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Hierarchical gold microspheres catalyst: Simultaneous synthesis and immobilization

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ABSTRACT

Without any other additives or additional energy, gold quasi microspheres with novel hierarchical structure have been successfully prepared and integrated simultaneously with a conducting polyaniline/polyacrylonitrile blend film via the in situ reduction of $AuCl_4^-$ on the film surface. The morphology and structure of the as-prepared gold microspheres are characterized, and its application as catalyst is also investigated. By controlling the concentration of $HAuCl_4$ and polyaniline content (or conductivity) of polyaniline/polyacrylonitrile blend films, the amount and size of gold microspheres can be effectively adjusted. It is suggested that the polyaniline chains of the blend films play both reducing and structure-directing roles during the formation of Au microspheres with hierarchical structure. The catalytic studies show that the hierarchical gold microspheres give highly catalytic activity when taking the reduction of p-nitrophenol as a mode reaction.

1. Introduction

Hierarchical micro/nanostructures with nanocrystals including nanoparticles, nanoplates, or nanopricks as building blocks have attracted considerable attention due to many promising applications [1–3]. Particularly, they are efficient for catalytic reaction system [4–9], because the hierarchical morphology affords high surface area, thus gives highly catalytic activity. Among lots of hierarchical materials, hierarchical noble metal micro/nanostructures, which combine the properties of noble metal and hierarchical materials, are particularly attractive in recent years. So far, a number of methods [3,10,11] have been developed for the synthesis of those micro/nanostructures. However, most of them usually demand additional reagents like reductant, surfactant, or rigorous conditions such as electrode, lighting and so on.

On the other hand, as catalysts, hierarchical noble metal micro/nanostructures require suitable supports to prevent them from aggregating during the reaction to be catalyzed. Although some powders such as inorganic particles, polymer microgels and so on, can be used as supports, the regeneration process including precipitation, filtering and redispersing, is complex and tedious in practice. A promising approach to make the regeneration of those noble metal catalysts with hierarchical structure convenient and efficient involves integrating them with a processable substrate. As a result of this need, extensive explorations have been done in recent years, however, most of the employed methods are restricted by a two-step route (synthesizing hierarchical noble metal micro/nanostructures firstly and then casting them on the surface of a processable substrate [1]). Alternatively, simultaneous synthesis and immobilization of micro/nanostructures on a processable matrix has been attractive due to great convenience and efficiency. However, as far as we know, little has been done in this respect besides our previous work [12].

Herein, based on a conducting polyaniline/polyacrylonitrile blend film, we demonstrate a convenient one-step route to the simultaneous synthesis and immobilization of hierarchical gold microspheres at room temperature. The employed method does not demand any additional steric stabilizer such as surfactants or other polymers, and any additional energy such as heating or agitation. Furthermore, the synthesis and immobilization of hierarchical Au microspheres happen at the same time. In our case, the obtained metallic Au particle has uniformly hierarchical morphology, thus exhibit high surface area, which gives highly catalytic activity.

2. Experimental

2.1. Materials

Aniline (ANI) monomers were purchased from Aldrich, and distilled under reduced pressure. Polyacrylonitrile (PAN)

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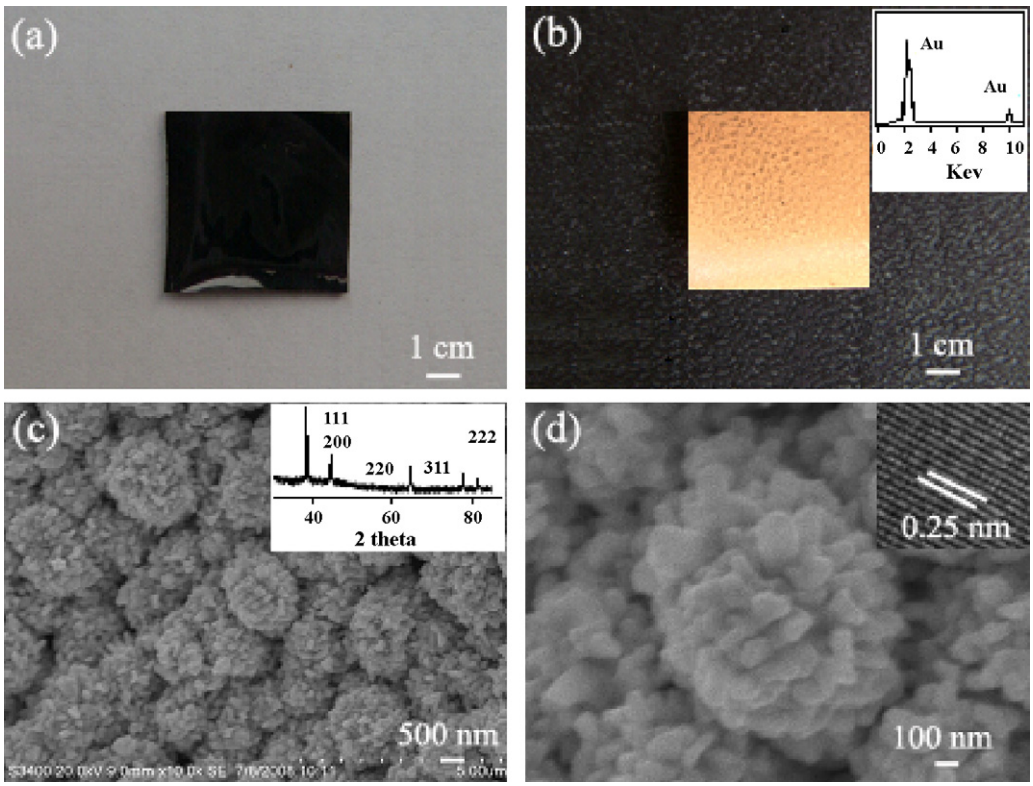

