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# Ultrasonic Synthesis of Highly Dispersed Au Nanoparticles supported on Ti-based Metal-organic Frameworks for Electrocatalytic Oxidation of Hydrazine

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In this work, Au nanoparticles supported on amino-functionalized Ti-benzenedicarboxylate metal-organic frameworks (Au/NH<sub>2</sub>-MIL-125(Ti)) were prepared by a facile ultrasonic method. The complex was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-vis absorption spectrum and electrochemistry method. The obtained nanocomposites exhibit excellent electrocatalytic activity toward hydrazine oxidation, which is attributed to the large specific surface area and good conductivity. In addition, we found that solution pH has an obvious effect on the electrocatalytic activity of Au/NH<sub>2</sub>-MIL-125(Ti) toward hydrazine oxidation. On this basis, we constructed a simple, sensitive, selective and inexpensive electrochemical method to detect hydrazine. A linear dynamic range of 10 nM to 100 μM with the detection limit of 0.5 nM was obtained. It was demonstrated that the fabrication of Au NPs on amino-functionalized Ti-based MOFs could be promising for the sensing of hydrazine. Our results imply the potential application of metal nanoparticles/MOFs nanocomposites in the field of electroanalytical chemistry.

## Introduction

Metal-organic frameworks (MOFs), also known as metal-coordination polymers, are a new class of organic-inorganic hybrid materials with an extended 3D network.<sup>1-4</sup> Due to the excellent characteristics of large surface area, tunable pore size, attractive electrical, optical, and catalytic properties, MOFs have shown a variety of potential applications in the past decades, such as heterogeneous catalysis,<sup>5-9</sup> gas storage and separation,<sup>10-13</sup> and drug delivery/release.<sup>14-17</sup> Especially, the excellent adsorbability, encapsulation capability, and high porosity make it an ideal candidate as an efficient solid matrix for biorecognition molecules as well as metal and metal oxide nanoparticles (NPs).<sup>7, 18-21</sup>

On the other hand, noble metal NPs have attracted much attention due to their excellent physical and chemical properties.<sup>22-26</sup> So it is reasonable to conclude that the combination of noble metal NPs and MOFs provides promising materials for various applications and

even exhibit enhanced performance. To date, there have been some typical examples about the preparations and applications of noble metal NPs/MOFs.<sup>27</sup> For instance, Sun et al. prepared different noble NPs supported on NH<sub>2</sub>-MIL-125(Ti) and investigated their photocatalytic activities toward CO<sub>2</sub> reduction.<sup>28</sup> Compared to pure NH<sub>2</sub>-MIL-125(Ti), Pt/NH<sub>2</sub>-MIL-125(Ti) showed an enhanced photocatalytic activity toward CO<sub>2</sub> reduction, whereas Au has a negative effect on this reaction. Wu et al reported the synthesis of Au NPs immobilized on the Zr(IV)-based metal-organic framework through a chemical wetting method and the Au@UIO-66 heterostructures exhibit high catalytic activity and stability for gas-phase CO oxidation.<sup>29</sup> Au NPs/MIL composites were also prepared through an encapsulation strategy and employed to catalyze the reduction of 4-nitrophenol, and possessed better catalytic activity than pure Au NPs.<sup>7</sup> Hu and his coworkers used Au/MIL-101 as highly sensitive SERS substrates to achieve high sensitive detection of p-phenylenediamine.<sup>30</sup> Tang's group synthesized interesting core-shell structured Au@MOF-5 NPs<sup>31</sup> and Pd@IRMOF-3<sup>32</sup> composites for SERS sensing of CO<sub>2</sub> and the catalysis of cascade reaction, respectively. The synthesis methods mentioned above were neither needs costly or time-consuming. However, the electrochemical properties of noble metal NPs/MOFs composites have been rare explored and exploited.<sup>33-35</sup> In this paper, we for the first time synthesized Au/NH<sub>2</sub>-MIL-125(Ti) by a simple, inexpensive and rapid ultrasonic method and investigated their electrochemical properties. We found the obtained composites exhibited excellent electrocatalytic activities toward hydrazine oxidation.

