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**Nanoporous gold film: fabricating and acting as a catalytic reactor***Youyi Xia\**, *Xiang Deng*, *Shuxin Yan*, *Chang Gao*, *Cong Ma*, *Ling Jin*

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**Abstract**

Nanoporous gold (NPG) is attractive due to highly catalytic activity. From an applied and economical point of view, fabricating thin NPG film is recognized to be an ideal approach. Herein, we report an interesting finding that thin NPG film with the thickness of 90 nm can be prepared on various substrates conveniently by using a seed-mediated growth. The film has a nanoporous characterization with 30-60 nm and 10-30 nm of ligament and pore size, respectively. The high cost-efficiency, adjustable substrates, easy and convenient operation would make this film reactor to be as a good candidate both for catalyzing oxidative and hydrogenation reaction.

**Keywords:** Nanoporous gold film, catalytic reactors, polypyrrole

**Introduction**

Nanoporous gold (NPG) is a kind of highly porous metallic structures characterized with comprehensive three-dimensional networks of nanoscale interconnected ligaments <sup>1</sup>. It is attractive due to highly catalytic activity even when the feature length of ligaments is larger than 30 nm. Importantly, high density of atomic steps and kinks are observed on the curved surfaces of NPG recently, comparable to 3-5 nm nanoparticles <sup>2</sup>, which provides a forceful

explanation for the activity of NPG<sup>3-5</sup>.

Within the last years, various NPG materials (film, foam and sponge) have been prepared successfully by dealloy<sup>6</sup>, template<sup>7</sup> as well as other techniques<sup>8-10</sup>. Among those materials, thin film is more attractive in the catalytic fields from an applied and economical point of view<sup>11,12</sup>. Particularly, if NPG film is on the order of 100 nm, the amount of Au would be less than 0.1 mg/cm<sup>2</sup><sup>13,14</sup>, which can be certainly acceptable in some catalytic fields, for example fuel cell. Also, the mass transplation in the thin NPG film is more easily, making it possible to further increase the catalytic activity of NPG for some reactions like the gas-phase synthesis whose reaction rate is controlled by diffusion.

Obviously, for the practical application, it is desirable to grow thin NPG film directly on the solid substrate, especially on the inwall of reactors because the film in that case would not only keep the high activity but also can be reused with great convenience. To realize the above assumption, herein, polypyrrole (PPY) film is firstly prepared via in-situ oxidation polymerization of pyrrole on the solid substrates. Then, thin NPG film is fabricated directly on the surface of PPY successfully by adjusting the doped acid in PPY and using a seed-mediated growth. Thus various, low-cost and easy-operation reactors with highly catalytic activity can be facilely constructed by changing the substrates.

## Experimental Section

### **Materials**

Tetrakis(hydroxymethyl)phosphonium chloride solution (80 wt.%) [(CH<sub>2</sub>OH)<sub>4</sub>P]Cl (THPC), thiohydraacrylic acid (TA), hydrogen tetrachloroaurate (III) hydrate (99.9%), 4-mercaptophenylboronic acid (4-MPBA), 4-mercaptobenzoic acid (4-MBA), mercaptosuccinic acid (MPA), ascorbic acid (AA), pyrrole (PY) and

(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (APS) were purchased from Aldrich in their reagent grades. All chemical reagents were used without further purification except PY, which was distilled under reduced pressure.

***Preparation of PPY film on the inwall of polypropylene centrifugal tube (PPCT)***

Typically, 1 ml of HCl solution (1M) and 10 µl of PY monomer were added into 1.5 ml of PPCT, followed by the addition of APS (0.03 g). After being shaken for 2 min, the mixed solution was dumped out. Thus, a black PPY film could be obtained on the inwall of PPCT after being washed with excessive ethanol and distilled water.

As for the preparation of PPY film on other substrates (such as ITO glass), it only needed to adjust the quantity of HCl, PY and APS to submerge the substrates according to the practical conditions. The other procedures were similar with the preparation of PPY film on the inwall of PPCT.