Fig. 1. The appearances of PANI/PAN blend film (a), hierarchical gold microspheres/PANI/PAN composite film (b), hierarchically quasi gold microspheres(c and d). Insets of b, c and d are the EDS spectrum, XRD pattern, and HRTEM image of the as-prepared Au quasi microspheres on the surface of composite film, respectively.

[$M_n = 7 \times 10^4$], was purchased from Anqing Petrochemical Group, China. $HAuCl_4$, 4-aminothiophenol, hydrochloric acid and $(NH_4)_2S_2O_8$ were analysis grades and used as received without further purification.

2.2. Fabrication of polyaniline (PANI) and polyaniline/polyacrylonitrile (PANI/PAN) blend films

PANI was synthesized by chemical oxidization polymerization. 10 ml of hydrochloric acid (5 wt.%) aqueous solution containing 0.2282 g of $(NH_4)_2S_2O_8$ oxidant was slowly added to 20 ml of distilled water containing 90 μl of aniline monomer. The mixture was stirred for 24 h at room temperature, and then filtrated, washed by distilled water and dried in vacuum at 40 °C. Thus, PANI was obtained.

For preparing PANI/PAN blend film, PAN (0.10 g) was dissolved in 50 ml of N,N′-dimethylformamide (DMF), to which 0.10 g of PANI was added. The mixture was stirred for 6 h at room temperature and then a black filtrate was collected via being filtered. By using the solution casting method, a PANI/PAN blend film on the surface of a glass plane was obtained. That blend film could be readily peeled off and cut using a blade like pure PAN film. The typical film thickness was about 200 μm. The PANI/PAN films with different polyaniline contents (or conductivities) could be obtained by adjusting the weight ratio between PANI and PAN.

2.3. Simultaneous synthesis and immobilization of hierarchical gold microspheres

Without any other additives added, the PANI/PAN blend film (10 mm × 10 mm × 0.5 mm, length × width × thickness) was immersed into 100 ml of $HAuCl_4$ aqueous solutions (1×10^{-2} mol l^{-1}) for 12 h at room temperature. Then, the film was withdrawn and washed by excessive distilled water. After drying under ambient temperature, simultaneous synthesis and immobilization of hierarchical gold microspheres was achieved, and the hierarchical gold microspheres/PANI/PAN composite film could be obtained. The hierarchical gold microspheres content was calculated by using the following expression:

$$\frac{W - W_0}{W} \times 100\%$$

where W and W_0 are the weights of hierarchical gold microspheres/PANI/PAN composite film and PANI/PAN blend film, respectively.

2.4. Catalytic activity of hierarchical gold microspheres/PANI/PAN composite film

Typically, a reaction mixture of water (8 ml), p-nitrophenol aqueous solution (5 ml, 1.5×10^{-3} mol l^{-1}), and 1 cm^2 of dried composite film (0.05 g) was first put in a beaker. To this stirring reaction mixture, 2 ml of $NaBH_4$ aqueous solution (1.5 mol l^{-1}) was then added. The progress of the conversion of p-nitrophenol to p-aminophenol was then monitored via UV–vis spectroscopy by recording the time-dependent absorption spectra of the reaction at a regular time interval of 5 min.