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As we known, hydrazine ( $N_2H_4$ ) has been widely applied in industry, farming, explosives, and so on.<sup>36,37</sup> Nevertheless, it is also a toxic material and has carcinogenic and hepatotoxic effect on human beings.<sup>38,39</sup> Thus it is of urgent importance for the sensitive detection of hydrazine.

Based on the above, we proposed a facile electrochemical sensor for hydrazine detection. The constructed sensor exhibited wide linear response range from 10 nM to 100  $\mu$ M and a low detection limit of 0.5 nM. Compared to other detection methods, such as spectrophotometric,<sup>40-42</sup> spectrophotometric flow injection,<sup>41,42</sup> liquid chromatography,<sup>45</sup> gas chromatography–mass spectrometry and Raman spectroscopy,<sup>46,47</sup> and Au,  $TiO_2$  or carbon materials based composites for electrochemical ways (as shown in supplementary information), our proposed method possesses many advantages, including high sensitivity, fast response, wide linear range and satisfactory detection limit.

## Results and discussion

### Characterization of $NH_2$ -MIL-125(Ti) and Au/ $NH_2$ -MIL-125(Ti)

The morphologies of  $NH_2$ -MIL-125(Ti) and Au/ $NH_2$ -MIL-125(Ti) were studied by SEM and TEM. As shown in Figure 1A, the as-synthesized  $NH_2$ -MIL-125(Ti) sample exhibits uniform shape and size distribution of around 300 nm. In comparison, Au NPs can be seen clearly on  $NH_2$ -MIL-125(Ti) in Figure 1B, indicating the successful synthesis of Au/ $NH_2$ -MIL-125(Ti) complex. The corresponding TEM image of the as-synthesized  $NH_2$ -MIL-125(Ti) and Au/ $NH_2$ -MIL-125(Ti) are shown in Figure 1C-D. It can be seen that Au NPs with an average diameter around 8 nm are not only loaded on the surfaces of  $NH_2$ -MIL-125(Ti) but also incorporated into the porous internal, which is in accordance with the results of SEM.

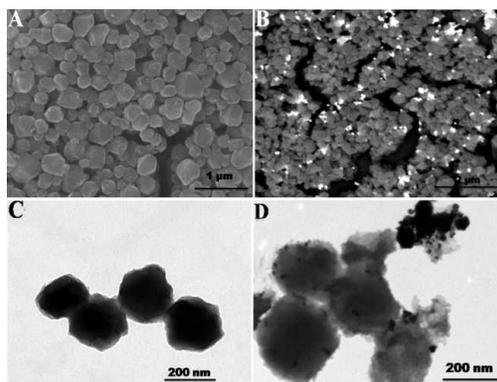


Figure 1 SEM and TEM images of the as-synthesized  $NH_2$ -MIL-125(Ti) (A, C) and Au/ $NH_2$ -MIL-125(Ti) (B, D).

The formation and the structure of the as-synthesized  $NH_2$ -MIL-125(Ti) and Au/ $NH_2$ -MIL-125(Ti) were further characterized by XRD and XPS. From Figure 2b, it can be observed that all diffraction peaks are consistent with those of the simulated patterns

of MIL-125(Ti) (Figure 2a), suggesting the successful preparation of  $NH_2$ -MIL-125(Ti).<sup>49-54</sup> For Au/ $NH_2$ -MIL-125(Ti) (Figure 2c), the characteristic  $\theta$  peak at 38.24 assigned to Au(111) is also observed, and the diffractions of the  $NH_2$ -MIL-125(Ti) can also be observed with a relatively weak intensity, which implies the successful synthesis of Au/ $NH_2$ -MIL-125(Ti) and  $NH_2$ -MIL-125(Ti) structure has not been destroyed after the loading of Au NPs.

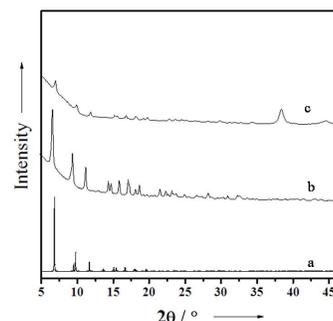


Figure 2 XRD pattern of the simulated MIL-125(Ti) (a),  $NH_2$ -MIL-125(Ti) (b) and Au/ $NH_2$ -MIL-125(Ti) (c).

