Supporting Information

Facile synthesis of functional bismuth-amino acid coordination polymer nano-structures

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Experimental Section:

1) Synthesis

In a typical synthesis, 9 mmol L-asparagine was dissolved in 20 ml deionized water at 40-45 ^{o}C. Then 2 mmol bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$) was added into the L-asparagine solution under stirring to obtain a transparent solution.

For the synthesis of BACP-1, the above transparent solution was left in a refrigerator at 10 ^{o}C for 12 days. The white precipitate was filtered and washed with deionized water and ethanol thoroughly. The yield of the product was 29%.

For the synthesis of BACP-2, the above transparent solution was transferred to a sealed conical beaker and was left in an oven at 80 ^{o}C for 24 h. Then the reaction mixture was cooled to room temperature, and the white precipitate was collected by centrifugation and washed with deionized water and ethanol thoroughly. The yield of the product was 25%.

For the synthesis of BACP-3, the above transparent solution was transferred to a Teflon-lined autoclave, sealed and hydrothermal treated in an oven at 160 ^{o}C for 24 h. The monolithic product was collected by filtration and washed with deionized water and ethanol thoroughly. The yield of the product was 26%.

For the preparation of Au@BACP-2, 0.2 g as-synthesized BACP-2 were immersed into 50 mL aqueous $HAuCl_4$ solution of desired concentration (corresponding to 1%wt of Au loading) and stirred at room temperature for 24 h. The resulted purple precipitate was filtered and washed with distilled water for several times. The sample was dried at 60 ^{o}C to obtain purple powder.

For the preparation of Pd(II)@BACP-2, 0.2 g as-synthesized BACP-2 was immersed into 50 mL aqueous H_2PdCl_4 solution of desired concentration (corresponding to 1%wt of Pd loading) and stirred at room temperature for 24 h. The resulted precipitate was filtered and washed with distilled water for several times. Without further reduction, the obtained precipitate was dried at 60 ^{o}C to obtain white powder

2) Suzuki reaction tests

To a screw-capped vial with a side tube were added 1 mmol of p-bromoacetophenone, 1.5 mmol of benzeneboronic acid, 3 mmol of K_2CO_3, 3 mL of ethanol, 2 mL of water and 0.05 g 1% Pd(II)@BACP-2. The mixture was degassed under nitrogen purge for 10 min at 0 ^{o}C. Subsequently, the vial content was placed in a preheated oil bath at a given temperature by and magnetically

stirred under nitrogen for a given time. After the reaction was completed, the reaction mixture was cooled to room temperature. The catalytic activity was assessed using HPLC analysis of the product yield.

3) Cell Viability assay

An MTT assay was used to determine the biocompatibility of the material. It is a useful method for evaluating the cytotoxicity of a material, owing to its simplicity, speed and precision. The cytotoxicity of BACP-2 was assessed by 3-(4,5-dimethylthiazol-2-yl)-2,5-biphenyltetrazolium bromide (MTT) viability assay. 3T3 cells were grown routinely in DMEM supplemented with 10% FBS and were maintained in a humid CO_2 incubator. For cytotoxicity assays, 3T3 cells were cultured (2000 cells per well) on 96-well plates for 24 h. Different concentrations of asparagine and BACP-2 were separately loaded into the 96-well plates. 3T3 cells cultured in the absence of above three solutions acted as controls. After being cultured for 24 h and 48 h separately, 10 μL MTT reagents was added to each well and incubated for 4h until a purple precipitate was visible. 100 μl DMSO was then added to each well and left in the dark at room temperature for 20 min. The absorbance of the resulting formazan solution was recorded at 570 nm with a Microplate System (Bio-Rad, USA).

4) FDA/PI staining

Cell viability was determined by Fluorescein Diacetate/ Propidium Iodide (FDA/PI) staining. FDA working solution (5 μg/mL) and PI working solution (100 μg/ml) were prepared freshly before use, then 300 μL FDA solution was added into each well, and cells were incubated at 37 ^{o}C for 5 min. Suck out the FDA solution and wash with PBS for two times, then add 300 μL PI solution and also incubated at 37 ^{o}C for 5 min. Photomicrographs were taken under fluorescence from three fields of each sample. The number of live (FDA-labeled) or dead (PI-labeled) cells were counted using Image Pro Plus software (Media Cybernetics, Bethesda, MI). The experiment was repeated three times.

5) Assessment of the digestion of pepsin on bull serum albumin by sodium dodecylsulfate-polyacrylamide gel electrophoresis (SDS-PAGE)

Electrophoresis of proteins was performed using regular SDS-PAGE (Bio-Rad, Hercules, CA) with 15% separating and 5% stacking gels. 10 μL of samples were added into 15% acrylamide (Sigma) gel for 1h at 150 V using a small electrophoresis chamber. In each gel a wide range

molecular weight marker (Sigma) was included. Proteins were stained with Coomasie Brilliant Blue R-250.

