nonuniform and the composition of the central region (20–80 nm) of the core is relatively uniform. Based on the above results of HRTEM, EDX, and EELS line scanning characterizations, it can be concluded that the nanoparticles in product B, with core-shell structure, are N-doped CSEINPs.

Figure 4(c) is the magnified image of the morphology of nanoparticle A corresponding to EELS line scanning measurement. In order to further investigate the uniformity of composition of nanoparticle A, seven representative points are selected along the track of the EELS line scanning measurement. P_1 and P_7 points are located at the midpoints of the upper and lower shells, respectively, P_2 and P_6 points are located at the inner sides of the interfaces between shell and core, P_3 and P_5 are located at the midpoints of the core radius, and P_4 is the center of the core.

Figure 4(d) shows the EELS spectra corresponding to P_1 – P_7 points, respectively. For the characteristic peaks of the C-K edge (~287–297 eV), the peak intensities of the spectra at P_1 and P_7 points are remarkably stronger than those at other five points, but the peak intensity at P_1 is obviously stronger than that at P_7 point; the peak intensities at P_2 and P_6 points take second place and the difference between them is not obvious; the peak intensities at P_3 , P_4 , and P_5 points are the weakest and the difference among them is also not obvious. For the characteristic peaks of the N-K edge (~398–415 eV), all the peak intensities at P_1 – P_7 points are very weak. For the characteristic peaks of the O-K edge (~530–560 eV), there are obviously weak peaks at P_2 and P_6 points and no

FIGURE 3: (a) HRTEM image of product B at low magnification. (b) Several nanoparticles with core-shell structure; (c) and (d) high magnification of the upper and lower shells of nanoparticle A in (b). (e) Histogram of size distribution of the nanoparticles.

FIGURE 4: (a) Image of the morphology corresponding to EELS line scanning measurement of nanoparticle A and (b) EELS line scanning spectra of nanoparticle A. (c) Magnified image of the morphology of nanoparticle A and (d) EELS spectra corresponding to P_1 – P_7 points in (c), respectively.

obvious peaks at other five points. For the characteristic peaks of the Fe-L edge (~ 709 – 722 eV), the peak intensities at P_1 and P_7 points are very weak and those at other five points are comparatively strong, but the peak intensities at P_3 , P_4 , and P_5 points are slightly stronger than those at P_2 and P_6 points. It is known from the above analysis that the EELS spectra at the points of the symmetrical positions are similar, except those at P_1 and P_7 points, but those at the different points of the asymmetrical ones show remarkably different peak intensities.

Figures 5(a)–5(d) show the fine structures of C-K, N-K, O-K, and Fe-L edges in the EELS spectra of P_1 – P_4 points, respectively. The peak intensities (287.9 eV and 297.4 eV) at P_1 and P_2 points are stronger than those at P_3 and P_4 points, as shown in Figure 5(a). These peaks reveal that the sp^2

hybridization of carbon atoms is present in the nanoparticle and the peak at 287.9 eV can be attributed to the electron transition of excitation from C1s core level to π^* band, and the sharper this peak is, the higher the degree of graphitization of the corresponding structure is; the broadband at ~ 297.4 eV is the characteristic peak of the electron transition of excitation from C1s level to σ^* band [29].

Figure 5(b) shows that, at P_1 point, there are three peaks at ca. 398.3 eV, 399.3 eV, and 401.6 eV, but the peak at 399.3 eV is very weak; at P_2 point, there are three peaks at 398.3 eV, 399.8 eV, and 401.8 eV, but the peak at 399.8 eV is stronger than the other two ones; at P_3 point, there are two peaks at 398.3 eV and 401.6 eV; at P_4 point, there are two peaks at 398.3 eV and 401.9 eV, but the latter is stronger than the former. The peaks at ~ 398.3 eV, 399.8 eV, and 401.8 eV should

FIGURE 5: Fine structures of C-K (a), N-K (b), O-K (c), and Fe-L (d) edges in the EELS spectra of P₁–P₄ points.

correspond to the π^* characteristic peaks of the pyridinic, pyrrolic, and graphitic nitrogen, respectively [30]. The peaks between 404 and 415 eV belong to the σ^* characteristic band of N-K edge [31]. The differences among the peak intensities and positions at the different points mean that the mechanisms of nitrogen taking part in the reactions during the process of formation of the nanoparticle may be different.

