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Au/montmorillonite/polyaniline nanoflake: facile fabrication by self-assembly and its application as catalyst

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Abstract By the self-assembly between citrate-stabilized Au nanoparticles (NPs) and dedoped montmorillonite (MMT) / polyaniline (PANI) core/shell nanoflakes, Au NPs/ MMT / PANI nanoflakes could be fabricated facilely. Importantly, hydrogen bonding between Au NPs and PANI shell of MMT/ PANI nanoflake was proposed to play a pivotal role in driving that self-assembly. The as-prepared product exhibited high catalytic activity when the reduction of p-nitrophenol was taken as a model reaction. Those novel findings of that self-assemblied mechanism and the preparation process of Au/ MMT/PANI nanocatalyst may shed some light on designing and preparing other functional Au NPs/conducting polymers composites by self-assembly.

Keywords Polyaniline; Au nanoparticles; Self-assembly; Hydrogen bonding

Introduction

Au nanoparticle (NP) is a fascinating topic due to its unique ability and high activity of catalysis, surface enhanced Raman scattering (SERS), et al [1-3]. However, it is well known that during the utilization, Au NP as well as other metallic NP is easily reduced and apt to form large particles, due to the inherent physical/chemical properties such as autocatalysis, mobility and so on, resulting in its poor dispersion and low activity. Loading or embedding Au NP on/into a support to form nanoflakes is one of most effective ways. So far, various materials such as inorganic compound and polymer [4-6] have been often reported as supports. By this method, the migration and aggregation of Au NP can be avoided, guaranteeing high activity of Au NPs during the practical application.

As a good candidate for supporting Au NP, besides possessing some general advantages, such as high surface area and porous structure, it is more desirable sometimes that electron transfer occurs through a direct or mediated mechanism between the support and Au NP, which has been proved for effectively enhancing the activity of Au NPs [7]. For this purpose, some electrical materials or semiconductors [8-10] have been selected as substrates for Au NP. Among them, conducting polymer, especially polyaniline (PANI), is becoming a promising matrix for loading Au NP to produce novel functional materials due to high conductivity and low cost. The introduction of Au NP to PANI can be realized by many methods. For example, Chattopadhyay et al. reported a method for synthesizing Au-PANI composites based on the use of H_2O_2 as the bifunctional reagent for the reduction of $HAuCl_4$ and oxidation of aniline [11]. Mallick and Feng et al found that $HAuCl_4$ could be applied as an oxidant for the polymerization of aniline to produce nanoflakes [12, 13]. By the reduction of PNAI nanofiber, Han et al prepared PNAI/Au composite nanofiber with high catalytic activity [14]. We also reported using sulfonated PANI-modified silk fibroin fiber to synthesize and load high density of Au NP [15]. Those one-step methods are very convenient, but the control of both the size distribution and dispersion of Au NPs is not easy even if by optimizing the experimental conditions. Pillalamarri et al. [16] reported the synthesis of Au-PANI composite by using γ-irradiation, in which highly uniform and well-dispersed Au NPs were found on PANI nanofibers, however, it was high-cost and not adapted to produce the composite in bulk.

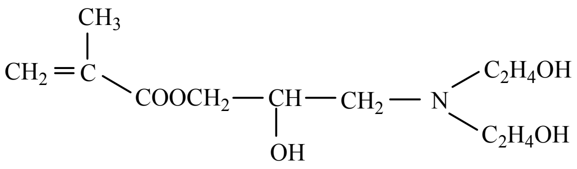
Recently, Yang's group [17] described a novel approach for generating Au NPs/PANI composite with a high density and uniform hot spot structure for SERS only by the self-assembly between citrate-stabilized Au NPs and HCl-doped PANI nanofiber. This method is simple and the size of Au NPs on the composite can be controlled by adjusting the Au NPs precursor. It was suggested that the formation was mainly ascribed to the electrostatic attraction between positively charged PANI and negatively charged Au NPs.

Herein, Au/MMT/PANI nanoflake, was synthesized by using a self-assembly method driven by hydrogen bonding. As an example, we investigated the catalytic activity by taking the reduction of p-nitrophenol as a model reaction. Those novel findings of that self-assemblied mechanism and the preparation process may shed some light on designing and preparing other Au NPs/conducting polymers composites.