Based on tests with different loadings (Fig. A), best result was obtained when the ratio of pepsin and BSA was between 1:100 and 1:250 (w/w), heavier loadings resulted in overlapping, broad band, so we chose the 1:150 as the experimental concentration[1].

1 D. Dhara and P. R. Chatterji, *J. Phys. Chem. B,* 1999, **103**, 8458

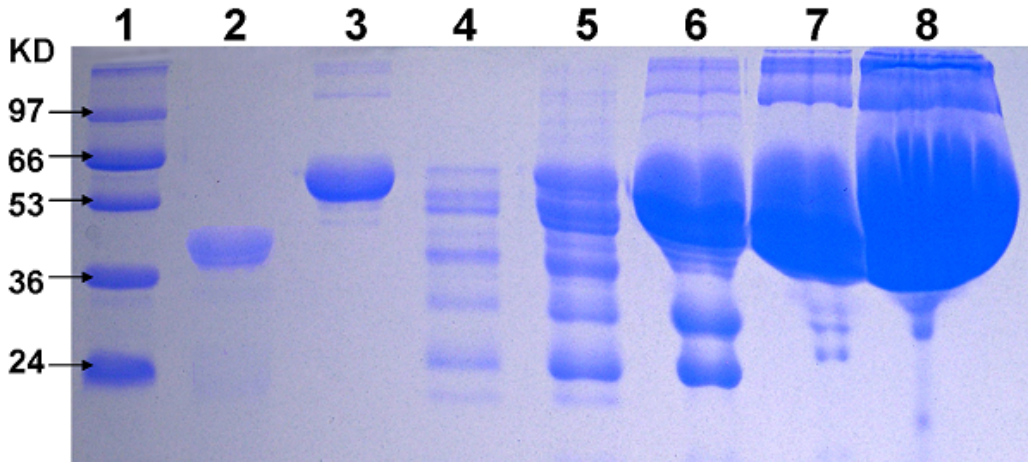


Figure A. The digestion of pepsin on different concentrations of bull serum albumin (BSA), separated by a 15% SDS-PAGE gel. The amounts in each wells are as follows: lane 1, protein molecular weight marker; lane 2, 4mg/ml pepsin; lane 3, 0.5mg/ml BSA; lane 4-8, pepsin:BSA (w/w) was 1:25, 1:100, 1:250, 1:500, 1:1000, respectively.

6）DiO staining

3,3’-dioctadecyloxacarbocyanine perchlorate (DiO) was one of the most common membrane fluorescent probes, which exhibited green fluorescence. The cells were cultured in DMEM supplemented with 10% FBS for 24 h as normal, then the DMEM was replaced by new DMEM containing different concentrations of Asn (0, 50,100,200 μg/mL). After 24 h, the cells were fixed by 4% paraformaldehyde for 10 min and then stained by 10 μg/mL DiO for 20 min. The results were observed under fluorescence microscope.

7) Characterization

The powder X-ray diffraction (XRD) patterns of the samples were measured on Bruker D8 Focus using CuKα (λ=0.1541 nm) radiation. Scanning electron microscopy (SEM) was measured

on Shimadzu SS-550 scanning electron microscope. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and selected-area electron diffraction (SAED) characterizations were carried out on a Philips Tecnai F20 instrument working at 200 kV. XPS spectra were obtained with a Kratos Axis Ultra DLD spectrometer. The thermogravimetry and differential thermal analysis (TG-DTA) of the samples were performed on a Rigaku TG-DTA thermal analyzer at a linear heating rate of 20 °C/min, and α-Al2O3 was used as a reference. Nitrogen adsorption and desorption isotherms were measured on a BELSORP-mini II sorption analyzer at 77 K. Specific surface area was calculated by BET (Brunauer-Emmett-Teller) method. UV-vis diffuse reflectance spectrums (DRS) of the samples were measured by using a Shimadu UV-2450 UV-vis spectrophotometer using an integrating sphere accessory. HPLC measurements were conducted on a LC-20AT equipped with a SPD-20A UV detector in which the absorbance was monitored at 254 nm. The separation was carried out on a reversed-phase packed column (250 mm×4.6 mm) using a 70:30 acetonitrile-water mixture and a flow rate of 1 mL/min.

