

Short Communication

In-situ Synthesis of Graphitic Carbon Nitride/Gold Nanoparticle Nanocomposites for Electrocatalytic Reduction of Iron(III)

Haitao Han¹, Dawei Pan^{1,*}, Mingyue Lin¹, Xueping Hu¹, Fei Li²

¹ Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences(CAS); Shandong Provincial Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai Shandong 264003, P. R. China

² The Key Lab in Molecular and Nano-materials Probes of the Ministry of Education of China, College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan Shandong 250014, P.R. China

*E-mail: dwpan@yic.ac.cn

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The graphitic carbon nitride/gold nanoparticle (g-C₃N₄/AuNP) nanocomposites were reported in this paper based on an in-situ synthetic method. After the protonation, ion-exchange, and chemical reduction processes, the g-C₃N₄/AuNP nanocomposites were successfully obtained. The proposed nanocomposites were investigated by various optical and electrical techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction spectroscopy (XRD), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), etc. The g-C₃N₄/AuNP nanocomposites showed excellent electrochemical properties and their preliminary applications toward electrocatalytic reduction of ferric iron were investigated. These nanocomposites exhibit promising prospects for practical application in electrochemical analysis.

Keywords: Graphitic carbon nitride, gold nanoparticle, in-situ synthesis, nanocomposites, iron

1. INTRODUCTION

As the most stable allotrope of carbon nitride, graphitic carbon nitride (g-C₃N₄) has attracted a great deal of attention from experimental and theoretical communities, mainly because of its fascinating properties such as appropriate band gap, excellent biocompatibility, and good chemical stability [1-3]. Particularly, due to its special semiconductor (band gap of 2.7 eV) and visible light

absorption properties [4], g-C₃N₄ has already been widely used as non-metal catalysts for light degradation of organic dyes, photolysis of water to obtain hydrogen, and photocatalytic organic reactions [5-7]. Nowadays, lots of nanocomposites based on g-C₃N₄, such as carbon-doped g-C₃N₄ and Ti-doped g-C₃N₄, and so on, have been proposed to enhance the catalytic activity of g-C₃N₄ [8,9]. As a result, several of methods have been developed to fabricate g-C₃N₄ based nanocomposites [10,11].

On the other hand, gold nanoparticles (AuNPs) possess excellent properties, such as large surface-to-volume ratio, outstanding electrical properties, high surface reaction activity, strong adsorption ability, and excellent biocompatibility [12-15]. In a word, AuNPs possess excellent electrochemical properties and have been widely used as the decorator for nanomaterials.

In this paper, an in-situ method was employed as the effective strategy to synthesize the g-C₃N₄/AuNP nanocomposites. Firstly, g-C₃N₄ was protonated by hydrochloric acid (HCl) to form g-C₃N₄-H⁺Cl⁻. And then, Cl⁻ in g-C₃N₄-H⁺Cl⁻ was ion-exchanged by chloroaurate ions (AuCl₄⁻) which was in-situ reduced to AuNPs by chemical reductant subsequently. The properties of the proposed nanocomposites were studied by various optical and electrical methods, including X-ray diffraction spectroscopy (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transformation infrared spectroscopy (FTIR), and cyclic voltammetry (CV). The preliminary application of g-C₃N₄/AuNP nanocomposites towards electrocatalytic reduction of Fe(III) was also investigated.

2. EXPERIMENTAL

2.1. Materials and apparatus

HAuCl₄ and melamine were supplied by Sinopharm Chemical Reagent Co., Ltd. Iron standard solution was purchased from Acros Organics (USA. <http://www.acros.com/>). All other chemicals are analytical reagents which used without further purification. The used deionized water (18.2 MΩ cm specific resistance) were obtained from Pall Cascada laboratory water system. The properties of the g-C₃N₄/AuNP nanocomposites were characterized by XRD (XRD-7000, Shimadzu Corporation), XPS (Kratos Amicus spectrometer), SEM (Hitachi S-4800), TEM (JEOL-1400), EDS (HORIBA EX-350), and FTIR (Nicoletis10). CHI 660E Electrochemical Work Station was used to carry out all the electrochemical experiments in which a conventional three-electrode cell was adopted. The g-C₃N₄/AuNP nanocomposites modified glassy carbon (GC) disk (3 mm in diameter) was used as the working electrode, with an Ag/AgCl electrode and platinum foil serving as the reference and counter electrodes, respectively.