***Synthesis of THPC-Au seeds***

For the growth of NPG film on the PPY, THPC-Au seeds were firstly synthesized according to the literature <sup>15</sup>. Typically, 45mL aliquot of distilled water was added into 0.5 mL of NaOH (1M) and 1 mL of THPC solution containing 12 µL of 80% THPC. The reaction mixture was stirred for 5 min. Then, 2.0 mL of 1% HAuCl<sub>4</sub> • 3H<sub>2</sub>O in distilled water was added quickly to the stirred solution. Thus, THPC-Au seeds with the diameter of ~5 nm were obtained.

***Growth of NPG film on the inwall of PPCT***

At room temperature, 1.5 ml of PPCT containing PPY film was redoped in TA aqueous solution (1.5 ml, 1M) for 10 min, followed by being washed with excessive distilled water. Then, it was filled with THPC-Au seeds solution for 5 h without stirring. Later, after being dumped and washed by water, it was loaded with 0.9 ml of water containing 100 µL HAuCl<sub>4</sub> (1 wt. %) with slight shaking. Subsequently, 0.1 ml

of AA (1 wt. %) was added drop by drop. The reaction was allowed for 30 min and the glaring NPG film could be obtained on the PPY film after being washed and dried at room temperature. According to the above procedures, NPG film can also be prepared on the other substrates only adjusting the amount of  $\text{HAuCl}_4$  and AA.

The Au amount ( $C_{\text{Au}}$ ) of NPG film was calculated according to equation 1. Where  $S_{\text{total}}$  was the inwall area of PPCT coated by NPG film, and  $W_{\text{NPG film}}$  was the weight of NPG film, which was calculated from the weight difference before and after the formation of NPG film on the inwall of PPCT.

$$C_{\text{Au}} = W_{\text{NPG film}} / S_{\text{total}} \quad (1)$$

#### ***Catalytic activity of NPG film for the reduction of p-nitrophenol***

1 mL of *p*-nitrophenol aqueous solution (0.085 mM) and 15 mg  $\text{NaBH}_4$  are added into PPCT containing NPG film at room temperature with slight inversion. The progress for the conversion of *p*-nitrophenol to *p*-aminophenol was then monitored by recording the time-dependent UV-vis spectra of the reaction at a regular time interval of 2 min.

#### ***Catalytic activity of NPG film for the oxidation of triethyl silicane***

Acetone (1.0 mL),  $\text{H}_2\text{O}$  (0.075 ml) and triethyl silicane (1mmol, 116 mg) were added to PPCT containing NPG film to carry out the oxidation reaction for 2 h at room temperature. The mixture was then concentrated under reduced pressure, followed by column chromatography on silica gel using hexane/ether (2:1) as eluent to obtain the product.

#### ***Instruments and measurements***

Scanning electron microscope (SEM) and optical microscope observations were carried out on JSM-5610 and XPT-7 microscopes, respectively. Catalytic activity of NPG film was investigated by UV-vis spectra, which were recorded on a UV-240

spectrometer (Shimadzu, Japan). Raman spectra were performed on a Bruker RFS100 Fourier transform Raman spectrometer with the resolution of  $1\text{ cm}^{-1}$ , which was equipped with an air-cooled Nd:YAG laser source (1064 nm), an output power of 30–200 mW and a Ge detector cooled by liquid nitrogen. Nitrogen adsorption isotherm was measured in a NOVA sorption apparatus and surface area calculation was carried out using the BET method.