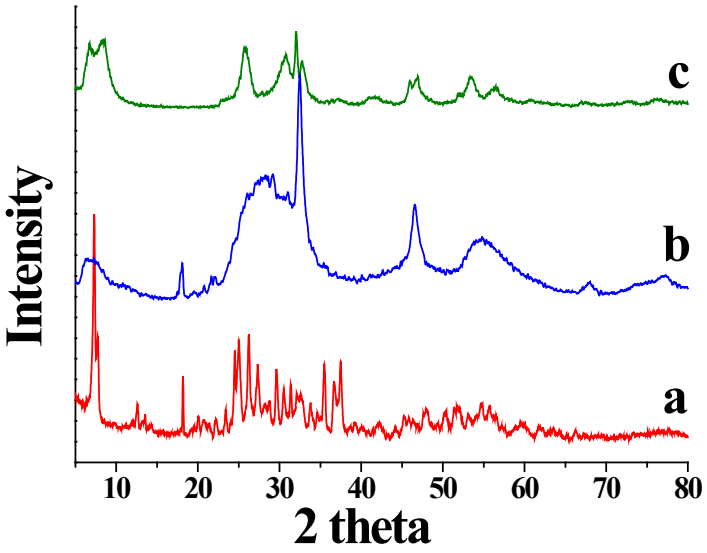


Figure S1. XRD patterns of the as-synthesized bismuth-asparagine coordination polymer (a) BACP-1, (b) BACP-2, (c) BACP-3.

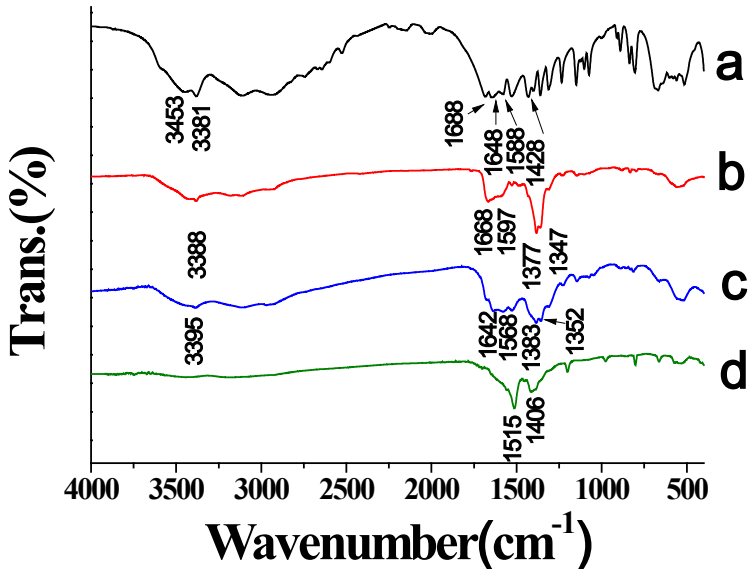


Figure S2. The FT-IR spectra of (a) pure L-asparagine, (b) BACP-1, (c) BACP-2 and (d) BACP-3.

Table S1. Assignments of peaks in the FT-IR spectra of of L-asparagine and BACPs.

Sample	Wavenumbers/cm^{-1}	Functional group assignment
L-Asparagine	3453	-OH (crystal water) stretching [1]
	3381	$-NH_2$ ($CONH_2$) stretching [1]
	1682	-C=O($CONH_2$) stretching [2,3]
	1644	NH_3^+(protonated α-amino) asymmetric deformation [2,4]
	1578	COO^- asymmetric stretching[5]
	1431	$-CH_2$-deformation [5]
	1400	-CH- in-plan bending [5]
	1359	
BACP-1	1666	NH_3^+ asymmetric deformation
	159	COO^- asymmetric stretching and
	1382	-CH- in-plan bending
	1360	
BACP-2	1667	NH_3^+ asymmetric deformation
	1577	COO^- asymmetric stretching and
	1384	-CH- in-plan bending
	1357	

[1] G. T. G. Giulio, D. Luigi, Thermochimica Acta, 1998, 311,129.

[2] S. Y. Venyaminov, N. N. Kalnin, Biopolymers, 1990, 30, 1259.

[3] K. Nomiya, H. Yokoyama, J. Chem. Soc., Dalton Trans., 2002, 2483.

[4] S. Ramaswamy, M. Umadevi, R. K. Rajaram, V. Ramakrishnan, J. Raman Spectroscopy, 2003, 34, 806.

[5] E. Podstawka, M. S´wiatłowska, E. Borowiec, L. M. Proniewicz, J. Raman Spectroscopy, 2007, 38, 356.

In the IR spectrum of the coordination polymers, the subtle bands of free amino acids from 1800 cm^{-1} to 1300 cm^{-1} disappeared while there display much broader and sharper bands, which is due to the coordination effect with Bi^{3+} ions.