The XPS survey of the as-synthesized Au/ $NH_2$ -MIL-125(Ti) was shown in Figure 3A, which mainly contains the peaks of C, N, O, Ti and Au, and the ratio of Au in the Au/ $NH_2$ -MIL-125(Ti) from XPS analysis was 0.46%. The spectrum of Au 4f of Au/ $NH_2$ -MIL-125(Ti) is displayed in Figure 3B. It can be observed that there are two peaks centered at 87.2 eV and 83.7 eV, which are ascribed to the peaks of Au 4f<sub>5/2</sub> and Au 4f<sub>7/2</sub>, respectively. As shown in Figure 3C, the peaks centered at 458.7 and 464.4 eV are consistent with the peaks of Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub>, respectively. The peak in the N1s region can be deconvoluted into three peaks at 399.3, 400.9 and 402.7 eV (Figure 3D). The peak at 400.9 eV can be assigned to the residual DMF in the framework, whereas the other two peaks can be assigned to the N of the amine functionality stretching out or protruding into the cavities.<sup>28</sup> These results confirmed the successful preparation of Au NPs/MOFs.

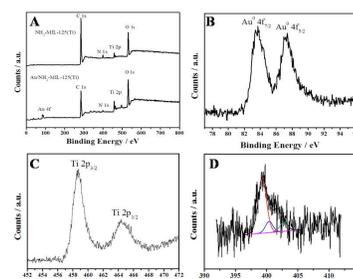


Figure 3 Survey XPS data for Au/ $NH_2$ -MIL-125(Ti) and  $NH_2$ -MIL-125(Ti) (A), Au 4f (B), Ti 2p (C) and the deviation of N 1s of Au/ $NH_2$ -MIL-125(Ti) (D).

Figure 4 shows the UV–Vis absorption spectra of the aqueous dispersion of  $\text{NH}_2\text{-MIL-125(Ti)}$  and  $\text{Au/NH}_2\text{-MIL-125(Ti)}$ . The absorption at 302 nm of  $\text{NH}_2\text{-MIL-125(Ti)}$  in Figure 4 a is induced by O to Ti ligand-to-metal charge transfer in  $\text{TiO}_3(\text{OH})$  inorganic clusters<sup>48</sup> and the broad adsorption at 400 nm is the adsorption of the organic linker  $\text{H}_2\text{ATA}$ .<sup>55</sup> After the introduction of Au NPs into  $\text{NH}_2\text{-MIL-125(Ti)}$ , there is obviously a new peak at about 550 nm (figure 4b), which further indicates the successful combination of Au NPs and  $\text{NH}_2\text{-MIL-125(Ti)}$ .

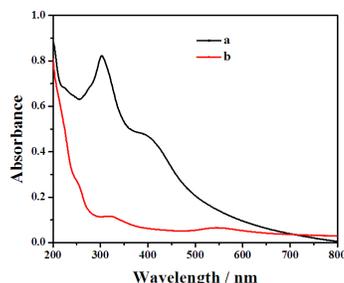
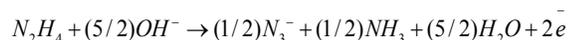


Figure 4 The UV–Vis absorption spectra of the aqueous dispersion of  $\text{NH}_2\text{-MIL-125(Ti)}$  (a) and  $\text{Au/NH}_2\text{-MIL-125(Ti)}$  (b).

#### Electrochemical behavior of hydrazine at $\text{Au/NH}_2\text{-MIL-125(Ti)}$ modified electrode

Firstly, the influence of solution pH for hydrazine was investigated over the pH range of 4–9. Figure 5 A depicts the CVs for 1mM hydrazine at  $\text{Au/NH}_2\text{-MIL-125(Ti)/GCE}$  in 0.1 M PBS with different pH values. It can be observed that at pH 7.0, the anodic current reached a maximum value with a negative potential, which is coincidence with the previous report that the electrolyte solution with pH 7 shows the improved electrocatalytic oxidation of hydrazine.<sup>56</sup> Therefore, pH 7.0 PBS was chosen as the optimum pH of hydrazine detection. This hydrazine oxidation process is similar to the reported literatures which involve a two electron transfer and can be concluded as the following equation:



Then, we employed cyclic voltammetry (CV) to evaluate the electrocatalytic performances of the as-synthesized composites in a three-electrode electrochemical cell. Figure 5B exhibits the cyclic voltammograms at bare GCE,  $\text{NH}_2\text{-MIL-125(Ti)/GCE}$ , Au NPs/GCE and  $\text{Au/NH}_2\text{-MIL-125(Ti)/GCE}$  in the presence of hydrazine. It can be found that a large anodic wave appears in the presence of hydrazine for  $\text{Au/NH}_2\text{-MIL-125(Ti)/GCE}$  with the onset potential around  $-0.034\text{ V}$  (vs.  $\text{Ag/AgCl}$ ), whereas the oxidation

of hydrazine at  $\text{NH}_2\text{-MIL-125(Ti)/GCE}$  started around 0.28 V, which is more positive than that of  $\text{Au/NH}_2\text{-MIL-125(Ti)/GCE}$ . In a control experiment, the electrocatalytic activity of Au NPs and bare GCE toward hydrazine were also investigated. Only large over-potential and small oxidation current were observed. These results demonstrate that the as-synthesized  $\text{Au/NH}_2\text{-MIL-125(Ti)}$  possesses excellent electrocatalytic activity toward hydrazine oxidation, providing an opportunity to construct electrochemical sensor for hydrazine.

Finally, CV measurements of electrocatalytic toward hydrazine oxidation at different scan rates were performed too. Figure 5C illustrates that the anodic currents of hydrazine are proportional to the scan rates in the range of 0.01–0.2 V/s in 0.1M PBS (pH 7.0), indicating the dominance of the adsorption process.

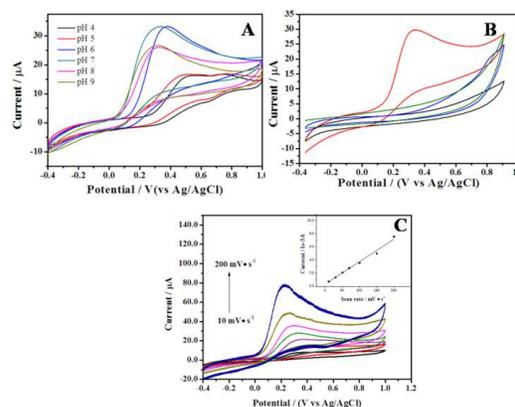


Figure 5 (A) Cyclic voltammograms at the  $\text{Au/NH}_2\text{-MIL-125(Ti)/GCE}$  in 1 mM hydrazine PBS at different pH values from 4 to 9 at a scan rate of  $100\text{ mV}\cdot\text{s}^{-1}$ . (B) Cyclic voltammograms at bare GCE (black line),  $\text{NH}_2\text{-MIL-125(Ti)/GCE}$  (blue line), Au NPs/GCE (green) and  $\text{Au/NH}_2\text{-MIL-125(Ti)/GCE}$  (red line) with 1 mM hydrazine in 0.1M PBS (7.0) at scan rate of  $100\text{ mV/s}$ . (C) Cyclic voltammograms at  $\text{Au/NH}_2\text{-MIL-125(Ti)/GCE}$  with 1 mM hydrazine in 0.1 M PBS (pH 7.0) with different scan rates. Inset: the peak currents vs. the square root of the scan rates.

#### Amperometric detection of hydrazine

Due to the excellent electrocatalytic property toward hydrazine oxidation at the as- prepared  $\text{Au/NH}_2\text{-MIL-125(Ti)}$ , a hydrazine sensor was successfully constructed. Figure 6A shows the typical current response of  $\text{Au/NH}_2\text{-MIL-125(Ti)/GCE}$  to subsequent additions of hydrazine in 0.1M PBS (pH 7.0) at an applied potential at 0.3 V, reaching a steady-state within 4s. As expected, it can be seen clearly that with the successive additions of hydrazine, the oxidation current increases. A graph for oxidation current vs.

hydrazine concentration with a good linear relationship is also plotted in Figure 6B. The linear range was from 10 nM–10  $\mu$ M ( $R^2 = 0.9942$ ) with the detection limit of 0.5 nM according to the experimental results and 10–100  $\mu$ M ( $R^2 = 0.9959$ ), which was comparable to other modified electrodes available in the literature (as shown in Table S1).