2.5. Instruments and measurements

Scanning electron microscope and optical microscope observations were carried out on JSM-5610 and XPT-7 microscopes, respectively.

X-ray diffraction (XRD) patterns were acquired with a Rigaku D/MAX-RC diffractometer using Cu Kα radiation in the 2θ range 5–55° at 45 kV.

The mechanical properties were measured at room temperature using an Instron 4301 (Instron, USA) universal testing machine.

Table 1
The electrical and stretching properties of different conducting films.

Samples[a]	Conductivity (S cm^{-1})	Stress at break (M Pa)	Strain at break (%)	Young's Modulus (M Pa)	PANI content (wt.%)
a	–	74.4 ± 0.5	6.4 ± 0.5	962.8 ± 25	–
b	10^{-6}	73.4 ± 0.5	6.3 ± 0.5	989.3. ± 25	13.9
c	10^{-5}	72.9 ± 0.5	6.1 ± 0.5	980.5 ± 25	20.5
d	10^{-4}	72.4 ± 0.5	5.9 ± 0.5	973.2 ± 25	32.6

[a] Sample a is the PANI/PAN blended film; samples b, c and d are all hierarchical quasi Au microspheres/PANI/PAN composite film.

Briefly, the film samples prepared according to the ASTM standard D 882-01 (45 mm × 5 mm × 0.2 mm, length × width × thickness) were tested at a rate of 10 mm min^{-1}. Young's modulus was calculated from the linear part of the initial slope. For each sample, the test was performed 5 times. The result was averaged and a standard deviation was reported.

Catalytic activity of hierarchical gold microspheres/PANI/PAN composite films was investigated by UV–vis spectra which were recorded on a UV-240 spectrometer (Shimadzu, Japan).

3. Results and discussion

3.1. The morphology of hierarchical gold microspheres

After a black PANI/PAN blend film (Fig. 1a) is immersed into $HAuCl_4$ aqueous solution for several minutes without any additives, the blended film exhibits a red-brown color as shown in Fig. 1b, indicating that the gold particles are simultaneously prepared and immobilization on the surface of blend film, as further confirmed by EDS pattern (inset of Fig. 1b). Thus, the Au particles/PANI/PAN composite film can be obtained. The morphologies of the resulted gold particles observed by SEM are shown in Fig. 1c and d. It can be seen that the gold particles are quasi Au microspheres with the size ranging from 1 to 2 μm, and possess hierarchical structure with the thickness of 80–200 nm nanoparticles as building blocks. In the XRD diffraction pattern (inset of Fig. 1c) of the composite film, several sharp diffraction peaks are observed at 38.3°, 44.9°, 64.3°, 77.4° and 81.6°, which can be assigned to diffraction from the 1 1 1, 2 0 0, 2 2 0, 3 1 1, and 2 2 2 planes [13] of gold crystal, respectively, corresponding to the face-centered cubic (fcc) structure (Joint Committee on Powder Diffraction Standards (JCPDS) file:04-0784). An additional inset, a HRTEM image, in Fig. 1d, corresponding to 1/3 {4 2 2} with a 2.5 Å spacing, is also observed. This indicates that those gold quasi microspheres are dominated by {1 1 1} facets [14,15], which accords with the result of XRD data. Our experimental result show the composite film have good stretching properties (Table 1). In addition, it can be made easily in different size according to the demand, handled handily in or cut into various shapes as the PANI/PAN blend film matrix depending on end use.

3.2. Formation of the gold microspheres with hierarchical structure

In general, the formation process of inorganic hierarchical architectures is a complex process, which is affected by crystal growth environments, crystal structures, surface energy and so forth [16,17]. From the SEM images (Fig. 2a–c) of immature Au microspheres formed during different periods, it can be believed that the formation process of the hierarchically quasi Au microspheres comprises mainly the formation of Au nanoparticles and the subsequent self-assembly of Au nanoparticles into hierarchical microspheres. When the conductive PANI/PAN film is immersed into the $HAuCl_4$ aqueous solution at ambient temperature, negatively charged $AuCl_4^-$ anions may be absorbed on the surface of conductive PANI/PAN film and reduced to Au atoms, forming gold nanoparticles in the presence of the conductive PANI chains of PANI/PAN blend film. The reaction can be represented as Eq. (1) according to some related reports [18,19]. At the same time, those Au nanoparticles formed on the surface of the conductive film matrix tend to undergo entropy-driven random aggregation [17,20] with spherical shape to minimize the surface energies. Thus, the quasi Au microspheres with hierarchical superstructure are finally obtained:

$$[(C_6H_4)NH]_X + AuCl_4^- \rightarrow [(C_6H_4)N]_X + Au + 4Cl^- + XH^+ \quad (1)$$