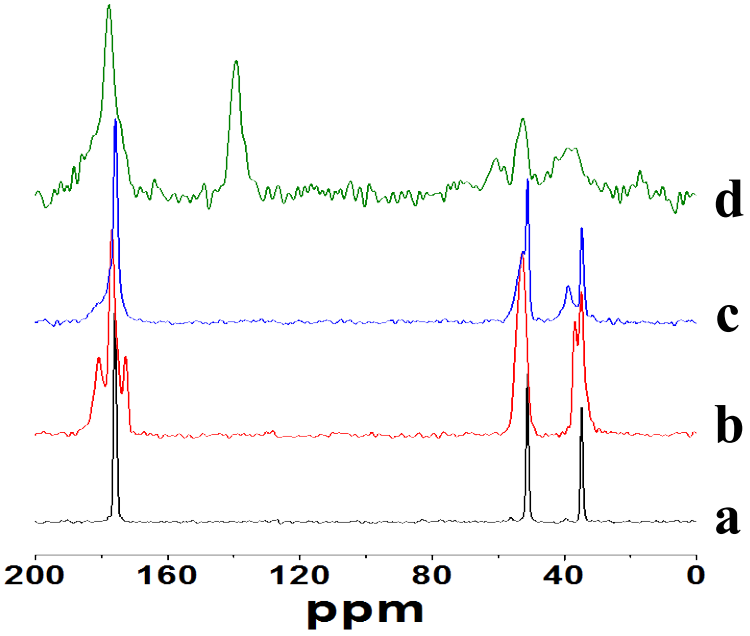


Figure S3. Solid state ^{13}C CP/MAS NMR spectra of (a) pure L-asparagine and (b) BACP-1, (c) BACP-2, (d) BACP-3.

Three sharp and intensive signals appear in the solid state ^{13}C CP/MAS NMR spectrum of pure L-asparagine. The 35 and 52 ppm signals could be assigned to CH_2 and CH, respectively. The low-field peaks at around 176 ppm could be ascribed to carboxyl/carbonyl.

a **b** **c**

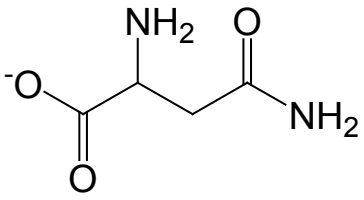
Figure S4. N1s XPS spectrum of BACPs: (a) BACP-1, (b) BACP-2, (c) BACP-3

Sample	α-amino group	Amide group	NO_3^-
BACP-1	399.2 eV	401.1 eV	406.3 eV
BACP-2	399.3 eV	401.2 eV	406.3 eV
BACP-3	399.5 eV	401.1 eV	406.3 eV

Table S2. The Elementary Analysis (EA) results of BACPs.

samples	Elemental	EA results	Thero. cal.	Chemical Formular
BACP-1	C	8.67	8.40	$Bi_3(NO_3)_3(Asn)_2(OH)_4$
	N	8.54	8.57	
	H	1.79	1.57	
BACP-2	C	15.01	14.94	$Bi_3NO_3(Asn)_4(OH)_4$
	N	9.19	9.80	
	H	3.01	2.80	

With the values of the weight of each element form EA, total amount of amino acid and nitrate radical can be calculated. Then the average molar ratio of amino acid/Bi^{3+} can be calculated.

