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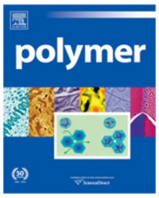

Gold microspheres with hierarchical structure/conducting polymer composite film: Preparation, characterization and application as catalyst

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ABSTRACT

Monodisperse gold microspheres with novel hierarchical structure and their composite integrated with a conducting film obtained from a new conducting copolymer, poly(acrylonitrile-co-vinyl acetate) -graft-poly(3,4-ethylenedioxythiophene), have been successfully prepared in one step via the in-situ reduction of $AuCl_4^-$ on the conducting film surface. The morphology and structure of the as-prepared composite film are characterized, and its catalytic effect on reduction of p-nitrophenol is investigated. By controlling the concentration of $HAuCl_4$ and the conductivity (or PEDOT content) of P(AN-co-VA)-g-PEDOT copolymer film, the amount and the size of gold microspheres can be effectively adjusted. It is suggested that the side poly(3,4-ethylenedioxythiophene) chains of the conducting copolymer play both reducing and structure-directing roles during the formation of Au microspheres with hierarchical structure.

1. Introduction

During the past few decades, great interest has been received to the morphological control of gold micro/nano materials because their shape and structure are closely related to their unusual catalytic, electronic and optical properties [1–4]. Among lots of gold micro/nano materials with varied morphologies, well-defined hierarchical gold micro/nanostructures have recently attracted considerable attention due to many potential applications. For example, hierarchically raspberry-like [5], meatball-like [6] and flower-like [7] gold microspheres assembled with nanoparticles, nanoplates or nanopricks as building blocks, can be applied in catalytic, superhydrophobic, surface enhanced material fields and so on.

A promising approach to exploiting the practicality of the hierarchically complex gold micro/nanostructures involves integrating them with a solid substrate to prepare composites. Alternatively, direct synthesis and immobilization of such micro/nanostructures on a selected matrix have been attractive due to the great convenience and high efficiency. However, little has been reported in this respect except electrochemical route (ECR) [7,8] which is restricted due to the limit of electrode dimension. In order to meet the requirements for practical applications, it is interesting and significative to introduce a novel method to realize more easily the above assumption.

Conductive polymers are attractive materials, as they cover a wide range of functions from insulators to metals and possess unique chemically reductive property at their oxidation state. However, as pure conductive polymers are usually insoluble and infusible, their applications are limited. Therefore, the fabrication of conducting copolymer with processability has become the aim of many recent investigations.

In the present work, a new conducting copolymer, poly (acrylonitrile-co-vinyl acetate) -graft- poly(3,4-ethylenedioxythiophene), named as P(AN-co-VA)-g-PEDOT, was successfully synthesized via expediently graft polymerization of 3,4-ethylenedioxythiophene (EDOT) in a colloid of P(AN-co-VA) within N, N′-dimethylformamide (DMF)/HCl solution. By using the P(AN-co-VA)-g-PEDOT film via the solution cast method from DMF, we further prepared the monodisperse gold microspheres with hierarchical structure and integrated them with the conducting copolymer film simultaneously without any additive. The as-prepared composite film could find many applications in catalyst, surface enhanced Raman scattering substrates, biosensors and so on. As an example, we investigated their catalytic activity detailedly by taking the reduction of p-nitrophenol as a model reaction.

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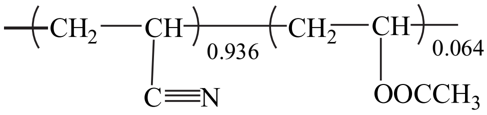
2. Experimental part

2.1. Materials

EDOT monomer was purchased from Aldrich. P(AN-co-VA) containing 90 wt% of AN units was supplied by Anqing Petrochemical Group, Anhui Province in China, and the chemical structure of which is given as



$$\left(\mathrm{CH_2}-\underset{\underset{\mathrm{C{\equiv}N}}{|}}{\mathrm{CH}}\right)_{0.936}\left(\mathrm{CH_2}-\underset{\underset{\mathrm{OOCCH_3}}{|}}{\mathrm{CH}}\right)_{0.064}$$

Also, it has a number average molecular weight (M_n) of 7.70×10^4 g/mol $HAuCl_4$, HCl, $(NH_4)_2S_2O_8$, DMF and p-nitrophenol were analysis grade and used as received without further purification.

2.2. Fabrication of pure P(AN-co-VA) film and P(AN-co-VA)-g-PEDOT film

Pure P(AN-co-VA) film was obtained by dissolving P(AN-co-VA) (0.20 g) in DMF (20 mL), casting the obtained solution in the glass dish and evaporating the solvent at about 30 °C.

P(AN-co-VA) (0.20 g) was dissolved in DMF (20 mL) containing 440 μL of EDOT monomers, to which HCl solution (36.5 wt%) was added to ensure that the reaction system is maintained under acidic environment (pH = 3–5). The formed P(AN-co-VA) colloid was stirred for 6 h at room temperature, then to which 60 mL of aqueous solution containing 2.8 g of $(NH_4)_2S_2O_8$ oxidant were added in 30 min. After continuously stirring for 24 h, the product was filtered, dried in vacuum at 40 °C and then dissolved in DMF again at 80 °C. Via being filtered, a homogeneous and deeply blue P(AN-co-VA)-g-PEDOT filtrate was collected. By using the solution casting method, a compact P(AN-co-VA)-g-PEDOT film on the surface of a glass plane was obtained, that could be readily peeled off and cut using a blade like pure P(AN-co-VA) film. The typical film thickness was about 200 μm. The P(AN-co-VA)-g-PEDOT films with different conductivities could be obtained by adjusting the weight ratio of EDOT monomer to P(AN-co-VA).