2. Experimental

2.1. Materials

Aniline (ANI) monomer was purchased from Aldrich, and distilled under reduced pressure. $HAuCl_4$, $(NH_4)_2S_2O_8$ (APS), p-nitrophenol (p-NP) and $NaBH_4$ were bought from Chinese Beijing Chem. Co. in their reagent grades, and used without further purification. 2-acrylamido-2-methylpropanesulfonic acid (AMPS) was kindly supplied by All-plus Chemical Co., Ltd (China). Pristine Na^+-MMT clay (PGW, cationic (Na^+) exchange capacity of 145 meq/100 g) was purchased from Nanocor Inc (USA). The polymerizable tertiary amine (GMA-DEA) used for clay surface modification, was synthesized as described elsewhere [18]and possessed the chemical structure as follows.



2.2. Surface modification of Na$^+$-MMT

Na$^+$-MMT was modified according to our previous report [19]. Typically, 15 g of Na$^+$-MMT clay was dispersed in 450 mL distilled water by stirring overnight at room temperature, into which 50 mL aqueous solution containing 6.45 g of GMA-DEA was added. The pH value of the mixture was adjusted to 3 by using hydrochloric acid. After being stirred for 6 h, the modified MMT clay (GMA-DEA-MMT) was filtrated, washed and then redispersed in 500 mL distilled water.

Later, 3.0 g AMPS was then added into 150 mL 2 wt% GMA-DEA-MMT dispersion. After the mixture was stirred for 30 min, the initiator (0.03 g APS) was finally introduced in the reactor and the polymerization was allowed to proceed at 70 ℃ for 4 h under a slow stream of nitrogen. The resulted product was centrifuged and washed repeatedly with distilled water to remove the ungrafted poly(AMPS), and then the novel modified MMT clay (PAMPS-g-MMT) can be obtained.

2.3. Preparation of dedoped MMT/PANI nanoflake

PAMPS-g-MMT (5 g) was dispersed in 80 mL of 0.5 mol/L hydrochloric acid, into which 0.8 g of ANI was added. After 30 min of stirring, the polymerization started by adding APS (1.96 g). An overnight reaction was allowed to ensure completion of polymerization. The resultant precipitate was filtered and sequentially washed with alcohol until the filtrate was clear. Thus the product, HCl-doped MMT/PANI nanoflake, could be obtained after being dried at 50 ℃ in an oven.

Dedoped product was obtained by the treatment of HCl-doped MMT/PANI nanoflake with $NH_3{\cdot}H_2O$ (5 wt.-%), followed by filtering, washing and drying.

2.4. Fabrication of Au/ MMT/PANI nanoflake by self-assembly

Citrate-stabilized Au NPs solution was firstly synthesized based on the reference [20]. Typically, 2 ml of sodium citrate solution (1 wt.-%) was added to a stirred $HAuCl_4$ boiling solution (250 mL, 0.001wt.-%). After about 75 S, the red solution of citrate-stabilized Au NPs with the diameter of ~ 15 nm was collected.

2 mg of dedoped PANI / MMT nanoflake was added to Au NPs solution (250 ml), and the mixture was stirred for 24 h or so to get adsorption equilibrium. Then, Au/ MMT/PANI nanoflake could be obtained by being filtered, washed using distilled water and dried at 50 ℃ in an oven.

2.5 Catalytic activity of Au/ PANI / MMT nanoflake

To study the catalytic activity, 1 mg of Au/ PANI / MMT nanoflake was dispersed in 100 mL p-NP aqueous solution (0.09 mM) at room temperature. Then, 10 mL of freshly $NaBH_4$ aqueous solution (1 M) was added. The progress of the reaction was monitored via UV-Vis spectroscopy by recording the time dependent absorption spectra at a regular time interval of 2 min at room temperature.