Asn:  M=131

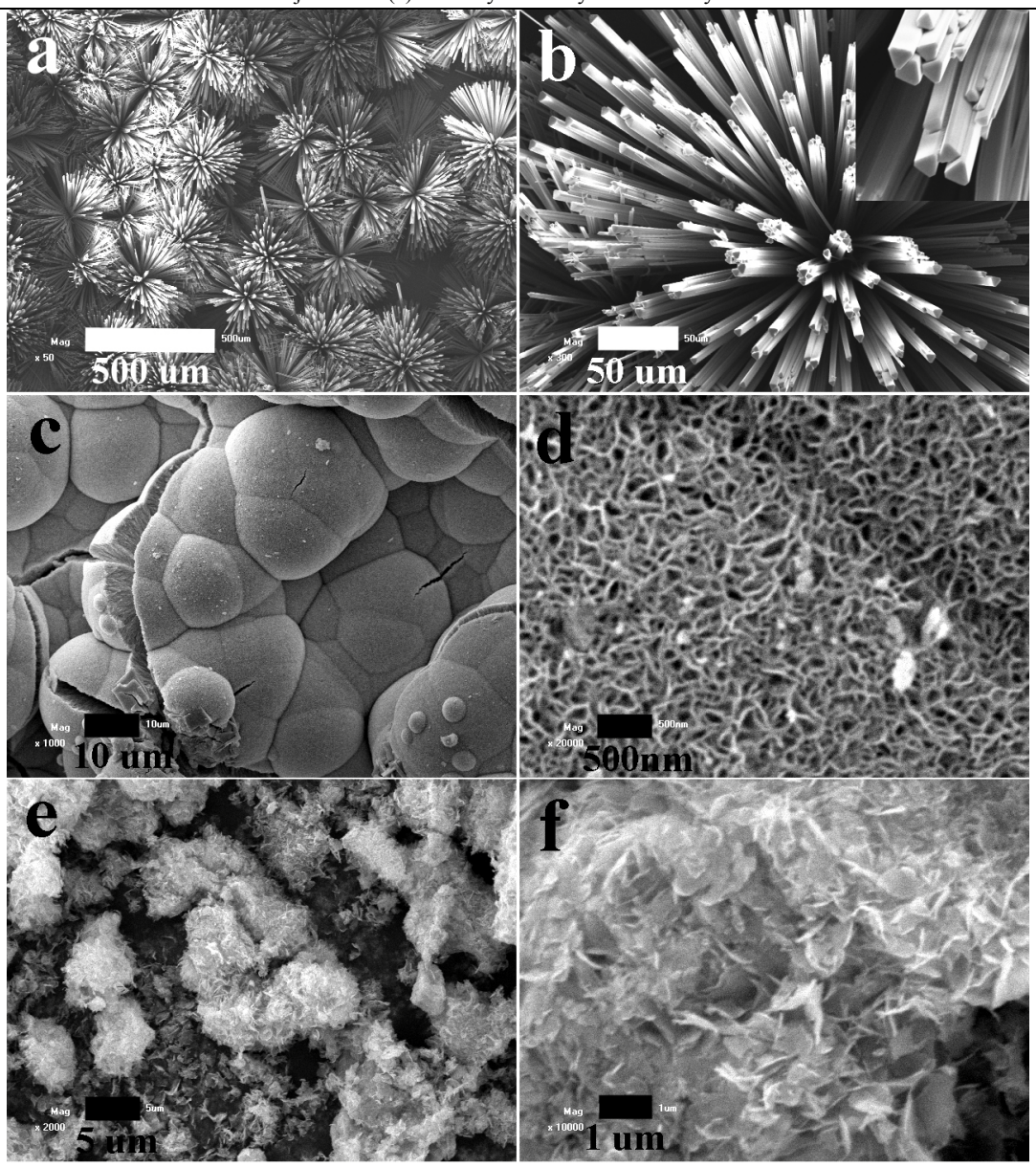


Figure S5. SEM images of (a and b) BACP-1', (c and d) BACP-2', (e and f) BACP-3'

Figure S5a and 5b show SEM images of BACP1' that a large quantity of uniform beautiful core-removed dandelion-like flower architectures assembled from much bigger well aligned 1D needle shaped crystallite were generated if the initial molar ratio of asparagine to bismuth was settled at 6:2. As the temperature of the reaction increased to 80 ^{o}C, the top view (Fig. S5c) shows the formation of micrometer-sized lumps ramblingly aggregated together. At higher magnification the lumps are covered by densely longitudinally packed BACP2' nanoplates, the thickness of the nanoplates are uniform with average value of ~30nm. When the reaction was proceded at 160 ^{o}C for 24 h, the resultant BACP3' nanostrucures become more discrete, they are composed of ultrathin nanoplates.