2.3. The grafted PEDOT content in the P(AN-co-VA)-g-PEDOT copolymer

According to the result of EDS analysis, the grafted PEDOT content (W_{PEDOT}) in the P(AN-co-VA)-g-PEDOT copolymer was estimated by the equation (1):

$$\frac{\dfrac{W_{PEDOT}\times 72}{M_{EDOT}^{-2}}+\dfrac{90\%\times(1-W_{PEDOT})\times 36}{M_{AN}}+\dfrac{10\%\times(1-W_{PEDOT})\times 48}{M_{VA}}}{\dfrac{W_{PEDOT}\times 32}{M_{PEDOT}^{-2}}}=\frac{W_C}{W_S} \tag{1}$$

where M_{EDOT}, M_{AN} and M_{VA} are the molecular weight of EDOT, AN and VA, respectively. W_S and W_C are the weight of carbon and sulfur in the P(AN-co-VA)-g-PEDOT copolymer.

2.4. Preparation of gold microspheres with hierarchical structure/conducting P(AN-co-VA)-g-PEDOT composite film

The P(AN-co-VA)-g-PEDOT film with conductivity of 10^{-3} S cm^{-1} was cut to the size of 1 cm^2 and immersed into 30 mL of $HAuCl_4$ aqueous solutions (1×10^{-2} mol L^{-1}) for 72 h at room temperature. Then, the film was withdrawn and washed by excessive distilled water. After drying under ambient temperature, the composite film of P(AN-co-VA)-g-PEDOT with the gold microspheres on its surface was thus obtained. The gold microspheres content was calculated by using the following expressions.

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

where W and W_0 are the weight of gold microspheres with hierarchical structure/conducting P(AN-co-VA)-g-PEDOT composite film and P(AN-co-VA)-g-PEDOT film, respectively.

2.5. Catalytic activity of gold microspheres with hierarchical structure/conducting P(AN-co-VA)-g-PEDOT composite film

Typically, a reaction mixture of water (8 mL), p-nitrophenol aqueous solution (5 mL, 1.5×10^{-3} mol L^{-1}), 1 cm^2 of purified and dried composite film (0.05 g) were 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.

2.6. Instruments and measurements

The morphologies of different films were observed by optical microscope (XPT-7) and scanning electron microscope [JSM-5610 and energy dispersive spectrometer (EDS) accessory for elemental measurement, Kevex-Sigma], respectively. Attenuated Total Reflectance Fourier transform infrared (ATR-FTIR) spectra of film samples were obtained on a BrukerVECTOR22 spectrometer with the resolution of 1 cm^{-1}. Raman spectra were recorded on a Bruker RFS100 Fourier transform Raman spectrometer with the resolution of 1 cm^{-1}, which is equipped with an air-cooled Nd:YAG laser source(1064 nm) and an output power of 30–200 mW and a Ge detector cooled by liquid nitrogen. Molecular weight and its distributions were determined by Gel permeation chromatography (Waters 1515) using a series of two linear Styragel columns HT3, HT4, and an oven temperature of 60.8 °C. Waters 1515 pump and Waters 2414 differential refractive index detector (set at 30.8 °C) were used. The eluent was DMF + 1 g/L LiBr at a flow rate of 1.0 mL/min. A series of six polystyrene standards with molecular weights ranging from 800 to 400,000 g/mol were used for calibration. X-Ray diffraction (XRD) patterns were acquired with a Rigaku D/MAX-RC diffractometer using Cu K_α radiation in the 2θ range 5–55° at 45 kV. The method used to determine conductivities of the P(AN-co-VA)-g-PEDOT films at room temperature was the standard four-point probe technique. The mechanical properties were measured at room temperature using an Instron 4301 (Instron, USA) universal testing machine. Briefly, the film samples prepared according to the ASTM standard D 882-01(45 × 5 × 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 gold microspheres with hierarchical structure/conducting P(AN-co-VA)-g-PEDOT composite film was investigated by UV–vis spectra which were recorded on a UV-240 spectrometer (Shimadzu, Japan).