2.2. Preparation of g-C₃N₄/AuNP nanocomposites

Firstly, g-C₃N₄ was synthesized through the condensation of melamine according to literature [1]. After, the synthesized g-C₃N₄ (0.5 g) was protonated by stirring with HCl (37%, 100 mL) for 3 hours at room temperature to form g-C₃N₄-H⁺Cl⁻. After filtered and thoroughly washed, g-C₃N₄-H⁺Cl⁻

was dispersed in 100 mL freshly deionized water once again with ultrasonication. Then, 2 mL HAuCl_4 (20 mmol L^{-1}) was added to the mixture with stirring, and the Cl^- was ion-exchanged by AuCl_4^- . After removing of the not ion-exchanged HAuCl_4 (centrifugal and washing), excess NaBH_4 was added to the suspension drop to drop with stirring. The $\text{g-C}_3\text{N}_4/\text{AuNP}$ nanocomposites were obtained after the suspension was centrifuged and washed sufficiently.

2.3. Fabrication of $\text{g-C}_3\text{N}_4/\text{AuNP}$ nanocomposites modified electrode

The $\text{g-C}_3\text{N}_4/\text{AuNP}$ nanocomposites modified GC ($\text{g-C}_3\text{N}_4/\text{AuNP}/\text{GC}$) electrode was prepared by dropping the $\text{g-C}_3\text{N}_4/\text{AuNP}$ suspension ($10 \mu\text{L}$) on the surface of GC electrode and drying with an infrared lamp.

2.4. Electrochemical procedure

The $\text{g-C}_3\text{N}_4/\text{AuNP}$ nanocomposites were electrochemically characterized by CV and differential pulse voltammetry (DPV). The CV experiments were carried out at a potential range of -0.2 to 1.5 V at a scan rate of 100 mV s^{-1} in $10 \text{ ml } 0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. The DPV responses of $\text{g-C}_3\text{N}_4/\text{AuNP}/\text{GC}$ and bare GC electrodes to the electrocatalytic reduction Fe(III) with different concentrations ($0, 10, \text{ and } 20 \mu\text{mol L}^{-1}$) were investigated in $0.1 \text{ mol L}^{-1} \text{ HCl}$ solution with the scan range from 0.7 to 0.35 V .

3. RESULTS AND DISCUSSION

Protonation of $\text{g-C}_3\text{N}_4$ can provide the Cl^- for subsequent ion-exchange and improve its dispersion and ionic conductivity [3,16]. Various optical and electrical methods were used to study the properties of the resulting nanocomposites.

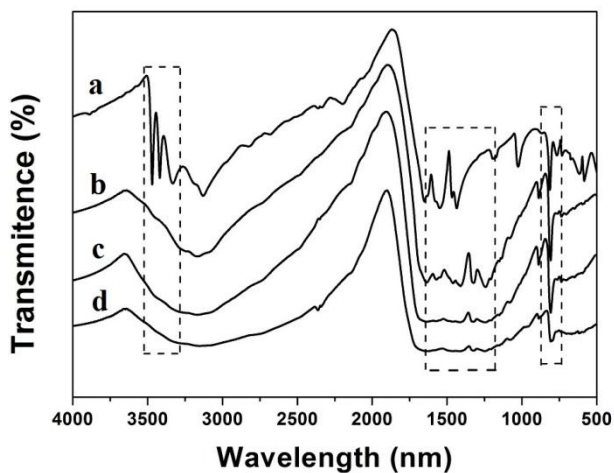


Figure 1. FTIR spectra of melamine (a), $\text{g-C}_3\text{N}_4$ (b), $\text{g-C}_3\text{N}_4\text{-H}^+\text{Cl}^-$ (c), and $\text{g-C}_3\text{N}_4/\text{AuNP}$ nanocomposites (d).