### Results and discussion

To demonstrate the formation of a thin NPG film, PPCT is firstly used as a substrate. Typically, 1 ml of HCl solution (1M) and 10  $\mu\text{l}$  of PY monomer are added into 1.5 ml of PPCT, followed by adding APS. Then, the resulted black PPY film (Figure 1a and Figure S1a) on the inwall of PPCT, is redoped by TA and allowed to adsorb THPC-Au seeds ( $\sim 5\text{ nm}$ , Figure S1b). Later,  $\text{HAuCl}_4$  and AA are added as reaction agents to carry out the seed-mediated growth. After 30 min, PPCT is opened with a scissors and its inside morphology is firstly observed by an optical microscope. As shown in Figure 1b, golden shine is obvious, indicating the formation of uniform Au film on the surface PPY. A further insight into the morphology of this Au film is from SEM images (Figure 1c and 1d). It can be clearly seen that the film is mainly made of interconnected ligaments and pores, and thus displays nanoporous characterization. The size of ligament and pore in that NPG film is about 30-60 nm and 10-30 nm, respectively. The thickness of NPG film is estimated about 90 nm from the cross-sectional image (Figure S2). Owing to the nanoporous structure, the film exhibits  $6.1\text{ m}^2/\text{g}$  of BET surface area by nitrogen adsorption measurement (Figure S3), which is 1.5 times higher than that ( $4.0\text{ m}^2/\text{g}$ ) of the typical NPG material prepared from dealloy method<sup>12</sup>. By increasing the size of tube, NPG film with large area can also be obtained

according to our experimental results. Moreover, NPG film can grow on other matrixes such as universal or conductive glass (Figure S4) very facilely from the same seed-mediated growth.

To understand the formation of NPG film on PPY, the evolution of morphology with time has been investigated firstly. Figure 2a clearly shows that Au seeds begin to grow and become large after 2 min of reaction. About 8 min, some interconnected structures are observed. With the increase of reaction time, those structures continue to grow (Figure 2b) and finally result in cross-linking and nanoporous thin film at 12 min (Figure 2c). Considering that acids could assist with the formation of noble metal nanostructure<sup>16</sup>, we also carry out the reactions by using different acids containing –SH as doped agents. As shown in Figure 2d and 2e, gold particles film is produced when TA is replaced by 4-MPBA and 4-MBA, respectively. However, when MPA is empolyed, the interconnected structures are also found although they are not perfect (Figure 2f). Those indicate that aliphatic acid may benefit the crosslinked structure and the explanation will be given later.

Based on those experimental results, the formation process of thin NPG film (Figure 3) on PPY is proposed and mainly comprises two steps according to the seed-mediated growth descibed eleswhere<sup>17-19</sup>: (i) The adsorption of Au-HTPC seeds on the PPY film. When PPY-doped with TA is immersed in Au-THPC seeds solution, electronic attractions<sup>20</sup> (Au-THPC NPs is negative and PPY chains is positive) and hydrogen bonding<sup>21</sup> among them (Au-THPC NPs provide many oxygen atoms and the PPY macromolecules contain lots of hydrogen atoms) would happen. Moreover, TA can also interact with Au-THPC NPs by Au-S bond. Those promote lots of Au seeds to be absorbed on the surface of PPY film; (ii) The

growth of Au-HTPC seeds to form thin NPG film. After the adsorption of Au-HTPC seeds on the PPY film is completed, the catalytic seeds growth may occur due to the Gibbs-Thomson equation once  $\text{HAuCl}_4$  and AA are added, which suggests a higher surface free energy involved for smaller nuclei<sup>22</sup>. When the aliphatic acid like TA and MPA is doped into PPY film, their flexible structures make them tend to lie on the surface of PPY film. Then, Au-HTPC seeds would prefer growing along the surface of PPY film to keep low surface energy due to the interaction of  $-\text{SH}$  and Au. With the increase in size during the growth process, Au nanoparticles begin to coalesce on the surface<sup>23</sup>, resulting in the interconnected structures and nanoporous morphology. This process could be like the modified silver-mirror reaction<sup>24,25</sup>. If the aromatic acid (4-MPBA or 4-MBA) is used as a doped acid, their conjugated and rigid structures make them upright, the isotropic growth of Au seeds happens. And thus lots of large and isolated Au nanoparticles instead of interconnected structures are obtained. Therefore, it could be concluded that both PPY film and the doped acid play important roles on the growth of NPG film. Because the NPG film is attached on the PPY, the strong interaction between them would happen, as can be detectable from the Raman signal (Figure S5). It is found that the intensities of several peaks related to PPY, are enhanced obviously (more than 10 times) after the formation of NPG film, implying the contribution of surface enhanced Raman scattering (SERS) effect of NPG film.