2.6. Instruments and measurements

The morphology observations and EDS spectrum of samples were carried out on scanning electron microscope (JSM-5610). UV-vis spectra of samples were recorded on a UV-240 spectrometer (Shimadzu, Japan). Zeta potential measurement was carried out on a zeta analyser (Malvern Zetasizer Nano ZS90). The thermal properties were measured on NETZSCH STA 449F3 thermal analyzer at a heating rate of 10℃ /min from 0 to 800℃. The nitrogen gas flow rate was 20 mL/min.

3. Results and discussion

The morphology and structure of Au/ PANI / MMT nanoflake

Au/MMT/PANI nanoflake is synthesized by the self-assembly between citrate-stabilized Au NPs and dedoped core/shell nanoflake of MMT/PANI, which is prepared via an *in-situ* polymerization of ANI after the modification of Na^+-MMT clay. As seen from Fig.1, this product keeps typically flake-like morphology and is decorated with Au NPs, which can be testified by the EDS spectrum (Inset of Fig.1d) (C, N, O, S and Cl coming from PANI). Those Au NPs do not aggregate together and display good dispersion on the as-prepared nanoflakes.

The formation process of Au/ PANI / MMT nanoflake

Under the experimental conditions, why and how to form Au/MMT/PANI nanoflake worth while investigating. Obviously, the formation process should not be ascribed to the electrostatic attraction because both dedoped PANI / MMT nanoflake (ζ= -1.0 mV) and citrate-stabilized Au NPs have negative property. In this case, it is proposed that hydrogen bonding interaction between Au NPs and the outside PANI shell of dedoped PANI / MMT drives that self-assembly process. The schematic demonstration is described in Fig.2, and the explanation is given as follows: Au NPs are surrounded by citrate molecules which provide many oxygen atoms, and PANI macromolecule contains lots of hydrogen. Those result in strong interaction by hydrogen bonding between Au NPs and PANI backbones, which is enough to complete the self-assembly and promotes Au NPs being absorbed on PANI shell, although single hydrogen bonding is weak.

To test the above proposal, we subsequently chose pure dedoped PANI to replace dedoped PANI / MMT nanoflake. As expected, Au/PANI composite can be also obtained. Au NPs display good dispersion on the pure dedoped PANI as that of the as-prepared nanoflakes (Fig.3).

The thermal property of Au/PANI /MMT nanoflake is measured, which can further help to understand the formation mechanism. As shown in Fig. 4, the TG curve of dedoped MMT/PANI nanoflake is usual. The process of weight loss can be explained according to the decomposition and carbonization of PANI shell on the MMT/PANI which has been reported elsewhere [21]. As to Au/MMT/PANI nanoflake, the rate of weight loss is quite different. Before 466℃, it is higher than that of dedoped MMT/PANI, while the opposite phenomenon is observed after 466℃. This can be ascribed to the existence of lots of citrate groups in Au/MMT/PANI nanoflake, which are resulted from the preparation process. Owing to the dual negative charge of dedoped MMT/PANI and citrate groups, hydrogen bonding interaction among -COO$^-$ of citrate groups and –NH– of MMT/PANI might only be a reasonable explanation. The higher content of citrate groups causes rapid weight loss before 466℃ due to the gradual water loss and decomposition of sodium citrate (m.p.: 230°), which may mainly happen around from 200℃ to 400℃ marked as green in Fig.3. After 466℃, the low rate of weight loss can be mainly contributed to Au nanoparticles on the surface of Au/MMT/PANI nanoflake. This result gives a forceful support that hydrogen bonding interaction is strong enough to anchor citrate-stabilized Au NPs on the dedoped PANI shell of MMT/PANI.

Catalytic activity of Au/MMT/PANI composite nanoflake

Some advantages such as small size and good dispersion of Au NPs on the as-prepared nanoflakes, would make it found potential application in the field of catalysis. To investigate the catalytic activity of those nanoflakes, the model catalytic reduction reaction of p-NP by $NaBH_4$ has been performed. This reaction is easily monitored by the absorption decrease of p-NP at 400 nm [22]. From Fig.6a, it can be found that the absorption of p-NP decreases obviously within 35 min after adding