3.1. FTIR spectrum of the $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites

FTIR spectroscopy was carried out to investigate whether this proposed synthesis process would damage the graphite-like structure of $g\text{-C}_3\text{N}_4$. Figure 1 shows the FTIR spectra of melamine (Figure 1a), $g\text{-C}_3\text{N}_4$ (Figure 1b), $g\text{-C}_3\text{N}_4\text{-H}^+\text{Cl}^-$ (Figure 1c), and $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites (Figure 1d). It can be concluded that after the condensation of melamine to $g\text{-C}_3\text{N}_4$, the bands of N–H ($3300\text{--}3500\text{ cm}^{-1}$) disappeared while the bands of C–N ($1240\text{--}1643\text{ cm}^{-1}$) and tri-s-triazine (810 cm^{-1}) retained. The FTIR spectra of $g\text{-C}_3\text{N}_4\text{-H}^+\text{Cl}^-$ and $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites is very similar to that of $g\text{-C}_3\text{N}_4$, which indicates that there is no damage to the graphite-like structure of $g\text{-C}_3\text{N}_4$ during the proposed in-situ synthesis process.

3.2. SEM images and EDS pattern of the $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites

To describe the morphology of the synthesized $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites, SEM images and EDS pattern were employed. Figure 2 illustrates the typical SEM photographs of $g\text{-C}_3\text{N}_4$ (Figure 2a), $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites (Figure 2b), and the EDS pattern of the $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites (Figure 2c). Obviously, $g\text{-C}_3\text{N}_4$ appears to have sheet structures in the SEM micrograph image, which is in accordance with the reported literature [17]. The morphology of the $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites is similar to that of $g\text{-C}_3\text{N}_4$, except for the uniformly distributed AuNPs on the $g\text{-C}_3\text{N}_4$ surface. The EDS pattern of the $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites indicates that C, N, Al, and Au are the major elements in the nanocomposites. C and N may come from $g\text{-C}_3\text{N}_4$, while Al may be attributed to the base aluminum foil. The presence of Au in the pattern confirms the existence of AuNPs on the $g\text{-C}_3\text{N}_4$ surface.

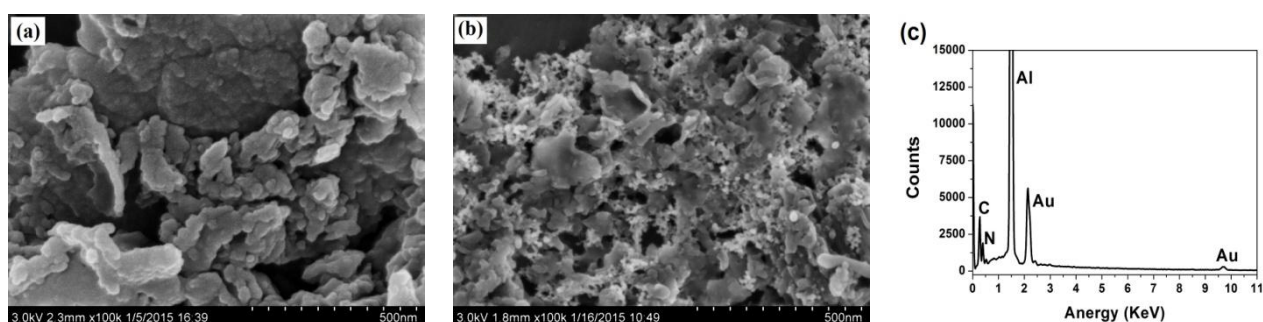


Figure 2. SEM images of $g\text{-C}_3\text{N}_4$ (a), $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites (b), and EDS pattern of $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites (c).

3.3. TEM images of the $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites

TEM images provide further evidence for the successful synthesis of the $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites. Figure 3 shows the TEM photographs of $g\text{-C}_3\text{N}_4$ (Figure 3a), and $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites (Figure 3b). It can be observed that $g\text{-C}_3\text{N}_4$ has sheet structures. As to the $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites, the morphology is clearly different from that of $g\text{-C}_3\text{N}_4$. The dispersion

of the sheet is more symmetrical and this may be caused by the cutting effect during the synthesis process. Furthermore, numerous uniform nanoparticles can be observed on the surface of g-C₃N₄/AuNP nanocomposites. In a word, almost 5 nm AuNPs were well distributed on the surface of g-C₃N₄.