To investigate the catalytic activity of NPG film, the oxidation reaction of an organosilane is carried out on the film surface. In this case, PPCT containing NPG film can be directly acted as a catalytic reactor, showing great convenience. As shown in Tab.1, the yield of  $\text{Et}_3\text{SiOH}$  can get up to 93.6 % after 1 h of reaction at the presence of NPG film. For NPG foam catalysis obtained by dealloying Ag-Au

foil, the yield was 94 %<sup>26</sup> for 1 mg of catalysis at the same experimental conditions. To evaluate the superiority-inferiority fairly, we calculate the weight of NPG film ( $W_{\text{NPG film}}=0.51$  mg) inside the PPCT. It indicates that the activity of our NPG film catalyst is about 1.96 times higher than the aforesaid NPG foam. The highly catalytic activity may be ascribed to the large surface area and high mass diffusion rate between raw and catalyst. Moreover, the electrical interaction of PPY and Au film as shown in Figure S5, may also play an important role. Further discussion is needed and will be done in the future work. Very importantly, this film catalyst is attached on the inwall of reactor, therefore it can be reused very conveniently only by washing with excessive water. As shown in Tab.1, no obvious decrease of catalytic activity is found after 10 cycles, which implies that NPG film attaches on the inwall of reactor firmly and can be used as a recycled catalyst.

So far, the catalytic activity of NPG materials are exclusively reported on the oxidative reaction such as oxidation of CO, methanol, ammonia borane, organosilanes and so on<sup>3-5, 27,28</sup>. To explore its novel application, herein the as-prepared thin film is deliberately employed to catalyze hydrogenation reaction by selecting the reduction of *p*-nitrophenol by NaBH<sub>4</sub> as a model, which is also carried out in 1.5 ml of PPCT containing NPG film. As shown in Figure 4a, it can be seen that the absorption of *p*-nitrophenol at 400 nm decreases obviously within 8 min in the presence of NPG film. By comparison, we use PPCT inside only with PPY film to carry out that reaction, and the result shows that the reactions does not occur even for lasting 5 h. Since the BH<sub>4</sub><sup>-</sup> concentration remains essentially constant throughout the reaction due to the excessive NaBH<sub>4</sub>, it is suggested that two principal species, *p*-nitrophenol and *p*-aminophenol influence the reaction

kinetics<sup>29</sup>. Therefore, in this case, pseudo-first-order kinetics could be applied for the evaluation of rate constant. In Figure 4b, The linear relation of  $\ln A$  versus time is observed, indicating that the reaction follows first-order kinetics. The rate constant ( $K_{app}=3.58 \times 10^{-1} \text{ min}^{-1}$ ) and activity factor ( $k=11.6 \text{ g}^{-1} \text{ s}^{-1}$ , the ratio of rate constant  $K_{app}$  to the total weight of the catalyst  $W$ ) can be estimated from the slope of straight line. The value of  $k$  is much higher than those of some supported Au catalysts<sup>30, 31</sup> and indicates highly catalytic activity of NPG film towards hydrogenation reaction.

For comparison with some reported NPG catalysis, the present NPG film has at least three advantages. (i) High cost-efficiency. Take the aforementioned reactor as an exmple, the area and weight of NPG film is about  $5.08 \text{ cm}^2$  (Figure S6) and  $0.51 \text{ mg}$ , respectively. Therefore, the Au amout ( $C_{Au}$ ) is estimated to be about  $0.104 \text{ mg/cm}^2$  according to our caculation. This value amounts to the ideal value ( $0.1 \text{ mg/ cm}^2$ ), which makes that that film can be accepted for the practical catalytic reaction. (ii) Adjustable substrates. Besides plastic matrixs, pyrrole can be easily polymerized on other kinds of substrates which makes that NPG film can be supported on different matrix facilely and used according to the practical need. For example, if for electrocatalytic oxidation, those thin films could be fabricated on ITO glass to carry out the reactions. (iii) Easy and convenient operation. The preparation of NPG film does not need any other tedious melting and dealloying process. Also, the regeneration process could be simplified only by excessive water washing. Those advantages would make the NPG film useful for the pratical applications.