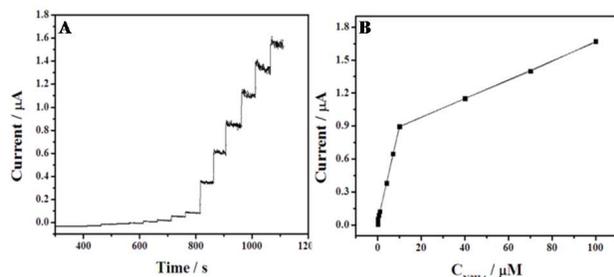


Figure 6 (A) The typical amperometric current responses at the Au/NH<sub>2</sub>-MIL-125(Ti)/GCE on successive injection of different amounts of hydrazine in stirring 0.1M PBS (pH 7.0). Applied potential: 0.30 V. (B) Plot of electrocatalytic current of hydrazine vs. its concentrations.

### Selectivity and stability

To assess the selectivity of the as-synthesized Au/NH<sub>2</sub>-MIL-125(Ti) for hydrazine oxidation over other potential interferences, an amperometric response was obtained by the successive injection of 1mM hydrazine and interferences (1mM AA, DA and glucose, respectively). As shown in Figure 7, after the addition of hydrazine, there was an obvious current response, however, the addition of interferences could only lead negligible signal change under the same condition, indicating the good selectivity in hydrazine sensing at the Au/NH<sub>2</sub>-MIL-125(Ti)/GCE. After the modified electrode was stored at room temperature for 7 days, the current decrease of 9.4 % was observed, demonstrating the good stability of hydrazine detection.

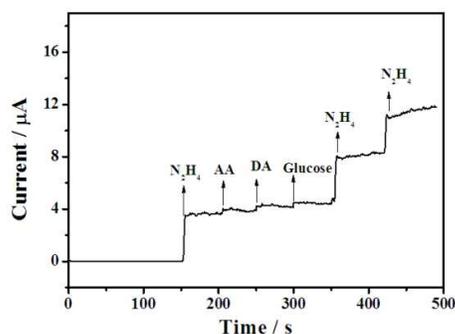


Figure 7 The typical amperometric current responses at the Au/NH<sub>2</sub>-MIL-125(Ti)/GCE upon addition of 1 mM hydrazine, 1 mM AA, 1 mM DA, 1 mM glucose, 1 mM hydrazine and 1 mM hydrazine. Applied potential: 0.30 V.

### Conclusion

In summary, we successfully synthesized the Au/NH<sub>2</sub>-MIL-125(Ti) nanocomposites by a simple and fast ultrasonic method, and investigated their electrochemical properties. We found that the obtained composites exhibited excellent electrocatalytic property toward hydrazine oxidation, which is ascribed to their high surface area and outstanding electrochemical activity. In addition, it is also confirmed that the hydrazine oxidation is a protons-participating process. Based on this point, we constructed a facile electrochemical sensor for hydrazine detection. The constructed sensor possessed the wide linear range from 10 nM to 100  $\mu$ M and low detection limit of 0.5 nM, which is superior to the reported works. Our work reported in this study not only provides a general way to synthesize other noble metal NPs/MOFs, but also broaden their applications.

## Experimental

### Chemicals and Reagents.

HAuCl<sub>4</sub> and 2-aminoterephthalate (H<sub>2</sub>ATA) were purchased from Alfa Aesar. Tetra-n-butyl titanate (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>) was purchased from Sinopharm Chemical Reagent Co., Ltd. hydrazine, ascorbic acid (AA), dopamine (DA), glucose and dimethylformamide (DMF) and trisodium citrate were purchased from Beijing Chemical Corp. All chemicals used were of analytical grade and used without further purification. Milli-Q ultrapure water (Millipore,  $\geq 18.2$  M  $\Omega \cdot$  cm) was used throughout the experiments.