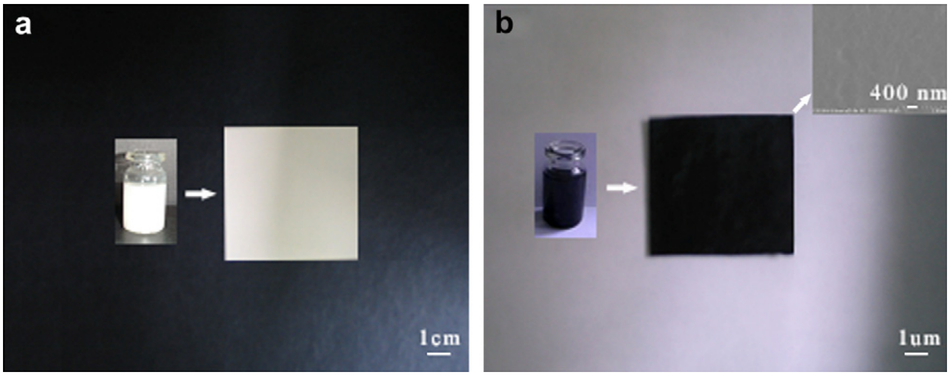


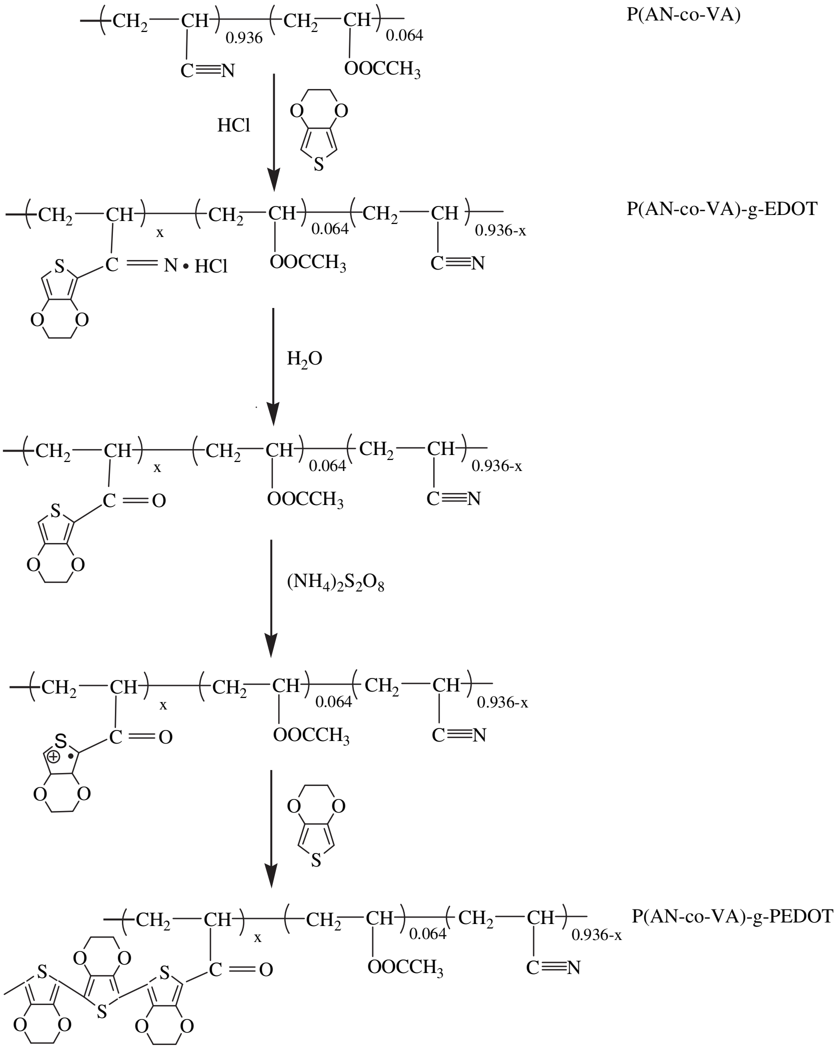
Fig. 1. The optical photographs of P(AN-co-VA) film (a) and P(AN-co-VA)-g-PEDOT film (b) (Inset is the SEM image of P(AN-co-VA)-g-PEDOT film).

3. Results and discussion

3.1. Synthesis and characterization of the conducting P(AN-co-VA)-g-PEDOT copolymer film

The conducting P(AN-co-VA)-g-PEDOT film is obtained by evaporation of DMF in the copolymer solution on glass substrate. Compared with the slightly yellow, pure and insulating P(AN-co-VA) film (Fig. 1a), the homogeneous P(AN-co-VA)-g-PEDOT film displays a deep blue color with metallic shine and a surface as smooth as that of P(AN-co-VA) film (Fig. 1b).

For the conducting P(AN-co-VA)-g-PEDOT copolymer, the detailed synthesis process and the proposed structure are described in Scheme 1. According to Friedel–Crafts reaction of



Scheme 1. Illustration of synthetic approach of P(AN-co-VA)-g-PEDOT copolymer.

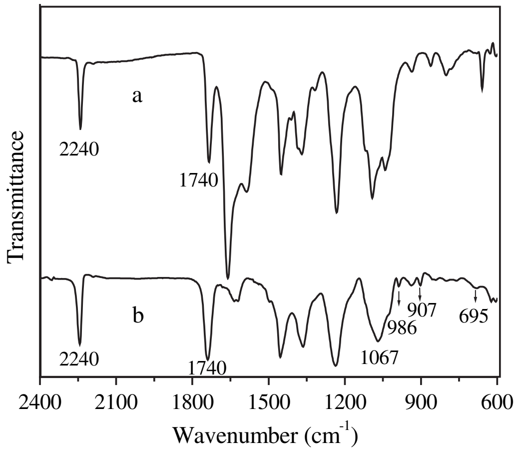


Fig. 2. FTIR spectra of P(AN-co-VA) (a) and P(AN-co-VA)-g-PEDOT (b) samples.