## Conclusions

In summary, we report an interesting finding that thin NPG film with

thickness of 90 nm can be prepared on various substrates to form a catalytic reactor conveniently by using a seed-mediated growth. Because of the nanoporous characterization, the film exhibits highly catalytic activity both for oxidative and hydrogenation reaction. Besides as a catalyst, it would be also found some other potential applications such as surface enhanced Raman scattering substrates, biosensors and so on due to the combination of several advantages (high cost-efficiency, adjustable substrates, easy and convenient preparation).

### Aknowlegements

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### References

- [1] Pedireddy, S.; Lee, H. K.; Tjiu, W. W.; Phang, I. Y.; Tan, H. R.; Chu, S. Q.; Troadec, C.; Ling, X.Y. One-step Synthesis of Zero-dimensional Hollow Nanoporous Gold Nanoparticles with Enhanced Methanol Electrooxidation Performance. *Nat. Comm.* **2014**, DOI: 10.1038/ncomms5947.
- [2] Fujita, T.; Guan, P.F.; McKenn, K.; Lang, X.Y.; Hirata, A.; Zhang, L.; Tokunag, T.; Arai, S.; Yamamoto, Y.; Tanak, N.; Ishikawa, Y.; Asao, N.; Yamamoto, Y. Atomic Origins of the High Catalytic Activity of Nanoporous Gold. *Nat. Mater.*, **2012**, *8*, 775-780.
- [3] Li, D.; Zhu, Y.; Wang, H.; Ding, Y. Nanoporous Gold as An Active Low Temperature Catalyst toward CO Oxidation in Hydrogen-rich Stream. *Sci. Rep.* **2013**, *3*, 3015-3020.
- [4] Nagle, L. C.; Rohan, J. F. Nanoporous Gold Catalyst for Direct Ammonia Borane

- Fuel Cells. *J. Electrochem. Soc.* **2011**, *158*, B772-B778.
- [5] X.Yan, F. Meng, Y. Xie, J. Liu, Y. Ding, Direct  $\text{N}_2\text{H}_4/\text{H}_2\text{O}_2$  Fuel Cells Powered by Nanoporous Gold Leaves. *Sci. Rep.* **2012**, *2*, 941-948.
- [6] J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, Evolution of Nanoporosity in Dealloying, *Nature* **2001**, *410*, 450-453.
- [7] G. W. Nyce, J. R. Hayes, A. V. Hamza, J. H. Satcher, Synthesis and Characterization of Hierarchical Porous Gold Materials. *Chem. Mater.* **2007**, *19*, 344-346.
- [8] M. Kim, G. H. Jeong, K. Y. Lee, K. Kwon, S. W. Han, Fabrication of Nanoporous Superstructures through Hierarchical Self-assembly of Nanoparticles. *J. Mater. Chem.* **2008**, *18*, 2208-2212.
- [9] K. Nishio, H. Masuda, Anodization of Gold in Oxalate Solution to Form a Nanoporous Black Film. *Angew. Chem. Int. Ed.* **2011**, *50*, 1603-1607.
- [10] Xia, H. B.; Ran, Y.; Li, H. S.; Tao, X. T.; Wang, D. Y. High Electrocatalytic Activity via Interfacial Self-Assembly and Overgrowth. *J. Mater. Chem. A*, **2013**, *1*, 4678-4686.
- [11] Q. F. Zhang, Y. K. Li, L. Zhang, L. Chen, Y. Liu, Y. Lu. Thin-sheet Microfibrillar-structured Nanoporous Gold/Al Fiber Catalysts for Oxidative Coupling of Methanol to Methyl Formate. *J. Catal.*, **2014**, *317*, 54-61
- [12] A. Wittstock, V. Zielasek, J. Biener, C. M. Friend, M. Bäumer, Nanoporous Gold Catalysts for Selective Gas-phase Oxidative Coupling of Methanol at Low Temperature. *Science* **2010**, *327*, 319-322
- [13] A. Wittstock, A. Wichmann, M. Bumer, Nanoporous Gold as a Platform for a Building Block Catalyst, *ACS Catal.* **2012**, *2*, 2199-2215.
- [14] X. M. Zhang, Y. Ding. Unsupported Nanoporous Gold for Heterogeneous

Catalysis, *Catal. Sci. Tech.*, **2013**, *3*, 2862.