Au/MMT/PANI nanoflakes. Based on this result and no catalytic ability of dedoped MMT/PANI nanoflakes, the reaction kinetics is further discussed (Fig.5b and 5c). Obviously, the linear relation of A (A is the absorbance at 400nm) versus time is observed for the a catalyst, indicating that the reaction is more fitted with first-order kinetics [23]. The rate constant ($K_{app}= 1.32\times10^{-3}$ s^{-1}) has been estimated from the slope of straight line and initial concentration of p-NP. To further evaluate our experimental result, the activity factor k (the ratio of rate constant Kapp over the total weight of the catalyst W) is calculated about 6.60 s^{-1} g^{-1} according to the reference [24], indicating a high catalytic activity comparable to some research results [25,26].

It's well known that the reusability is one of the most advantages of using heterogeneous catalyst rather than homogeneous catalyst. As a result, the reusability of Au/MMT/PANI nanoflake as a catalyst toward the reduction of p-NP in the presence of $NaBH_4$ is also discussed. By simple centrifugation and washing after completion of the first cycle, the catalyst can be recovered and reused in the next cycle. As shown in Tab.1, the experimental result confirms that Au/MMT/PANI nanoflake can be used as a recycled catalyst although the catalytic reaction time increase slightly with cycles, which may result from the loss of catalysts during centrifugation and purification processes of catalyst.

Conclusions

In summary, Au/MMT/PANI nanoflake has been fabricated by the hydrogen bonding-induced self-assembly between negative dedoped MMT/PANI nanoflakes and citrate-stabilized Au NPs. The as-prepared product displays highly catalytic activity and good reusability when the reduction of p-nitrophenol is taken as a model reaction. Those novel insights of that self-assemblied mechanism and the preparation process of Au/ MMT/PANI nanocatalysis may shed some light on designing and preparing other functional Au NPs-based composite materials for many potential applications such as sensors and surface-enhanced Raman scattering (SERS) substrate.

Acknowledgements

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Tab.1. The activity factor *k* in different cycles of catalytic reduction of p-NP in the presence of $NaBH_4$ with Au/MMT/PANI

The number of cycles	1	2	3	4	5
The activity factor k(s^{-1} g^{-1})	6.60	5.68	5.35	5.20	5.09

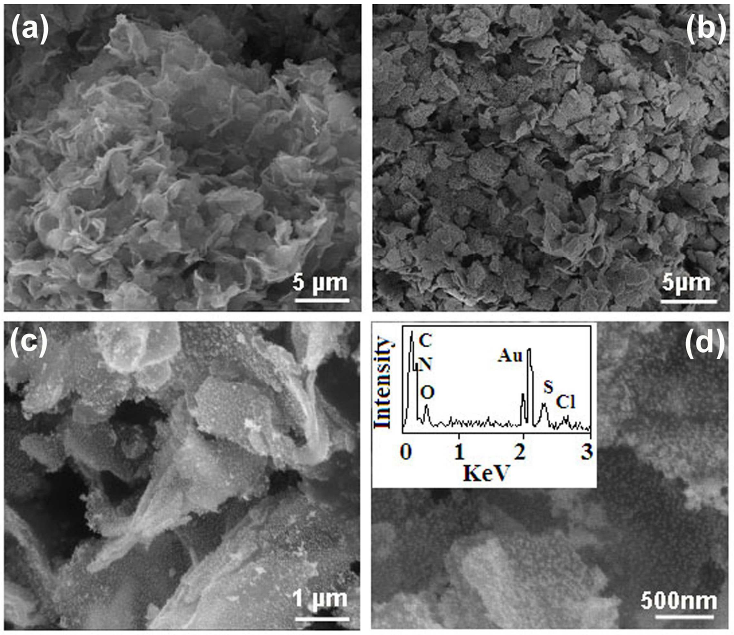


Fig.1 SEM images of dedoped MMT/PANI nanoflake (a) and Au/ MMT / PANI nanoflake prepared by using ~ 15 nm Au NPs (b, c, d).