### Apparatus.

Transmission electron microscopy (TEM) was performed on a HITACHI H-600 Analytical TEM with an accelerating voltage of 100 kV. An XL30 ESEM scanning electron microscope (SEM) equipped with an energy-dispersive X-ray analyzer was used to determine the morphology and composition of the as-prepared materials. XRD patterns were recorded on a D8 ADVANCE (BRUKER, Germany) diffractometer using Cu  $\text{K}\alpha$  radiation with a Ni filter ( $\lambda = 0.154059$  nm at 40 kV and 40 mA). X-ray

photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB-MKI I spectrometer (VG Co., United Kingdom) with Al K $\alpha$  X-ray radiation as the X-ray source for excitation. UV–Vis detection was carried out on a Cary 50 UV–Vis-NIR spectrophotometer (Varian, USA). All the electrocatalytic measurements were performed with a CHI 832 electrochemical workstation (Chenhua Instruments Corp, Shanghai, China). A conventional three-electrode cell was used, including a KCl saturated Ag/AgCl electrode as reference electrode, a platinum wire as counter electrode, and a glassy carbon electrode (GCE) with a diameter of 2.6 mm as working electrode, respectively.

### Synthesis of NH<sub>2</sub>-MIL-125(Ti)

NH<sub>2</sub>-MIL-125(Ti) was synthesized according to the reported literature.<sup>48</sup> Briefly, 2-aminoterephthalate (H<sub>2</sub>ATA) (0.543g, 3 mmol) was dissolved in a solution containing DMF (9 ml) and MeOH (1 ml). Then tetra-n-butyl titanate Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> (0.26 ml, 0.75 mmol) was added into the solution. The above mixture was sonicated at room temperature for 10 min, then transferred into a 50 ml Teflon liner and heated at 150°C for 72 h. Finally, the obtained yellow powder was collected by centrifugation, washed with DMF and MeOH, respectively, and dried at 60 °C under vacuum.

### Synthesis of Au/NH<sub>2</sub>-MIL-125(Ti) and Au NPs

The Au/NH<sub>2</sub>-MIL-125(Ti) complex was synthesized through ultrasonic method. Firstly, 5 mg of NH<sub>2</sub>-MIL-125(Ti) was dissolved in 5.76 mL water under ultrasonic. Secondly, 120  $\mu$ L of HAuCl<sub>4</sub> (1%) was added and kept sonicating for 5 min. At last, 360  $\mu$ L of trisodium citrate was quickly added into the solution and sonicated for another 20 min until the color of the solution turned into stable dark purple. The product was collected by centrifugation, washed with methanol and water several times, and then dispersed in 1 ml water.

Au NPs were synthesized by the same procedure described above for Au/NH<sub>2</sub>-MIL-125(Ti) without addition of NH<sub>2</sub>-MIL-125(Ti).

### Fabrication of Au/NH<sub>2</sub>-MIL-125(Ti) modified glassy carbon electrode

Before modification, GCE was polished with 1, 0.3 and 0.05  $\mu$ m alumina slurry, respectively, and rinsed thoroughly with ultrapure water between each polishing step. Then, it was washed successively with alcohol/water (1:1) mixture in an ultrasonic bath and dried in

air. At last, 5  $\mu$ L of the above synthesized Au/NH<sub>2</sub>-MIL-125(Ti) was carefully cast on GCE and dried in air, noted as Au/NH<sub>2</sub>-MIL-125(Ti)/GCE.

### Acknowledgements

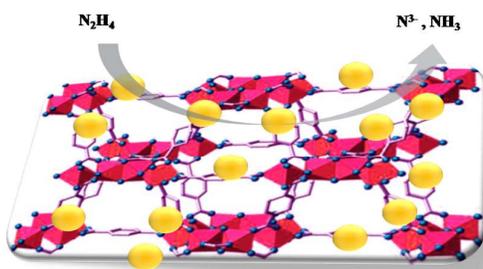
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## Table of contents



Au/NH<sub>3</sub>-MIL-125(Ti) composites, synthesized by a simple, rapid ultrasonic method, shows excellent electrocatalytic oxidation of hydrazine.