Figure 5(c) shows that the characteristic peaks of O-K edge are weak at P₁, P₃, and P₄ points, but those at P₂ point are strong, especially the two peaks at 530.8 eV and 540.0 eV. The peak at 530.8 eV corresponds to the electron transition from O1s core state to the unoccupied orbitals formed by the interaction of the O2p with the Fe3d states; the other three peaks at 540.0 eV, 549.6 eV, and 558.9 eV are generally attributed to the electron transition from the O1s to the vacant orbitals formed by the interaction of the O2p with the Fe4s and 4p states [32, 33]. The remarkable difference between the peak intensity at P₂ and those at P₁, P₃, and P₄ means that the main range of temperature of oxygen taking part in the reactions during the process of formation of the nanoparticle may be limited.

Figure 5(d) shows that the characteristic peaks of Fe-L edge are very weak at P₁ point, but the characteristic peaks of L₃ (709.4 eV) and L₂ (722.4 eV) edges at P₂–P₄ points are obviously strong and their intensities gradually increase from P₂ to P₄ points. These two peaks should correspond to the electron transitions from the two levels, formed due to the spin-orbital splitting of 2p orbitals, to the 3d ones ($2p_{3/2} \rightarrow 3d$ and $2p_{1/2} \rightarrow 3d$), respectively [32, 34]. The remarkable difference between the peak intensities at P₂–P₄ and that at P₁ means that the degree of iron taking part in the reactions should gradually decrease from the center of core to the interface between core and shell and then sharply declines during the formation of shell.

The above analysis shows that there are some differences among the bonding states between the distinct elements at the different points of the nanoparticle A, concerning the mechanism, degree, and temperature range of the different elements taking part in the reactions during the process of arc discharge. Such information should be a kind of true reflection for the mechanism of formation of the as-prepared core-shell nanoparticles, like the information found in fossil,

FIGURE 6: XRD pattern of the product B (Co K α).

FIGURE 7: TG-DSC curves of product B.

by which one can guess what may happen or exist in the ancient time.

Figure 6 shows the XRD pattern of products B. The diffraction peak at 30.96° is matched well with graphite carbon (PDF Card Number 75-2078). The peaks at 44.19° , 46.74° , 50.96° , 53.94° , 57.86° , 61.26° , 64.47° , and 68.68° can be ascribed to Fe_3C (PDF Card Number 72-1110); those at 52.40° and 77.41° can be assigned to Fe (PDF Card Number 87-0721); those at 50.968° and 59.47° can be attributed to $\text{CFe}_{15.1}$ -Austenite (PDF Card Number 52-0512). The above results reveal that the phase composition of products B includes graphitic carbon, Fe, Fe_3C , and Austenite $\text{CFe}_{15.1}$. The XRD patterns of the products A, D, and E (see Figure S5 in Supplementary Material) show the similar profile with that in Figure 6; that is, they have the similar phase composition with the product B.

Figure 7 shows the TG-DSC curves of the products B. The TG curve shows that from room temperature to about 220°C the sample did not have obvious weight change; from 220°C to 675°C , it had a remarkable weight gain; from 675°C to 1100°C , it had only a small weight gain. The DSC curve shows

FIGURE 8: Magnetic hysteresis loop of product B at room temperature.

one strong and two weak exothermic peaks. The strong peak that appeared at 556°C is due to the oxidation of amorphous carbon and iron species [35], and the weak peaks which appeared at 656°C and 840°C are due to the oxidation of graphite carbon and the deep oxidation of little iron species [36, 37], respectively. As the sample had finally weight gain, it is inferred that the weight gain of oxidation of iron species is larger than the weight loss of oxidation of graphite carbon. The Fe content of product B was calculated to be about 85.6 wt.%, supposing that the final sample (residue) is Fe_2O_3 [38]. The TG-DSC curves of the products A, D, and E (see Figure S6 in Supplementary Material) are somewhat different from those in Figure 7, but the Fe contents in A and E are 85.4 wt.% and 85.7 wt.%, respectively, very close to that in product B, and the Fe content in D is a bit low (80.4 wt.%). This means that there may be some difference among the microstructures of the products A, B, D, and E.