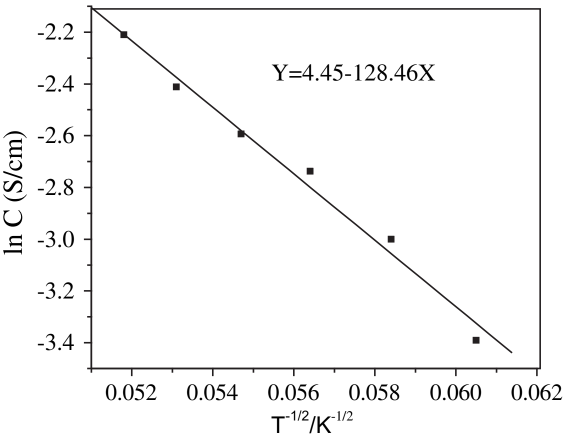


Fig. 3. Variation of logarithmic conductivity of the P(AN-co-VA)-g-PEDOT film with $T^{-1/2}$.

heterocyclic thiophene [9], it is known that the nitrile groups as the grafted sites induct the EDOT monomer and its cation radical to propagate gradually, getting the conjugated PEDOT branch chains on the P(AN-co-VA) backbone. The evidence for the graft copolymerization could be obtained from the FTIR spectra. Compared with the spectrum of P(AN-co-VA) (Fig. 2a), besides the characteristic band at 2240 cm^{-1} for –CN stretching and 1740 cm^{-1} for –CO stretching, some characteristic absorption peaks (1067, 986, 907 and 695cm^{-1}) related to PEDOT are observed in the FTIR spectrum of P(AN-co-VA)-g-PEDOT sample (Fig. 2b). These results indicate that PEDOT is successfully grafted onto P(AN-co-VA). The P(AN-co-VA)-g-PEDOT films with different conductivity can be obtained by adjusting the weight ratio of EDOT monomer to P(AN-co-VA). The measured molecular weight, the electrical and stretching properties of the as-prepared conducting films are listed in Table 1. As can be seen, the P(AN-co-VA)-g-PEDOT copolymers with different conductivity all have the higher molecular weight compared with pure P(AN-co-VA), confirming PEDOT grafting successfully onto P(AN-co-VA). It is noticeable that the conductivities of these P(AN-co-VA)-g-PEDOT copolymers increase with the increasing molecular weight, which demonstrates that the more or longer PEDOT branch chains favor the increase of conductivity of the graft copolymers. In our case, the maximum PEDOT content in the copolymer is estimated ca.52.6 ± 0.1 wt% from the C/S weight ratio of 4.92 in P(AN-co-VA)-g-PEDOT. Although this PEDOT content may be slightly over-estimated due to the presence of doped sulfur-containing anions which resulted from ammonium persulfate oxidant, it can be believed that there are many PEDOT branch chains on the P(AN-co-VA) backbone. It is these PEDOT branch chains that form the conductive routeway and promote the transfer of charge carrier in or among the conductive PEDOT segments. The conductivities $C(T)$ of the P(AN-co-VA)-g-PEDOT film samples treated in the temperature (T) ranging from 273 K to 373 K for 5 h were measured. As shown in Fig. 3, the relationship between the temperature and conductivity follows quasi one-dimensional (1D) variable range hopping (VRH) model, which is described as follows:

$$C(T) = C_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/2}\right] \tag{2}$$

where T_0 is a measure of the potential barrier height, as carriers get thermally activated hopping among localized states at different energies [10]. C_0 is related to their size contribution, mean volume occupied by the conducting grains in the material, etc. [11].

3.2. Preparation and characterization of the gold microspheres with hierarchical structure/conducting P(AN-co-VA)-g-PEDOT copolymer composite film

By immersing the P(AN-co-VA)-g-PEDOT film into $HAuCl_4$ aqueous solution without any additives, we have obtained easily Au/P(AN-co-VA)-g-PEDOT composite film. Typically, the composite film exhibits a red-brown color as shown in Fig. 4a, indicating that the gold particles are formed on the surface of P(AN-co-VA)-g-PEDOT film matrix, as further confirmed by EDS pattern (Fig. 4d). The morphologies of the resulted gold particles observed by SEM are shown in Fig. 4b and c. It is seen that the gold particles are perfect Au microspheres with the size of about 6 μm, and possess hierarchical structure with the thickness of 200–250 nm nanoplates as building blocks. In the XRD diffraction pattern (Fig. 4e) of the composite film, several sharp diffraction peaks are observed at 38.2°, 44.8°, 64.5°, 77.5° and 81.7°, which can be assigned to diffraction from the 111, 200, 220, 311, and 222 planes [12] of gold crystal, respectively, corresponding to the face-centered cubic (fcc) structure (Joint Committee on Powder Diffraction Standards (JCPDS) file:04-0784). It is worth noting that the intensity ratio (0.36) of the 200 plane peak to 111 one is lower than the conventional value (0.52) of usual gold powder. Similar result is found for the intensity ratio (0.21) of the 220 plane peak to 111 one (the conventional value is 0.32)[13,14]. These observations imply that the deposited gold microspheres tend to grow with the surface dominated by the lowest energy111 facets [15]. Identical with the

Table 1
The molecular weight, the electrical and stretching properties of different conducting films.