[15] T. Pham, J.B. Jackson, N. J. Halas, T. R. Lee, Preparation and Characterization of Gold Nanoshells Coated with Self-Assembled Monolayers. *Langmuir*, 2012, *18*, 4915-4920.

[16] Li, S. W.; Xu, P.; Ren, Z. Q.; Zhang, B.; Du, Y. C.; Han, X. J.; Mack, N. H.; Wang, H. L. Fabrication of Thorny Au Nanostructures on Polyaniline Surfaces for Sensitive Surface-Enhanced Raman Spectroscopy. *ACS Appl. Mater. Interfaces*, **2013**, *5*, 49-53.

[17] Pham, T.; Jackson J. B.; Halas N. J.; Lee T. R. Preparation and Characterization of Gold Nanoshells Coated with Self-Assembled Monolayers. *Langmuir*, **2002**, *18*, 4915.

[18] He, J.T., Wang, Y.W., Y.H. Feng, Qi, X.Y., Zeng Z.Y., Liu, Q., Teo, W. S., Gan, C. L., Zhang, H.; Chen, H.Y. Forest of Gold Nanowires: A New Type of Nanocrystal Growth, 2013, *7*, 2733.

[19] Lim, B., Jiang, M.J.; Camargo, P.H.C.; Cho, E.C.; Tao, J.; Lu, X.M.; Zhu, Y.M.; Xia, Y.Y. Pd-Pt Bimetallic Nanodendrites with High Activity for Oxygen Reduction, *Science*, 2009, *6*, 1302.

[20] Qian, K.; Liu, H. L.; Yang, L. B.; Liu, J. H. Designing and Fabricating of Surface-enhanced Raman Scattering Substrate with High Density Hot Spots by Polyaniline Template-assisted Self-assembly, *Nanoscale*, **2012**, *4*, 6449-6454.

[21] Xia, Y.Y.; Li, T.J.; Ma, C.; Gao, C.; Chen, J. Au/montmorillonite/polyaniline Nanoflakes: Facile Fabrication by Self-assembly and Application as Catalyst. *RSC Adv.*, **2014**, *4*, 20516-20520.

[22] Jin, Y.D.; Kang, X.F.; Song, Y.H.; Zhang, B.L.; Cheng, G.J.; Dong, S.J. Controlled Nucleation and Growth of Surface-Confined Gold Nanoparticles on a

(3-aminopropyl)trimethoxysilane-Modified Glass Slide: A Strategy for SPR Substrates. *Analy. Chem.*, **2001**, *73*, 2843.

[23] Oldenburg, S.J.; Averitt R.D.; Westcott, S.L.; Halas N.J. Nanoengineering of optical resonances. *Chem. Phys. Lett.*, **1998**, *288*, 243.

[24] Huo, S.J.; Xue, X.K.; Li, Q.X.; Xu, S.F.; Cai, W.B. Seeded-Growth Approach to Fabrication of Silver Nanoparticle Films on Silicon for Electrochemical ATR Surface-Enhanced IR Absorption Spectroscopy. *J. Phys. Chem. B*, **2006**, *110*, 25721.

[25] Shen, L.Y.; Ji, J.; Shen, J.C. Silver Mirror Reaction as an Approach to Construct Superhydrophobic Surfaces with High Reflectivity. *Langmuir*, **2008**, *24*, 9962.

[26] Asao, N.; Ishikaw, Y.; Menggenbateer, N. H.; Yamamoto, Y.; Chen, M.W.; Zhang, W.; Inoue, A. Nanostructured Materials as Catalysts: Nanoporous-Gold-Catalyzed Oxidation of Organosilanes with Water. *Angew. Chem. Int. Ed.* **2010**, *49*, 10093-10095.