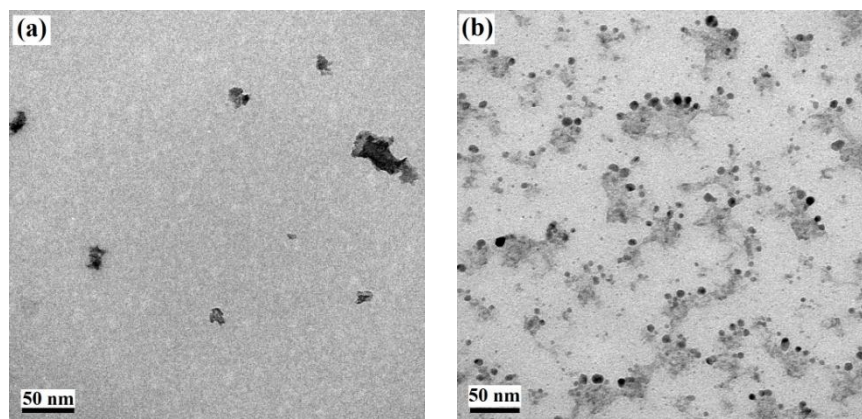


Figure 3. TEM images of g-C₃N₄ (a), and g-C₃N₄/AuNP nanocomposites (b)

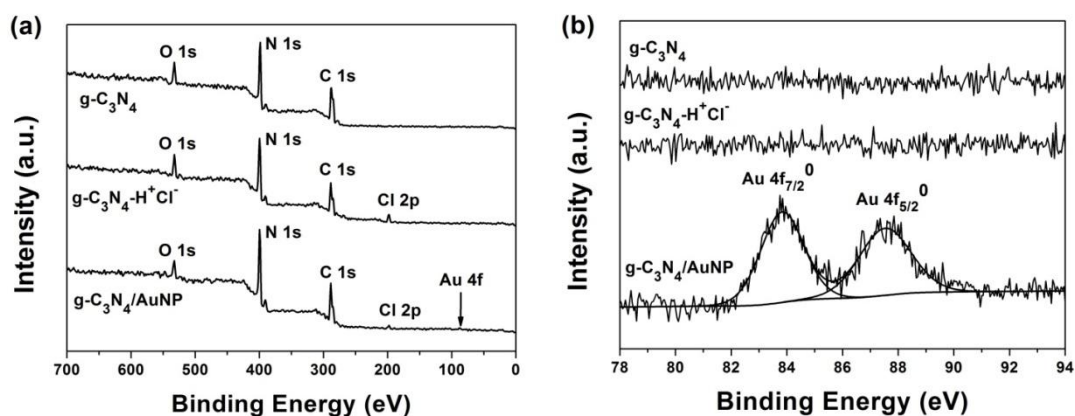


Figure 4. Survey (a) and Au 4f (b) XPS spectra of g-C₃N₄, g-C₃N₄-H⁺Cl⁻, and g-C₃N₄/AuNP nanocomposites.

3.4. XPS spectrum of the g-C₃N₄/AuNP nanocomposites

To further confirm the in-situ synthesis of the g-C₃N₄/AuNP nanocomposites, XPS was conducted. Figure 4 shows the survey (Figure 4a) and Au 4f (Figure 4b) XPS spectra of g-C₃N₄, g-C₃N₄-H⁺Cl⁻, and g-C₃N₄/AuNP nanocomposites. The appearance of Cl 2p in g-C₃N₄-H⁺Cl⁻ proves the successful protonation of g-C₃N₄. The Au 4f XPS spectrum of the g-C₃N₄/AuNP nanocomposites displays a doublet for Au⁰ due to Au 4f_{7/2} and Au 4f_{5/2} spin-orbit coupling, which proves the presence of AuNPs. The decrease of Cl 2p peak in g-C₃N₄/AuNP nanocomposites may be caused by the ion-exchange between Cl⁻ and AuCl₄⁻, which proves that in-situ growth of AuNPs. Moreover, the C/N ratios of g-C₃N₄, g-C₃N₄-H⁺Cl⁻, and g-C₃N₄/AuNP nanocomposites are (56/44, 51/45, and 52/46

respectively) very close, which indicates that the component and graphite-like structure of $g\text{-C}_3\text{N}_4$ were not damaged during the proposed in-situ synthesis process.