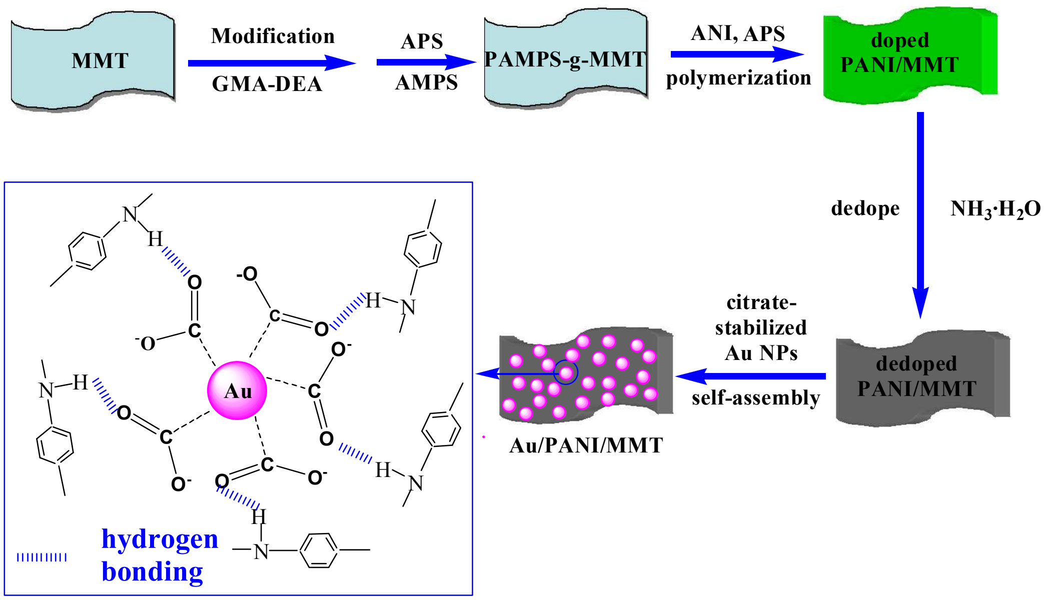


Fig.2 Schematic demonstration of formation of Au/ MMT / PANI nanoflake

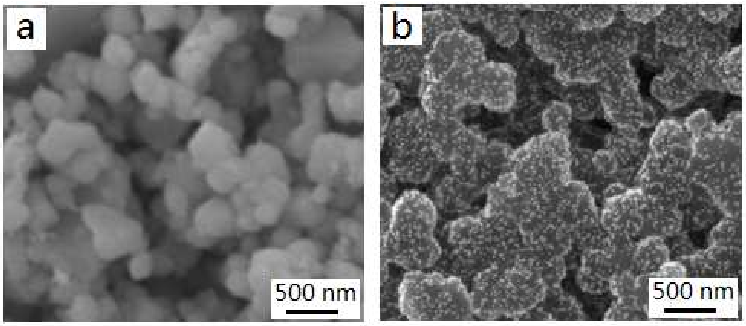


Fig. 3 The SEM images of doped PANI (a) and Au/ dedoped PANI nanocomposites (b) prepared by the self-assembly between dedoped PANI and Au NPs (~15 nm).

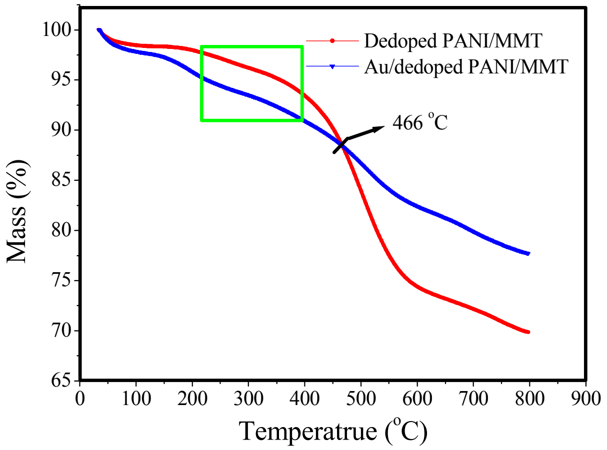


Fig.4. TGA patterns of dedoped MMT / PANI nanoflake and Au/ MMT / PANI nanoflake prepared by using ~ 15 nm Au NPs.