Samples[a]	Mn	Conductivity (S cm^{-1})	Stress at break (M Pa)	Strain at break (%)	Young's Modulus (M Pa)	PEDOT content (wt%)
a	7.70×10^4	–	31.5 ± 0.2	22.3 ± 0.2	1257 ± 25	–
b	9.06×10^4	10^{-5}	31.2 ± 0.3	21.6 ± 0.2	1299 ± 5	14.8
c	1.17×10^5	10^{-4}	31.0 ± 0.2	20.3 ± 0.3	1352 ± 5	36.4
d	1.45×10^5	10^{-3}	31.5 ± 0.2	19.5 ± 0.2	1443 ± 5	52.6

[a] Sample a is the pure P(AN-co-VA) film; samples b, c and d are all conductive P(AN-co-VA)-g-PEDOT films.

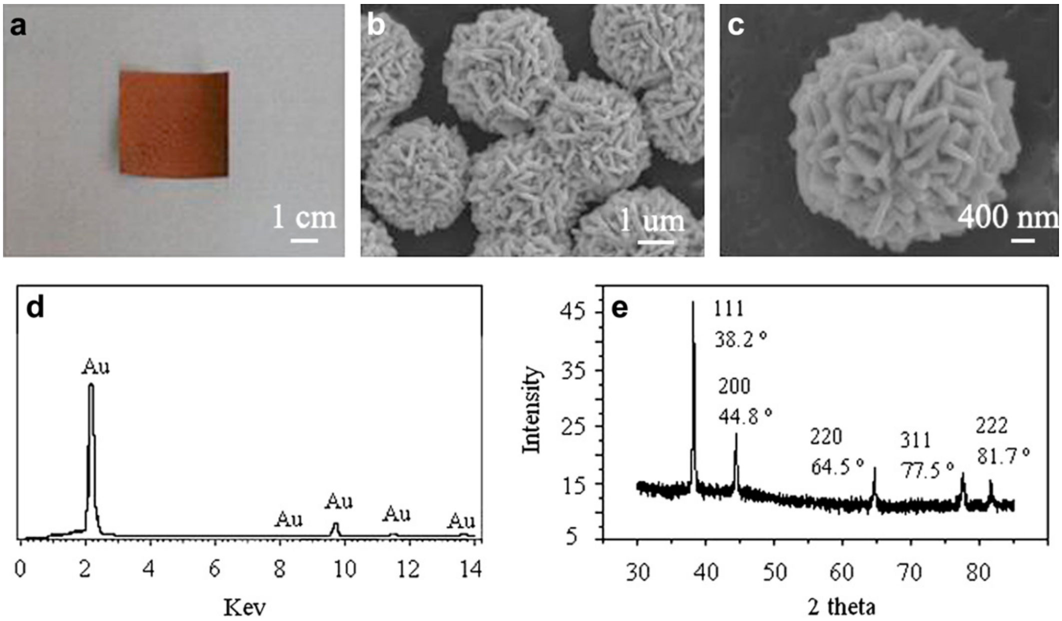


Fig. 4. The optical micrograph (a), SEM images (b, c), EDS (d) and XRD (e) patterns of Au microspheres with hierarchical structure/P(AN-co-VA)-g-PEDOT composite film.

P(AN-co-VA)-g-PEDOT film matrix, the composite film has excellent stretching strength, and can be made easily in different size and cut into various shapes depending on the end use.

3.3. *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. 5a–c) of immature Au microspheres formed during different periods, it can be believed that the formation process of the hierarchical Au microspheres comprises mainly the formation of Au nanoplates and the subsequent self-assembly of Au nanoplates into the hierarchical microspheres. When the conductive P(AN-co-VA)-g-PEDOT film is immersed into the $HAuCl_4$ aqueous solution at ambient