The magnetic hysteresis loop (MHL) of the product B, measured at room temperature, demonstrates the ferromagnetic behavior, as shown in Figure 8. The M_s value of product B is 130 emu/g, estimated from the full MHL of product B (see Figure S7 in Supplementary Material), which is much larger than that of product B_{II} ($M_s = 89$ emu/g) [39]. The main reason may be that the shells of these two kinds of core-shell nanoparticles consist of different compositions and structures, as the Fe content of B is only slightly larger than that of B_{II} (Table 1). The shells of the nanoparticles in B_{II} consist of three to seven layers of graphite and graphite is diamagnetic material, leading to the decrease of M_s value [40]. The shells of the nanoparticles in B are the composite one containing C, Fe, O, and N elements, and Fe_3C is the weakly ferromagnetic phase ($M_s = \sim 140$ emu/g [39]), Fe_3N is the ferromagnetic phase [41], austenite is the paramagnetic phase [42, 43], and iron oxide is the superparamagnetic phase, leading to the larger M_s value [44]. But both the two M_s values are smaller than that of the bulk iron ($M_s = 222$ emu/g) [39]. This is because both B and B_{II} are mainly composed of the nanoparticles with core-shell structure.

TABLE 1: Fe contents, shell structures, and magnetic properties of the products B and B_{II}.

Sample	Fe content (wt.%)	Av. particle size (nm)	Shell structure	<i>Ms</i> (emu/g)	<i>H_c</i> (Oe)	<i>Mr/M_s</i>	Reference
B	85.6	20.8	Composite shell	130	194	0.062	This work
B _{II}	82.6	20.6	3–7 layers of graphite	89	240	0.124	[39]

The *H_c* value of product B is 194 Oe, which is smaller than that of B_{II} (240 Oe) [39] (both of the *H_c* values are much larger than that of the bulk iron (*H_c* = ~1 Oe) [45]). The reason may be the same as the above one for the difference between two *Ms* values, as the difference between the average sizes of the nanoparticles of B and B_{II} is not large. The magnetic properties of the material can also be characterized by the ratio of remanent magnetization to saturation one (*Mr/M_s*). When the ratio is less than 0.25 or the particle sizes of the materials are smaller than the value of their magnetic single domain (about 20 nm for Fe and 60 nm for Fe₃C) [46, 47], the materials will show superparamagnetism at room temperature [46]. Although the *Mr/M_s* value (0.062) of B is much smaller than 0.25, it shows ferromagnetic behavior. This may be because the sizes of about 39.2% nanoparticles of the product B are larger than 20 nm (Figure 3(e)).

Figure 9(a) shows the removal efficiency of MB solution (*C*₀ = 10 mg/L) with the N-doped CSEINPs under natural light. It can be observed that the MB adsorption on the N-doped CSEINPs is very fast at the first 3 min and it almost reaches the adsorption equilibrium in 10 min. The insets in Figure 9(a) show the color change of the MB solution before (left) and after (right) being treated with the N-doped CSEINPs. Figure 9(b) shows that the adsorption capacity of MB increases from 19.9 to 44.3 mg/g in 300 min, with the increase of the *C*₀ from 10 to 60 mg/L. The inset in Figure 9(b) shows that the MB adsorption on the N-doped CSEINPs is also very fast at the first 3 min for all of the MB solutions and the adsorption amount of MB obviously increases with the increase of the *C*₀, neglecting the experimental error. The results may be attributed to an increase in the driving force of concentration gradient with the increase of the *C*₀.