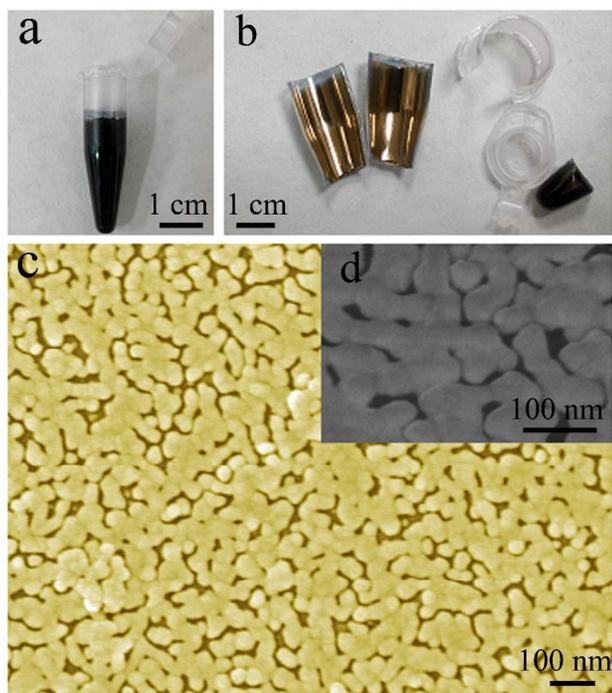
[27] Xu, C.X.; Su, J.X.; Xu, X.H.; Liu, P.P.; Zhao, H.J.; Tian, F.; Ding, Y. Low Temperature CO Oxidation over Unsupported Nanoporous Gold. *J. Am. Chem. Soc.*, **2007**, *129*, 42-43.

[28] Yan, M.; Jin, T.N.; Ishikawa, Y.; Minato, T.; Fujita, T.; Chen, L.Y.; Bao, M.; Asao, N.; Chen, M.W.; Yamamoto, Y. Nanoporous Gold Catalyst for Highly Selective Semihydrogenation of Alkynes: Remarkable Effect of Amine Additives. *J. Am. Chem. Soc.*, **2012**, *134*, 17536-17538.

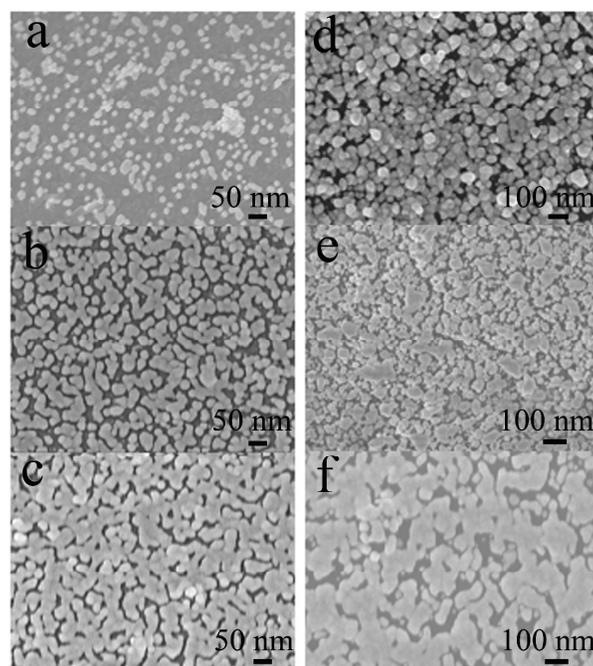
[29] Rashid, M. H.; Mandal, T. K. Templateless Synthesis of Polygonal Gold Nanoparticles: an Unsupported and Reusable Catalyst with Superior Activity, *Adv. Funct. Mater.* **2008**, *18*, 2261-2271.

[30] Kuroda, K.; Ishida, T.; Haruta, M. Reduction of 4- nitrophenol to 4-aminophenol over Au NPs Deposited on PMMA, *J. Mol. Catal. A: Chem.*, **2009**, *298*, 7-11.