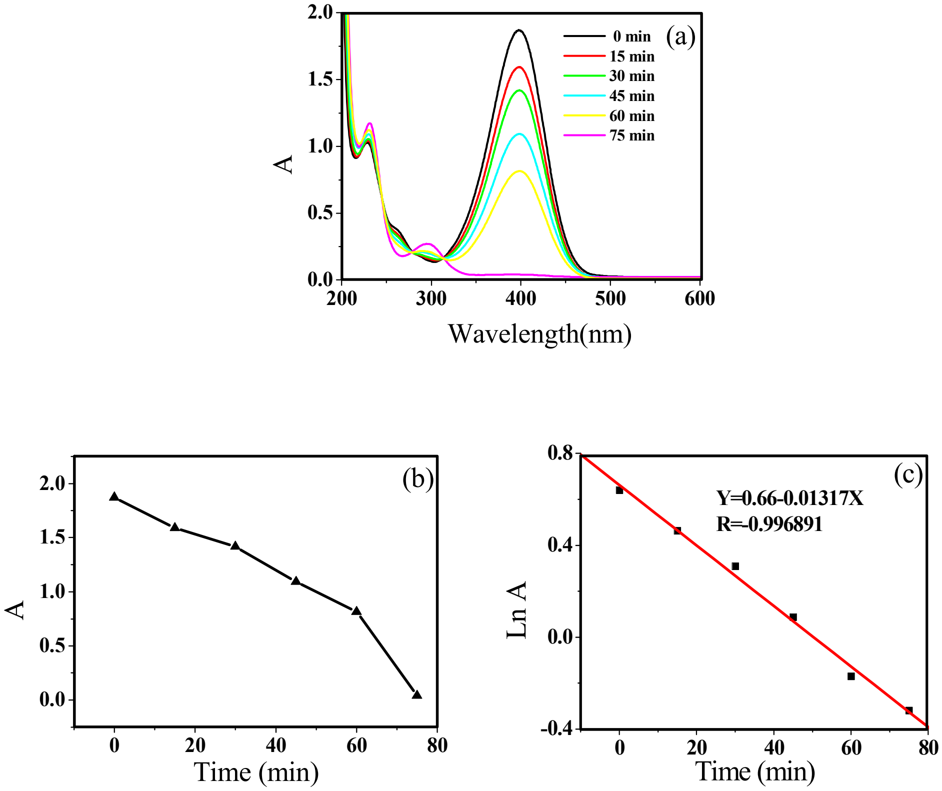
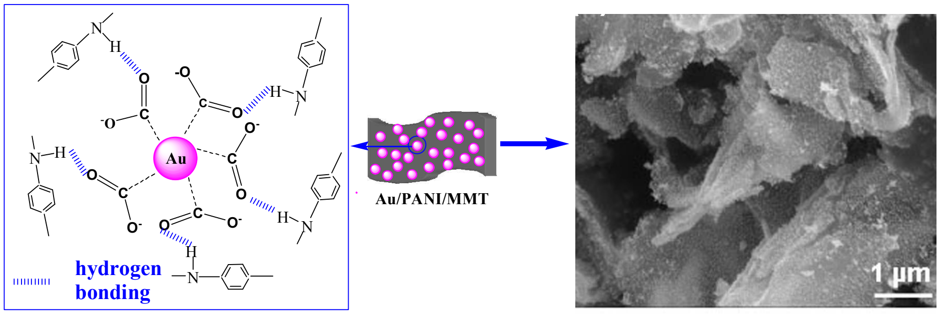


Fig.5. Catalytic activity of Au/ MMT / PANI nanoflake prepared by adding 2 mg of dedoped MMT / PANI nanoflake into 250 ml Au NPs (~15 nm) solution, respectively.(a) The absorption of the mixed solution at different times; (b) Plot of A versus time; (c) Plot of lnA versus time.

Graphic abstact



Hydrogen bonding between citrate-stabilized Au NPs and PANI backbone is proposed to play a pivotal role in driving that self-assembly between Au NPs and doped or dedoped PANI, from which a high catalytic Au NPs/PANI/ MMT nanocomposites, was then synthesized.