3.3. The effects of experimental conditions on the formation of gold microspheres with hierarchical structure

To further investigate the self-assemblied processes of hierarchical Au microspheres, and the influences of the concentration of $AuCl_4^-$ and PANI content (or conductivity) of the employed PAN/PAN film matrix on the construction of hierarchical structures have been investigated. Although both the shape and size of quasi Au microspheres are independent of the concentration of $AuCl_4^-$ and PANI content, it is found that the density of quasi Au micro-

Table 2
The rate constants of different reaction systems of reduction of p-nitrophenol using different Au microspheres with hierarchical structure/PANI/PAN composite films as catalysts.

Composite film samples	Experimental conditions	Au content (wt.%)	Rate constants (min^{-1})
1#	PANI/PAN film: 10^{-4} S cm^{-1} $HAuCl_4$ aqueous solution: 20 mM	6.00 ± 0.05	1.68×10^{-2}
2#	PANI/PAN film: 10^{-5} S cm^{-1} $HAuCl_4$ aqueous solution: 20 mM	8.01 ± 0.05	2.03×10^{-2}
3#	PANI/PAN film: 10^{-6} S cm^{-1} $HAuCl_4$ aqueous solution: 20 mM	10.28 ± 0.05	2.43×10^{-2}
4#	PANI/PAN film: 10^{-4} S cm^{-1} $HAuCl_4$ aqueous solution: 10 mM	9.59 ± 0.05	2.25×10^{-2}
5#	PANI/PAN film: 10^{-4} S cm^{-1} $HAuCl_4$ aqueous solution: 5 mM	8.35 ± 0.05	2.10×10^{-2}
6#	PANI/PAN film: 10^{-4} S cm^{-1} $HAuCl_4$ aqueous solution: 1 mM	6.34 ± 0.05	1.88×10^{-2}

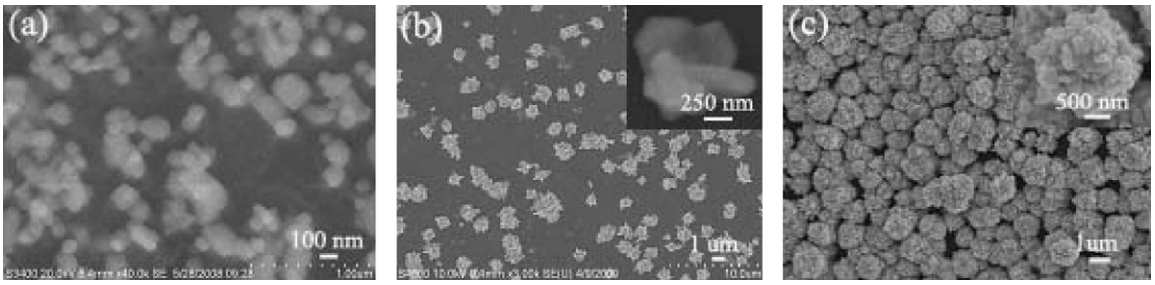

Fig. 2. TEM images of hierarchically quasi Au microspheres obtained at different periods: (a) 10 min, (b) 15 min, and (c) 30 min. Insets of b and c are the magnified images of the corresponding Au quasi microspheres, respectively.

spheres on the surface of composite film tends to increase with the increases of $AuCl_4^-$ and PANI content (or conductivity) (Table 2), indicating that hierarchical Au microspheres can be obtained easily and also controlled.