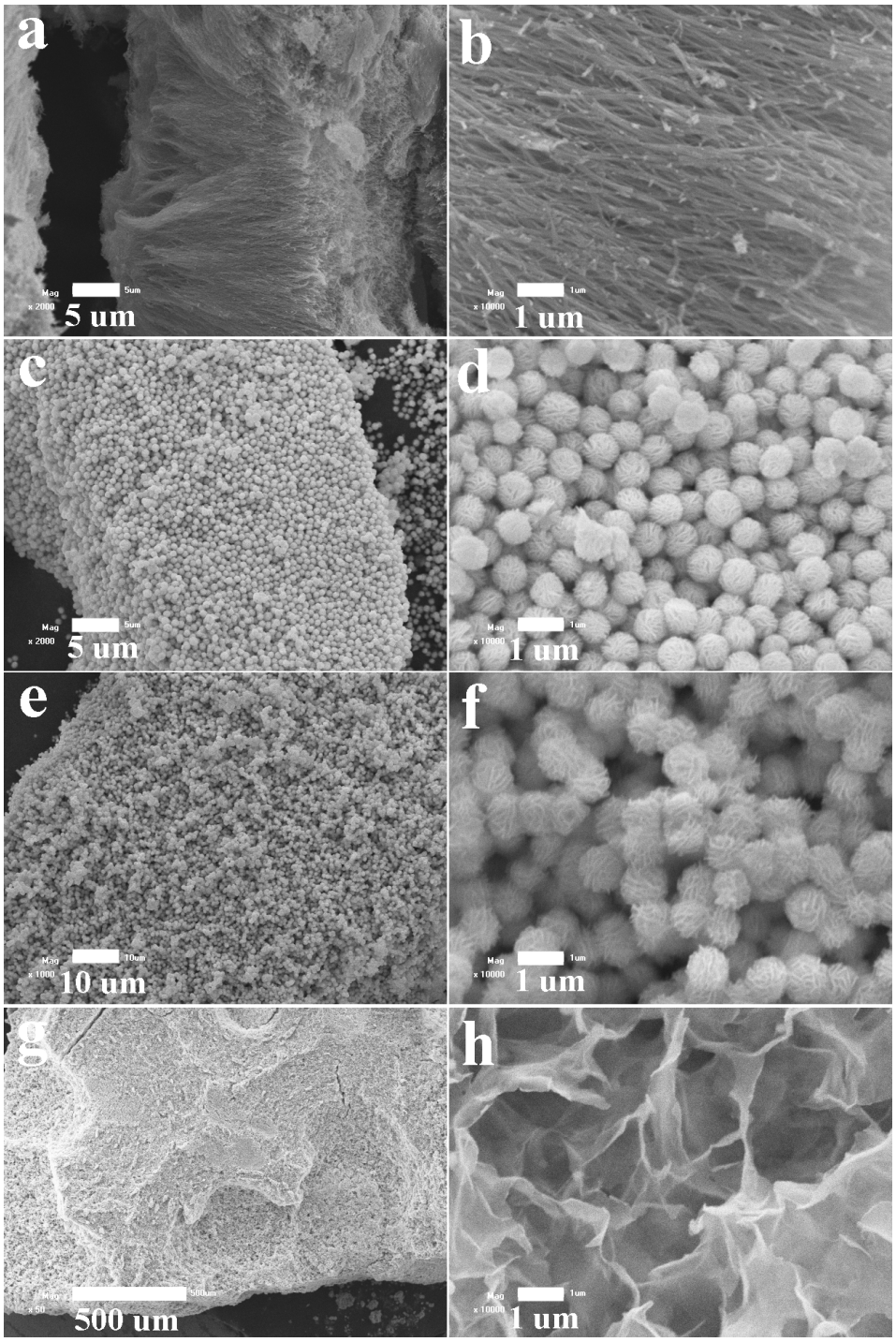


Figure S6. SEM images of BACPs synthesized at different temperature for 7 days. (a and b) 10 ^{o}C, (c and d) 80 ^{o}C, (e and f) 120 ^{o}C, (g, h) 160 ^{o}C. The initial molar ratio of the reaction solution is same to that of BACP-1. The results indicate that the reaction temperature is important to control the morphology of the BACPS.