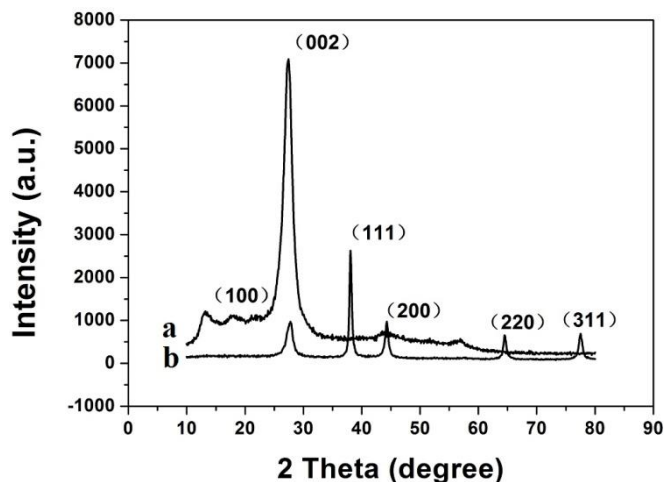


Figure 5. XRD patterns of $g\text{-C}_3\text{N}_4$ (a) and $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites (b).

3.5. XRD pattern of the $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites

XRD is a powerful and effective method for investigating the crystalline properties of the as-synthesized nanomaterials. Figure 5 shows the XRD patterns of $g\text{-C}_3\text{N}_4$ (Figure 5a), and $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites (Figure 5b). In Figure 5a, a typical $g\text{-C}_3\text{N}_4$ structure is suggested by two obvious peaks. The strongest peak at $2\theta = 27.48^\circ$ is a characteristic interlayer stacking peak of aromatic systems, and can be indexed as the (002) plane for graphitic materials [1]. The calculated interplanar distance of aromatic units is $d = 0.324$ nm. The relatively weak peak at $2\theta = 13.52^\circ$ indexed as (100) plane can be associated with an in-plane structural packing motif. As to the $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites, the typical diffraction peaks at $2\theta = 38.11^\circ$, 44.29° , 64.51° and 77.51° corresponding to the (111), (200), (220), and (311) lattice planes of the gold face-centered cubic crystal appear attractively except for the (002) characteristic peak of $g\text{-C}_3\text{N}_4$ [18,19].

From all the results discussed above, it can be concluded that the $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites were synthesized successfully through the in-situ strategy and the graphite-like structure of $g\text{-C}_3\text{N}_4$ was retained during the synthesis process.

3.6. Electrochemical behaviors and potential application of the $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites

To investigate the electrochemical properties of the target $g\text{-C}_3\text{N}_4/\text{AuNP}$ nanocomposites, CV curves of the bare GC, and $g\text{-C}_3\text{N}_4/\text{AuNP}/\text{GC}$ electrodes in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution from 0.2 to 1.5 V with a scan rate of 100 mV s^{-1} are presented in Figure 6. It can be observed that there is no redox peak obtained for the bare GC electrode (Figure 6a). However, a sharp reduction peak and an oxidation peak can be seen from the $g\text{-C}_3\text{N}_4/\text{AuNP}/\text{GC}$ electrode (Figure 6b). Obviously, the peaks were caused by the redox of AuNPs. Moreover, AuNPs can facilitate electron transfer to improve the electroconductivity of the synthesized nanomaterials.

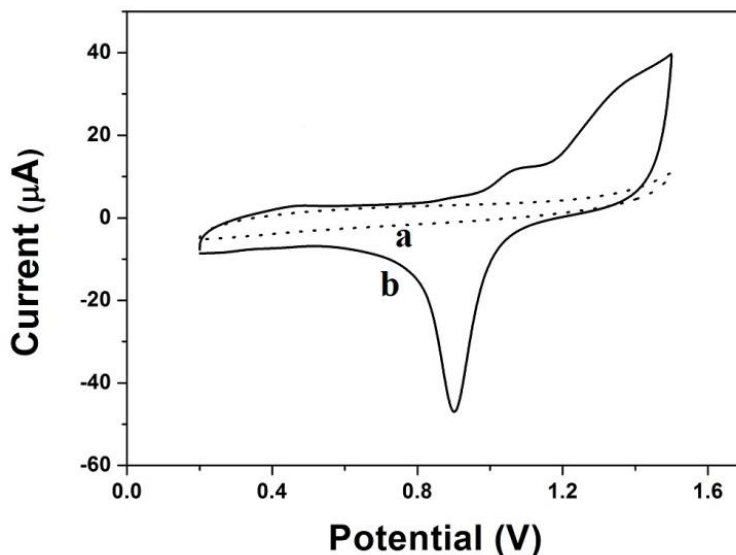


Figure 6. Cyclic voltammograms of bare GC (a) and g-C₃N₄/AuNP/GC (b) electrodes in 0.5 mol L⁻¹ H₂SO₄ solution.