3.4. Catalytic activity of gold quasi microspheres with hierarchical structure/PANI/PAN composite film

In order to investigate the catalytic activity of the as-prepared gold quasi microspheres, different composite films are employed for the catalytic reduction of p-nitrophenol by $NaBH_4$. The composite film samples with the same size of 1 cm^2 are used in each reaction. We confirm that this reaction does not occur using the PANI/PAN blended film, even for lasting 24 h. Fig. 3a shows a typical UV–vis absorption change of the reaction mixture by the addition of composite film which prepared from 10^{-4} S cm^{-1} of PANI/PAN blended film and 10 mM of $HAuCl_4$ aqueous solution. From these spectra, it can be seen that the absorption of p-nitrophenol at 400 nm decreases obviously within 70 min after the addition of composite film, indicating the excellent catalyst activity. Due to the excessive $NaBH_4$ throughout the reaction, it is suggested that two principal species, p-nitrophenol and p-aminophenol influence the reaction kinetics. Therefore, pseudo-first-order kinetics could be applied for the evaluation of rate constants in this case. In Fig. 3b, the ratio of C_t to C_0 (C_t and C_0 are p-nitrophenol concentrations at time t and 0) is measured from the relative intensity of respective absorbance, A_t/A_0. The linear relation of $\ln(C_t/C_0)$ versus time is observed for the composite film catalyst, indicating that the reaction follows first-order kinetics. The rate constant ($K = 2.25 \times 10^{-2}$ min^{-1}) has been estimated from first-order reaction kinetics using the slope, indicating a high catalytic reduction rate comparable to some research results [21,22]. According to the same experimental method, the catalytic ability of a series of composite films is examined and the corresponding results are also listed in Table 2. As can be seen, the rate constant varies from 2.43×10^{-2} to 1.68×10^{-2} min^{-1} as the gold content of the composite film decreases from 10.28 ± 0.05 to 6.00 ± 0.05%. Explanations may be that more Au microspheres with hierarchical structure result in the bigger surface area, promoting the catalytic reaction. Moreover, our experiments show that those Au quasi microspheres with hierarchical structure are firmly integrated with the conductive PANI/PAN blended film matrix even in the case that they are washed by water repetitiously. This fact implies that these composite films can be used repeatedly. To support this point, we have repeated utilization produces for 25 times and have not found obvious change of the catalyst reaction rate constant.

In our previous researches, we used some polymer micro/nanoparticles as supports to prepare several kinds of noble metals catalysis with good catalytic activity such as Ag@poly(3,4-ethylenedioxythiophene) yolk/shell structure [23], Ag/poly(acrylonitrile-co-vinyl acetate) composite microspheres [24] and so on. For comparison with those catalysis and some reported gold catalytic materials including bared, core–shell micro/nanostructures or other powder matrix decorated with gold micro/nanostructures [25–27], the present Au microspheres with hierarchical structure/PANI/PAN composite films have an obvious advantage of easy and convenient operation in the practical catalytic reaction system. For instance, the composite film can be processed to different shape according to the practical need, and put into or out from the catalytic reaction system freely. Moreover, the tedious regeneration process including precipitating, filtering and redispersing could be simplified by washing only with excessive water. Therefore, this composite film is indeed a good material for promoting the practical catalytic application.

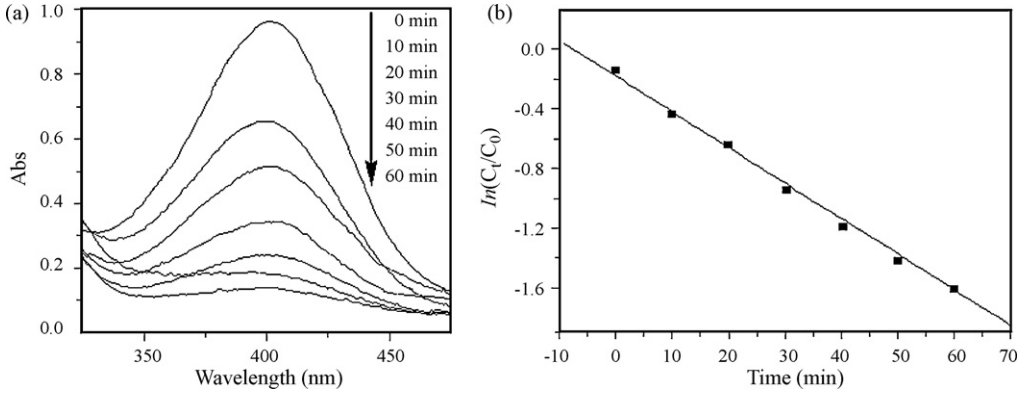

Fig. 3. Catalytic activity of quasi Au microsphere with hierarchical structure/PANI/PAN composite film prepared under 10 mM of $HAuCl_4$. (a) Time-dependent UV–vis spectral changes of the catalyzed system and (b) plot of $\ln(C_t/C_0)$ versus time.

4. Conclusions

In this paper, we report an interesting and facile approach for simultaneous synthesis and immobilization of hierarchical gold microspheres by using a conductive blended film as reducing and structure-directing agent. The size and amount of the gold microspheres with nanoparticles as building blocks on the surface of the composite film can be easily controlled by varying the content of PANI in PANI/PAN blend film and concentration of $HAuCl_4$. These composite films can be used as an advanced catalyst material due to their high catalysis, convenient operation and regeneration process in the practical application.

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