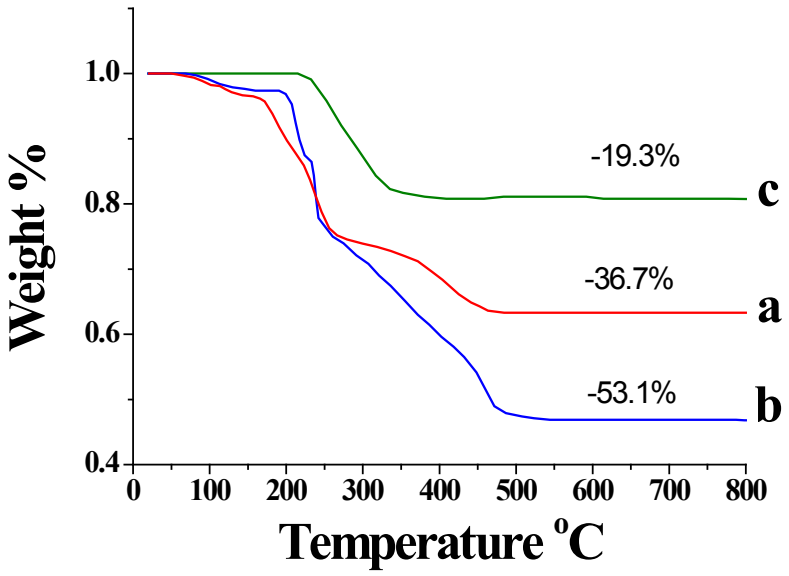


Figure S7. TGA of BACPs: (a) BACP-1, (b) BACP-2, (c) BACP-3

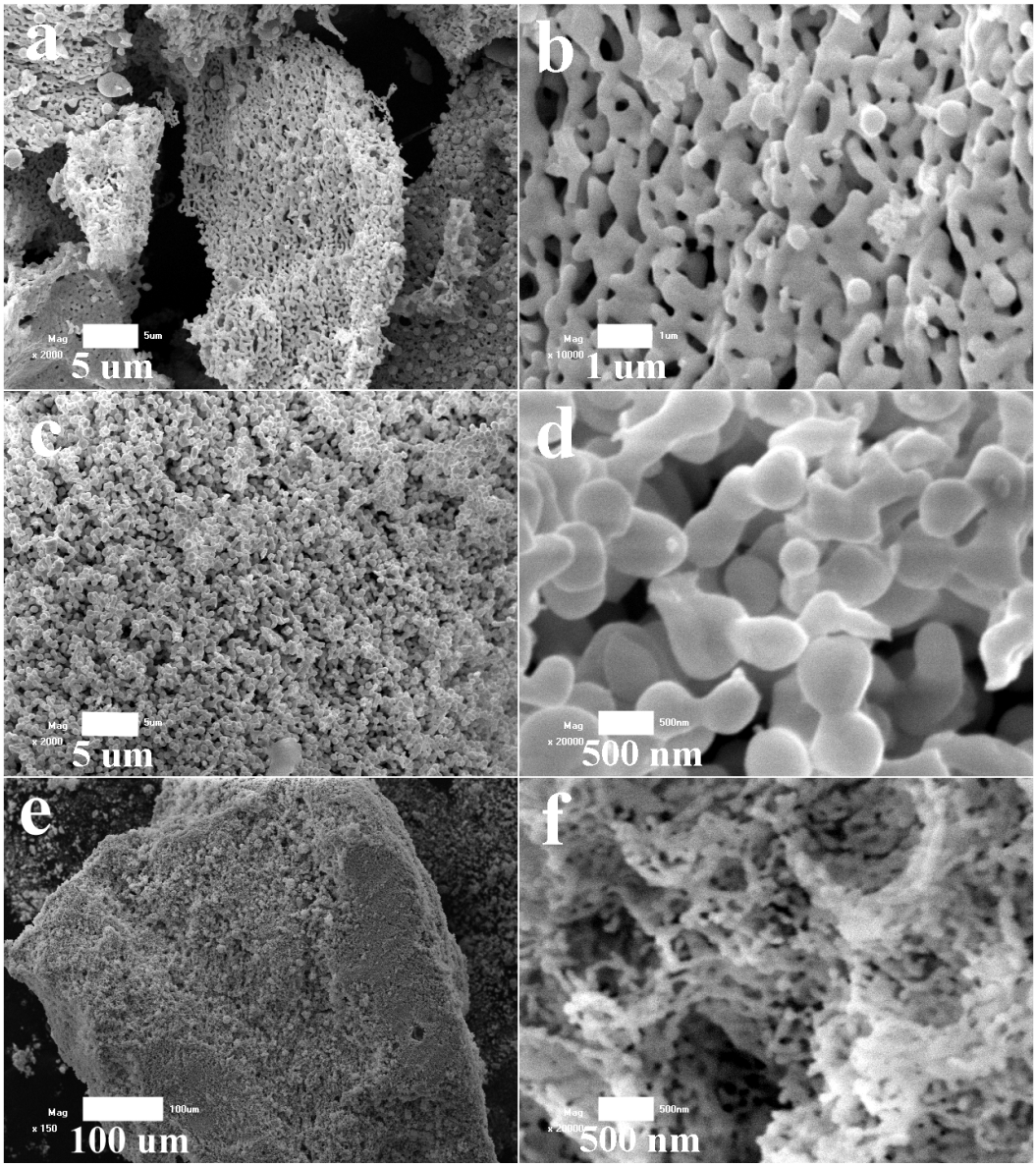


Figure S8. SEM images of the oxides obtained by calcinations, (a and b) BACP-1C, (c and d) BACP-2C, (e and f) BACP-3C

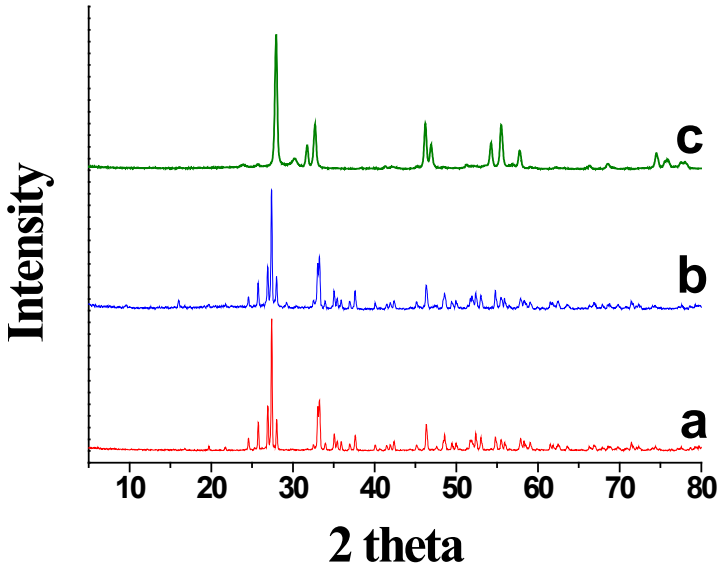


Figure S9. XRD patterns of the oxides obtained by calcinations, (a) BACP-1C, (b) BACP-2C, (c) BACP-3C