The kinetic data were analyzed using pseudo-second-order kinetics, which was defined as follows [18]:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}, \quad (3)$$

where *q_t* and *q_e* are the adsorption amounts of MB at the time *t* and equilibrium (mg/g), respectively. *k₂* is the pseudo-second-order rate constant of the kinetic model (g/mg·min).

Figure 9(c) shows the kinetic curves of *t/q_t* against *t* and the values of kinetic parameters are listed in Table 2. It is observed from Figure 9(c) that the slope of the curve decreases with the increase of *C*₀. The correlation coefficients *R*₂ in Table 2 are higher than 0.99 and the experimental value *q_e* (*q_e-exp*) is in accordance with the calculated one *q_e* (*q_e-cal*). This means that the adsorption of MB on the N-doped CSEINPs fits the pseudo-second-order kinetic model [22, 27, 48].

The above adsorption performance of the N-doped CSEINPs may be ascribed to the defects and dangling

bonds on the surfaces of them, as they formed under the conditions of large temperature and concentration gradients. In addition, as aqueous MB is a cationic monovalent dye [49], the electrostatic interactions between the positively charged dye and oxygen-containing functional groups on the surface of N-doped CSEINPs also play an important role in the adsorption [50].

Figure 10(a) shows the curves of the removal rate of MB (*C*₀ = 10 mg/L), without and with the N-doped CSEINPs. In the blank experiment, the concentration of MB shows no change, with no IVL. The concentration of MB gradually decreases with the extension of IVL (the decrement is ca. 13% in 150 min). This may mean that MB has a little photolysis under IVL [50]. The adsorption equilibrium was reached in 10 min in the dark and the corresponding removal rate of MB was ca. 66%, in presence of the N-doped CSEINPs. The removal rate of MB gradually increased with the extension of IVL and reached about 90% in 150 min. Figure 10(b) shows the adsorption spectra of MB solution at different adsorption and IVL time with the N-doped CSEINPs. The intensity of the characteristic absorption peak of MB at 664 nm decreased sharply at 10 min after the N-doped CSEINPs were added and then gradually decreased with the extension of IVL.

To evaluate the reusability of the N-doped CSEINPs, the recycling test for the adsorption and photocatalytic degradation of MB with the N-doped CSEINPs was carried out, and the results are shown in Figure 11. After the first cycle, the abilities of the adsorption and photocatalytic degradation decrease obviously, and then they gradually decrease with the increase of the number of cycles. In the fourth cycle, only about 50% of MB can be removed with the N-doped CSEINPs. The reasons for the above results may be that some residual MB molecules adsorbed on the N-doped CSEINPs hindered the adsorption and reduced the active sites.

Figure 12(a) shows the FTIR spectrum of the N-doped CSEINPs. The strong broad peak at ~3442 cm⁻¹ is attributed to stretching vibration of hydroxyl groups (-OH groups) of adsorbed water. The weak peaks at ~2921 cm⁻¹ and 1391 cm⁻¹ are associated with stretching vibration and flexural vibration of C-H bonds, respectively. The peak at ~1627 cm⁻¹ is related to C=O group. The peaks at ~1116 and 1044 cm⁻¹ are ascribed to -C-OH groups. The peak at ~598 cm⁻¹ is characteristic of the Fe-O vibrations [27]. Those hydrophilic functional groups result in the enhanced hydrophilia of the obtained composite. Figure 12(b) shows the FTIR spectrum of the N-doped CSEINPs-MB complex. The latter is obviously different from the former; that is, some peaks in the former sharply decrease or almost disappear, and the characteristic peaks of MB molecules appear, shifting to the lower wavenumbers (ca. 1581 and 1326 cm⁻¹) [51]. The changes in FTIR spectra indicate that ionic interactions between cationic dyes and the

FIGURE 9: (a) The removal efficiency of MB ($C_0 = 10$ mg/L) with the N-doped CSEINPs versus time; the insets show the photographs of the MB aqueous solution before (left) and after (right) being treated with the N-doped CSEINPs. (b) Curve of the adsorbed amount of MB with the N-doped CSEINPs versus time ($C_0 = 10$ –60 mg/L). (c) Kinetics curves of adsorption of MB on the N-doped CSEINPs.