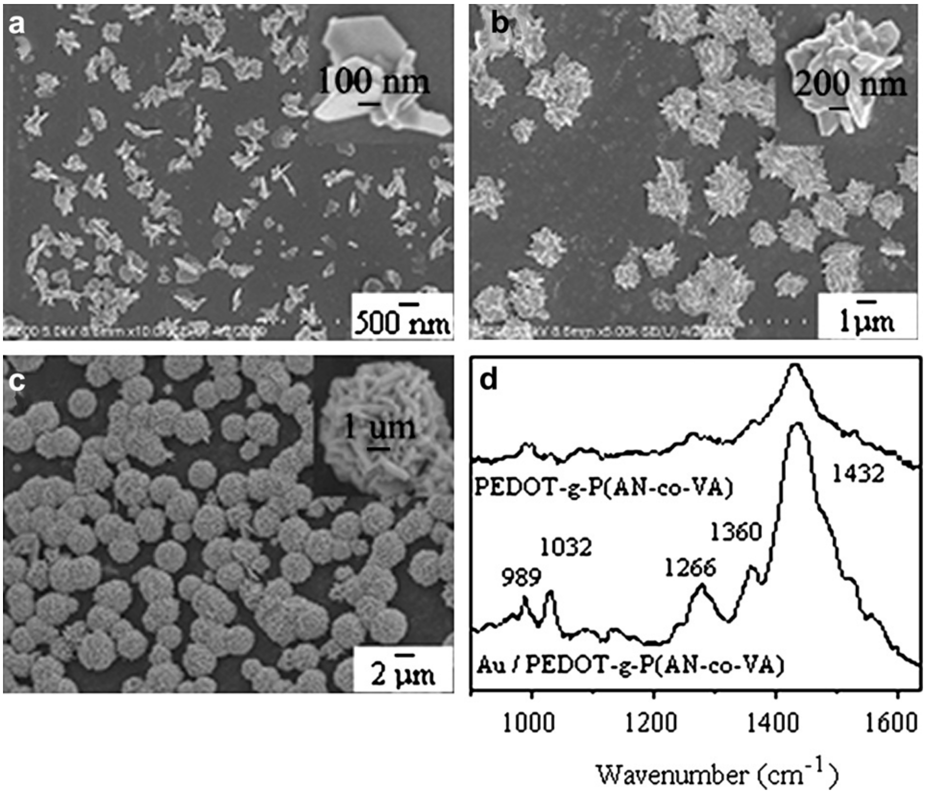


Fig. 5. The SEM images of Au microspheres formed during different periods (a: 2 h; b: 4 h; c: 6 h) and the Raman spectrum (d) of Au microspheres with hierarchical structure/P(AN-co-VA)-g-PEDOT composite film.

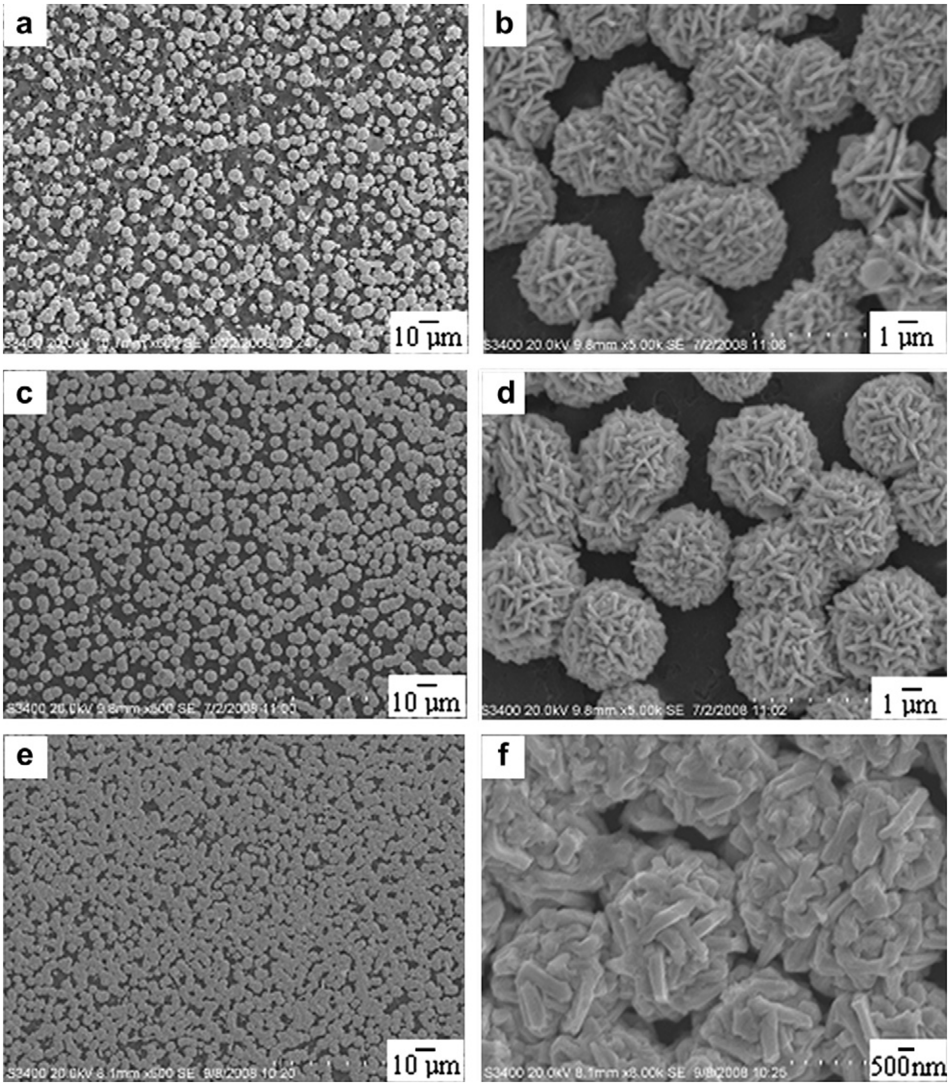


Fig. 6. The SEM images of Au microspheres with hierarchical structure/P(AN-co-VA)-g-PEDOT composite film prepared in the different concentration of $HAuCl_4$ aqueous solution: a, b) 1 mM; c, d) 5 mM; e, f) 10 mM. Other conditions: 10^{-3} S cm $^{-1}$ of P(AN-co-VA)-g-PEDOT film, room temperature, 72 h.