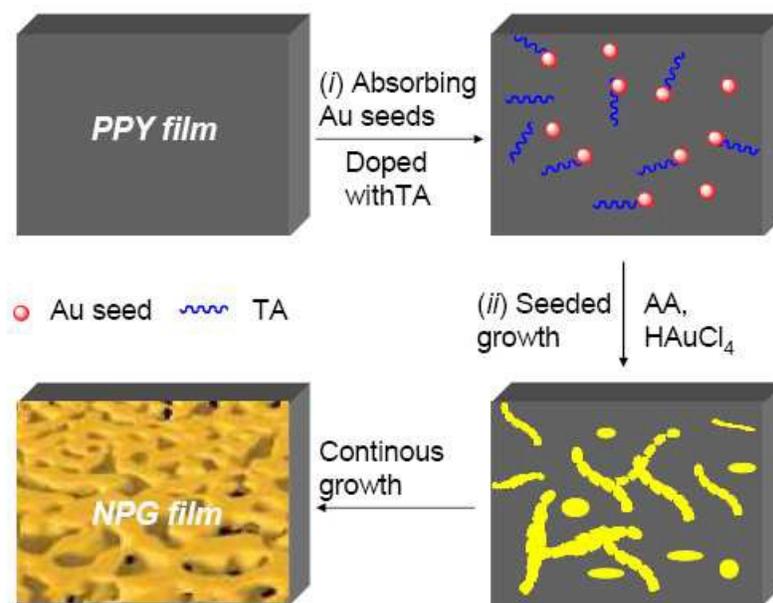
[31] Mdrashid, H.; Bhattacharjee, R. R.; Kotal, A.; Mandal, T. K. Synthesis of Spongy Gold Nanocrystals with Pronounced Catalytic Activities, *Langmuir*, **2006**, *22*, 7141-7143.



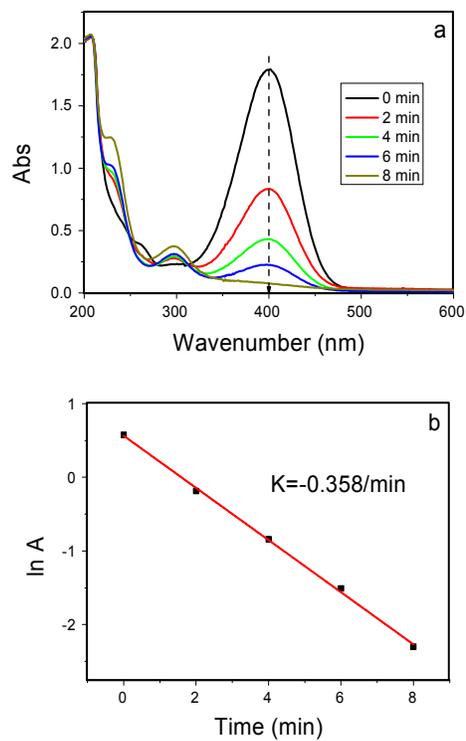
**Figure 1.** The appearances of PPCT with PPY film on its inwall (a) and thin NPG film (b, c, d, e) which grows on the PPY film.



**Figure 2.** The effects of time (a, b, c) and doped acid (d, e, f) on the evolution of NPG morphology. (a) 2 min; (b) 8 min; (c) 12 min; (d) 4-MPBA; (e) 4-MBA; MPA.



**Figure 3.** The formation demonstration of thin NPG film on PPY



**Figure 4.** Catalytic activity of NPG film catalyst. (a) Time-dependent UV-vis spectral changes of the catalyzed system; (b) Plot of  $\ln A$  versus time.

**Graphic abstract**

Thin NPG film with thickness of 90 nm can be prepared on various substrates to form a catalytic reactor conveniently by using a seed-mediated growth. Because of the nanoporous characterization, the film exhibits highly catalytic activity both for oxidative and hydrogenation reaction. The high cost-efficiency, adjustable substrates, easy and convenient operation would make the film reactor useful for practical applications.