TABLE 2: Parameters of pseudo-second-order kinetic model of MB adsorbed by the N-doped CSEINPs.

Concent. ratio (mg/L)	q_{e-exp} (mg/g)	q_{e-cal} (mg/g)	k_2 (g/mg·min)	R_2
10	19.95	19.98	1.18×10^{-1}	0.999
20	28.35	28.69	1.14×10^{-2}	0.999
30	32.56	32.84	8.08×10^{-3}	0.999
40	36.02	36.38	4.42×10^{-3}	0.998
50	40.25	40.93	3.93×10^{-3}	0.998
60	44.27	45.20	2.81×10^{-3}	0.997

FIGURE 10: (a) Curves of the removal rate of MB versus time, without (blank) and with the N-doped CSEINPs, in the dark and then under IVL. (b) Changes of the UV-vis spectra of the MB aqueous solution versus time, without and under IVL, in presence of the N-doped CSEINPs.

FIGURE 11: Recycling test for the photocatalytic degradation of MB with the N-doped CSEINPs.

negatively charged groups were formed and MB molecules were adsorbed on the surfaces of the N-doped CSEINPs.

Figure 13 shows the HRTEM images of the N-doped CSEINPs after being used in the recycling test. Compared with Figures 3(a) and 3(b), it is found that the morphology and structure of the nanoparticles have changed significantly; that is, many of the nanoparticles are already not approximately spherical and do not have the core-shell structure, and the dispersion of the nanoparticles becomes bad. The result of EDX measurement shows that the atomic percent contents of the elements C, Fe, O, and N at the region inside the red circle in Figure 13(b) are 4.20%, 35.73%, 57.43%, and 2.64%,

respectively (see Figure S8 in Supplementary Material); that is, the composition of the nanoparticles has also changed obviously.

The XRD pattern of the N-doped CSEINPs after being used in the recycling test is shown in Figure 14, which reveals that the phase composition includes graphitic carbon, Fe, Fe_3C , Fe_3O_4 , and Austenite $\text{CFe}_{15.1}$. Compared with Figure 6, the peaks of the primary phases still exist, but the peaks of Fe_3O_4 and amorphous carbon (ca. 23°) appear. These changes are consistent with the disappearance of the core-shell structure and the atomic percent contents of C, Fe, O, and N elements obtained by EDX characterization (Figure S8). The reasons for the above changes of morphology, microstructure, and phase composition may be that the

FIGURE 13: HRTEM images of the N-doped CSEINPs after being used in the recycling test.

FIGURE 14: XRD pattern of the N-doped CSEINPs after being used in the recycling test (Cu K α).

interaction between the nanoparticles and MB molecules is strong and the core-shell structure of the nanoparticles is metastable, leading to the oxidization of Fe in the shell and the disappearance of the core-shell structure. Such changes may also be some of the reasons which result in the decreases of the adsorption and photocatalytic degradation abilities of the nanoparticles.

It was reported that the mechanisms of gas-liquid-solid model [52], surface diffusion [53], gas phase nucleation [54], carbon dissolution model [55], and particle self-assembling growth [56] could be used to explain the formation mechanism of some of the carbon-coated metal nanoparticles. These mechanisms have some reference significance for the understanding of the formation mechanism of N-doped CSEINPs. On the basis of the results in the references

and our experimental ones, especially those of the EELS characterization, the possible formation mechanism of N-doped CSEINPs is supposed as follows.