temperature, negatively charged $AuCl_4^-$ anions may be absorbed on the surface of conductive P(AN-co-VA)-g-PEDOT film and reduced to Au atoms, forming gold nuclei in the presence of the conductive side PEDOT chain of P(AN-co-VA)-g-PEDOT copolymer. In the process of gold nuclei growth, side PEDOT chains may also play a capping agent role to lower the surface energy of gold 111 facets through the direct interaction with the gold surface, resulting in a very slow growth along the 111 orientations. Such interaction between the PEDOT side chains and gold surface is detectable from the Raman signal of conductive P(AN-co-VA)-g-PEDOT film, as shown in Fig. 5d. It can been found that the intensities of several peaks related to PEDOT, such as symmetry $C_\alpha{=}C_\beta(-O)$ stretching at 1432 cm^{-1}, $C_\beta{-}C_\beta$ stretching at 1360 cm^{-1}, $C_\alpha{-}C_{\alpha'}$ inter-ring stretching at 1266 cm^{-1}, C–O–C deformation at 1032 cm^{-1} and oxyethylene ring deformation at 989 cm^{-1},[18] are enhanced obviously after the formation of hierarchical Au microspheres, implying the contribution of surface enhanced Raman scattering effect. Since no peak related to Au–S bond is found in the Raman spectrum of the composite film, it is considered that the interaction between the gold particles and the copolymer film surface may be physisorption. As we know, anisotropic metal plates could be readily obtained by operating at a slow reduction rate (under kinetic control) [19]. In this work, the employed reductant, conductive P(AN-co-VA)-g-PEDOT copolymer film, has mild reduction activity because of its moderate reduction potential provided by the side PEDOT chains, which may also play an important role in controlling the formation and shaping of Au nanoplates. Therefore, it is suggested that both reducing and structure-directing roles of the side PEDOT chains on the backbone of P(AN-co-VA)-g-PEDOT lead to the formation of Au nanoplates. At the same time, those Au nanoplates 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 glomerate Au microspheres with hierarchical superstructure are finally obtained.

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

To further understand the self-assemblied process of gold microspheres on the surface of the conductive polymer film, the influences of the synthesis conditions, such as the concentration of

$HAuCl_4$ and the conductivity (or PEDOT content) of P(AN-co-VA)-g-PEDOT copolymer, on the construction of 3D Au microstructure have been systematically investigated. For P(AN-co-VA)-g-PEDOT film matrix with a conductivity of 10^{-3} S cm^{-1}, due to the lower concentration of $HAuCl_4$ (lower than 1 mM), some immature Au microspheres are observed on the surface of conductive film with the size ranging from 2 to 6 μm(Fig. 6a and b). With the increase of $HAuCl_4$ concentration, the density of Au microspheres with hierarchical structure increases gradually and Au microspheres also become more perfect (Fig. 6c and d). Bulk quantities of Au microspheres which tend to connect with each other on the surface of the composite film are obtained when the concentration of $HAuCl_4$ is increased to 10 mM (Fig. 6e and f). Also, the Au nanoplates become thicker due to more doped $AuCl_4^-$ ions lying along the PEDOT side chains, resulting in Au microspheres with more compact structure. Continuous increase of concentration of $HAuCl_4$ does not obviously increase the content of gold microspheres and the thickness of Au microsheets because all the side PEDOT chains themselves have been oxidized in the process [21]. The conductivity (or PEDOT content) of employed P(AN-co-VA)-g-PEDOT film matrix is another important factor that significantly affects the growth of Au microspheres. For example, in the same 20 mM of $HAuCl_4$ aqueous solution, with the increase of conductivity (or PEDOT content), more Au microspheres form and the structure of Au microsphere becomes more compact. It is therefore concluded that the composite film containing high density and perfect morphology of Au microspheres with hierarchical structure can be obtained easily by controlling the concentration of $HAuCl_4$ aqueous solution and the conductivity (or PEDOT content) of employed P(AN-co-VA)-g-PEDOT film.

3.5. Catalytic activity of gold microspheres with hierarchical structure/conducting P(AN-co-VA)-g-PEDOT composite film

Due to the hierarchical structure, the Au microspheres exhibit high surface area. As an example, these Au microspheres with hierarchical structure/P(AN-co-VA)-g-PEDOT composite films have been employed for the catalytic reduction of p-nitrophenol by $NaBH_4$. The composite film sample with the same size of 1 cm^2 is used in each reaction. It is well known that this reaction is simple and fast in the presence of metallic surface [22–25]. Fig. 7a shows a typical UV–vis absorption change of the reaction mixture by the addition of composite film which prepared from 10^{-3} S cm^{-1} of P(AN-co-VA)-g-PEDOT film and 10 mM of $HAuCl_4$ aqueous solution. Usually, the absorption decrease of p-nitrophenol at 400 nm can be used to evaluate catalyst activity [26]. From these spectra, it can be seen that the absorption of p-nitrophenol at 400 nm decreases obviously within 50 min after the addition of composite film, indicating the excellent catalyst activity. By comparison, the P(AN-co-VA)-g-PEDOT film matrix is also used, and results show that this reaction does not occur even for lasting 72 h. Since the BH_4^- concentration remains essentially constant throughout the reaction due to the excessive $NaBH_4$, it is suggested that two principal species, p-nitrophenol and p-aminophenol influence the reaction kinetics. In this case, pseudo-first-order kinetics could be applied for the evaluation of rate constants. In Fig. 7b, 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 ($K = 3.65 \times 10^{-2}$ min^{-1}) has been estimated from first-order reaction kinetics using the slope, indicating a high catalytic reduction rate comparable to some research results [22,27]. According to the same experimental method, the catalytic ability of a series of composite films is examined and the corresponding results are listed in Table 2. As can be seen, the rate constant varies from 3.68×10^{-2} min^{-1} to 2.48×10^{-2} min^{-1} as the gold content of the composite film decreases from 10.90 ± 0.01% to 6.01 ± 0.02%. Explanations may be due to the more Au microspheres with hierarchical structure that result in the bigger surface area, promoting the catalytic reaction. Moreover, our experiments show that those Au microspheres with hierarchical structure are firmly integrated with the conductive P(AN-co-VA)-g-PEDOT composite 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 repeated utilization produces for 20 times and did not find obvious change of the catalyst reaction rate constant.