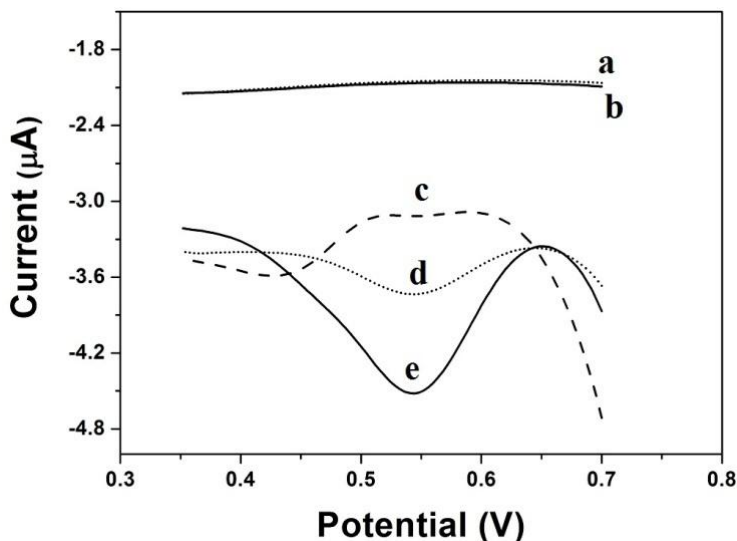


Figure 7. Differential pulse voltammograms of bare GC electrode without (a) and with (b) 10 $\mu\text{mol L}^{-1}$ Fe(III), g-C₃N₄/AuNP/GC electrode without (c), with 10 $\mu\text{mol L}^{-1}$ (b) and 20 $\mu\text{mol L}^{-1}$ (e) Fe(III) in 0.1 mol L⁻¹ HCl.

Figure 7 shows the differential pulse voltammetry (DPV) responses toward Fe(III) reduction at two different electrodes in 0.1 mol L⁻¹ HCl. There is no reduction peak at the bare GC electrode without and with 10 $\mu\text{mol L}^{-1}$ Fe(III) (Figure 7a, b). In other words, it is not possible to detect 10 $\mu\text{mol L}^{-1}$ Fe(III) using the unmodified GC electrode. However, at the g-C₃N₄/AuNP/GC electrode, contrast to the DPV response without Fe(III) (Figure 7c), a sharp reduction peak at about 0.54 V was observed when 10 $\mu\text{mol L}^{-1}$ (Figure 7d) and 20 $\mu\text{mol L}^{-1}$ (Figure 7e) Fe(III) was added. Distinctly, the reduction peak was due to the reduction of Fe(III) and this shows the excellent electrocatalytic activity of the g-

C₃N₄/AuNP nanocomposites towards the reduction of Fe(III). This makes it feasible to determinate the Fe(III) concentration with the modified electrode. Additionally, it should be noted that the reduction peak potential is almost at 0.54 V, which means that the nanocomposites modified electrode has much higher onset reduction potential than most of the electrodes in the electrocatalytic reduction of Fe(III) [20,21]. And this also shows the high electrocatalytic activity of the proposed nanocomposites. The excellent electrochemical properties of the g-C₃N₄/AuNP nanocomposites exhibit a promising prospect for the electrochemical detection of iron.

4. CONCLUSIONS

An in-situ method based on ion-exchange was reported here to successfully synthesize the g-C₃N₄/AuNP nanocomposites. The g-C₃N₄ was protonated by HCl and ion-exchanged by AuCl₄⁻ and then reduced to the target nanocomposites in-situ. Extensive characterizations of the g-C₃N₄/AuNP nanocomposites were studied and the results showed that AuNPs were well distributed on the surface of the g-C₃N₄. Additionally, the nanocomposites have good electrocatalytic responses to Fe(III) reduction and can be used for development of iron sensors.

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