During the process of arc discharge, there is a large temperature gradient between the center of arc discharge zone and the inner wall of cooling copper pipe (the average temperature gradient is about $87.5\text{--}94.4^\circ\text{C}\cdot\text{mm}^{-1}$ [57]); under the function of arc blowing force [58], the species formed by evaporation or sublimation of the anode spread from the center of arc discharge to the surrounding space and a concentration gradient is formed. With the sharp decrease of temperature, the mixture vapor condenses to form many tiny droplets mainly containing C and Fe elements and maybe small amounts of O and N elements, most of C ions or atoms react with Fe ions or atoms to form Fe_3C , and small amount of C atoms may separate out and diffuse to the droplet surfaces; N ions react with Fe and C ions or atoms to form Fe_xN_y and C_xN_y , respectively, and O ions or atoms react with Fe ions or atoms to form Fe_xO_y . As the droplets may be in an approximately rotating state during the process of the continued diffusion, the approximately spherical cores mainly containing Fe and Fe_3C are formed due to the condensation of small droplets, with the further decrease of the temperature [52].

As the diameter of anode used in this work is larger about 1.6 mm than that reported in the reference [39] (the iron content of the former is ca. 75.5 wt.% (Figure S2) and that of the later is ca. 85.5 wt.% [39]; other experimental conditions are similar), the density of species formed by evaporation or sublimation of the anode during the process of arc discharge will increase, leading to the increase of probability of collision among the species and consequently the probability of reaction among them will increase [59]. But the increasing degree of the reaction rates between C and Fe, O, and N three elements should be significantly larger than that between C and C atoms; therefore the shell formed is the composite one containing C, Fe, O, and N elements, rather than the one composed of graphite structure. As the

shell surface has no obvious amorphous structure, the shell should be formed in the liquid phase or the region near to the boundary between liquid and solid phases.

Arc discharge can generate high temperature corresponding to tens of eV and thus some of nitrogen molecules may be dissociated (the dissociation energy of nitrogen molecule is 9.76 eV) [60]. According to the results of EELS characterization (Figures 4(b) and 5(b)), it is speculated that the main temperature range of N ions taking part in the reactions should correspond to that of formation of the region between the core-shell interface. The O element may be derived from the residual air in the arc discharge chamber (only a mechanical vacuum pump was used to wash the chamber), as well as the anode (Figure S1). Similarly, according to the results of EELS characterization (Figures 4(b) and 5(c)), the main temperature range of O ions or atoms taking part in the reactions is speculated to correspond to those of formation of the regions on both sides of the interface between core and shell. Although the exact temperature ranges cannot be determined by the present techniques, it is known from the above related analysis and discussion that it may be very important to modify the temperature gradient in the arc discharge chamber for controlling the composition, structure, and morphology of the products formed by DC arc discharge.

On the bases of the experimental materials, characterization results, and the above discussions, it is inferred that the following reactions may happen during the process of arc discharge:

During the process of arc discharge, as all of the reactions may occur instantaneously and the whole system is in a dynamic nonequilibrium state, and, moreover, the temperature is very high, and it is unable to detect various intermediates of reactions and the exactly existent forms of some products can not be determined at present; the exact temperature ranges of formation of core and composite shell have yet to be verified. All these issues need to be studied further in the future.

4. Conclusions

In summary, we successfully prepared the N-doped CSEINPs by DC arc discharge under nitrogen atmosphere at 800°C. The shells of N-doped CSEINPs are composed of homogeneously amorphous structure containing C, Fe, O, and N elements. The product shows typically ferromagnetic behavior at room temperature and its M_s and H_c values are 130 emu/g and 194 Oe, respectively. The adsorption capacity of MB with the N-doped CSEINPs increases from 19.9 to 44.3 mg/g, with the increase of the initial concentration from 10 to 60 mg/L, and ca. 90% of MB can be degraded under IVL in 150 min. It

is found that the adsorption of MB on the N-doped CSEINPs fits the pseudo-second-order kinetic model. The reusability of the as-prepared nanoparticles is not good, as only about 50% of MB can be removed with the nanoparticles in the fourth cycle. The core-shell structure of them disappears due to the interaction between them and MB molecules. This study presents a method to prepare the N-doped composite shells and thus the properties of the iron nanoparticles with core-shell structure may be easily controlled and modified. Therefore, their areas of application may be expanded further.

Disclosure

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Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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