For comparison with some reported gold catalytic materials including bared, core-shell micro/nanostructures or other powdery matrix decorated with gold micro/nanostructures [26,28,29], the present Au microspheres with hierarchical structure/P(AN-co-VA)-g-PEDOT 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. Because the metallic catalytic activity is mainly determined by the size as well as the amount other than the shape of the catalytic species, the present hierarchical structure does not raise the catalytic rate obviously. Nevertheless, this composite film is indeed a good material for promoting the practical catalytic application.

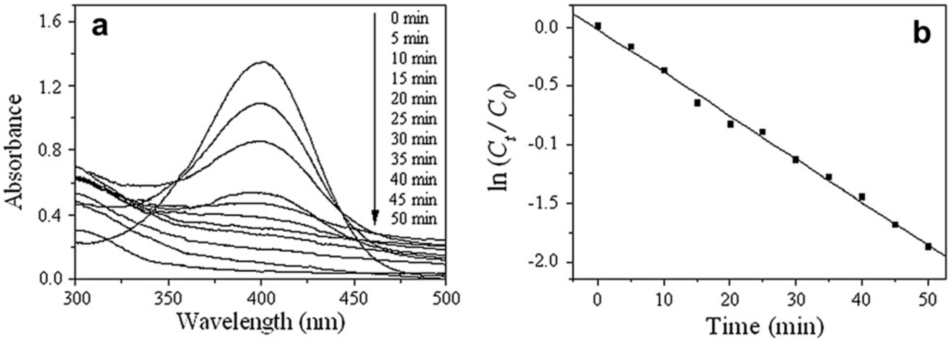


Fig. 7. Catalytic activity of Au microspheres with hierarchical structure/P(AN-co-VA)-g-PEDOT composite film which prepared from 10^{-3} S cm^{-1} of P(AN-co-VA)-g-PEDOT film and 10 mM of $HAuCl_4$ aqueous solution.

Table 2
The rate constants of different reaction systems of reduction of p-nitrophenol using different Au microspheres with hierarchical structure/P(AN-*co*-VA)-*g*-PEDOT composite films as catalyst.

Composite film samples	Experimental conditions	Au content (wt%)	Rate constants (min^{-1})
1#	P(AN-co-VA)-g-PEDOT film: 10^{-3} S cm^{-1} $HAuCl_4$ aqueous solution: 20 mM	10.90 ± 0.01	3.68×10^{-2}
2#	P(AN-co-VA)-g-PEDOT film: 10^{-4} S cm^{-1} $HAuCl_4$ aqueous solution: 20 mM	8.01 ± 0.01	3.03×10^{-2}
3#	P(AN-co-VA)-g-PEDOT film: 10^{-5} S cm^{-1} $HAuCl_4$ aqueous solution: 20 mM	6.28 ± 0.02	2.63×10^{-2}
4#	P(AN-co-VA)-g-PEDOT film: 10^{-3} S cm^{-1} $HAuCl_4$ aqueous solution: 10 mM	10.59 ± 0.01	3.65×10^{-2}
5#	P(AN-co-VA)-g-PEDOT film: 10^{-3} S cm^{-1} $HAuCl_4$ aqueous solution: 5 mM	8.24 ± 0.01	3.10×10^{-2}
6#	P(AN-co-VA)-g-PEDOT film: 10^{-3} S cm^{-1} $HAuCl_4$ aqueous solution: 1 mM	6.01 ± 0.02	2.48×10^{-2}

4. Conclusions

In summary, we report an interesting finding in this contribution that monodisperse gold microspheres with novel hierarchical structure/conducting polymer composite film material can be prepared facilely by using a conductive graft copolymer film as reducing and structure-directing agent. The size and amount of the gold microspheres with the nanoplate structure as building blocks on the surface of the as-prepared composite film can be easily controlled by varying the content of PEDOT in P(AN-co-VA)-g-PEDOT copolymer and the 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. Also, the combination of unique hierarchical morphology of the monodisperse gold microspheres and processability as well as high-strength of the novel conducting copolymer matrix, could make these functional composite films find other potential applications such as surface enhanced Raman scattering substrates, biosensors and so on.

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