Sample	Calcination	Crystal phase
BACP-1C	475 ^{o}C 3h	Monoclinic α-Bi_2O_3
BACP-2C	475 ^{o}C 3h	Monoclinic α-Bi_2O_3
BACP-3C	275 ^{o}C 5h	Tetragonal β-Bi_2O_3

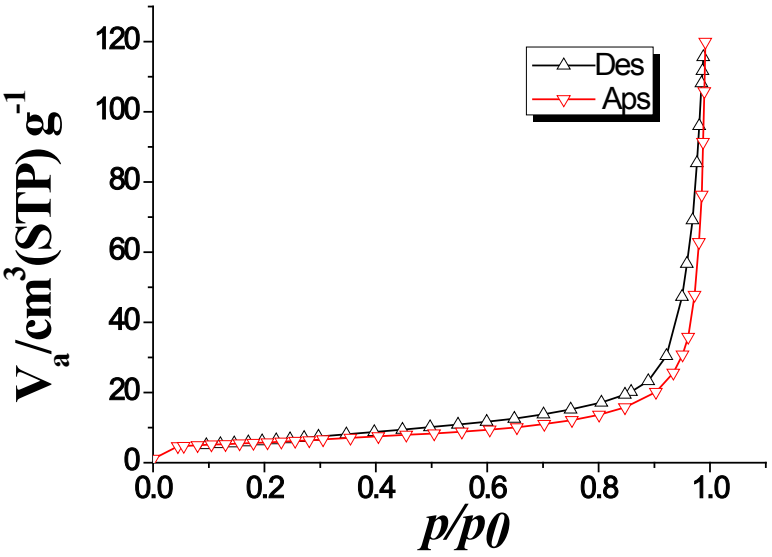


Figure S10. N_2 adsorption-desorption isotherms of BACP-3C.

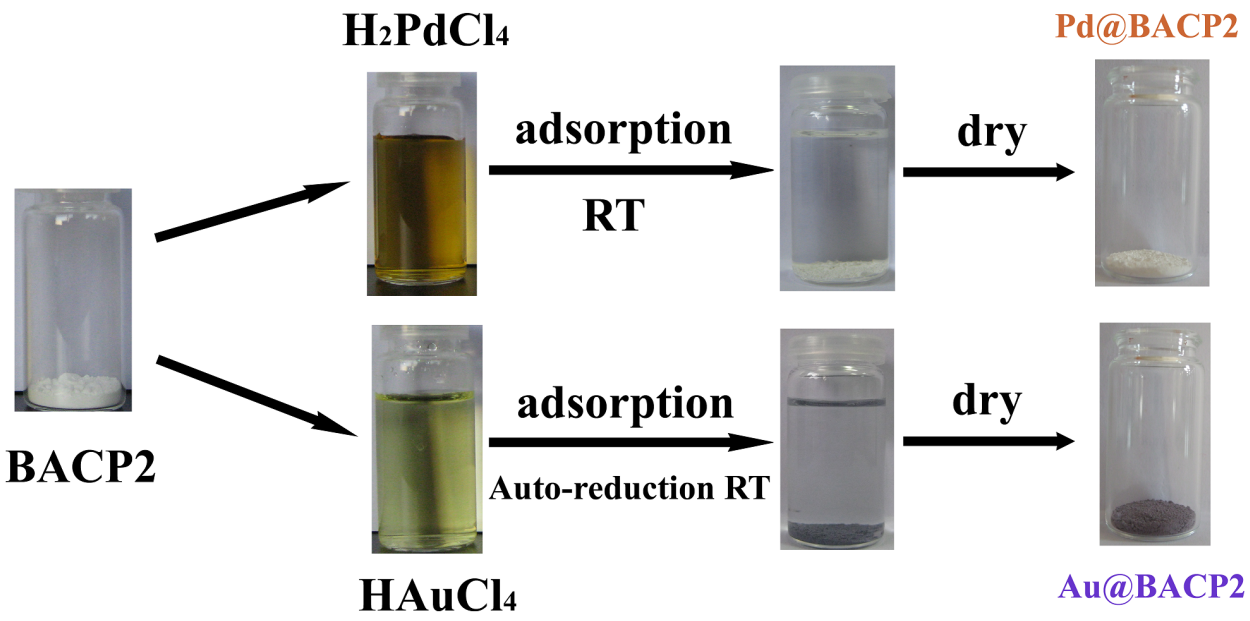


Figure S11. Photographs of preparation procedure of BACP-2 supported noble metal catalysts.

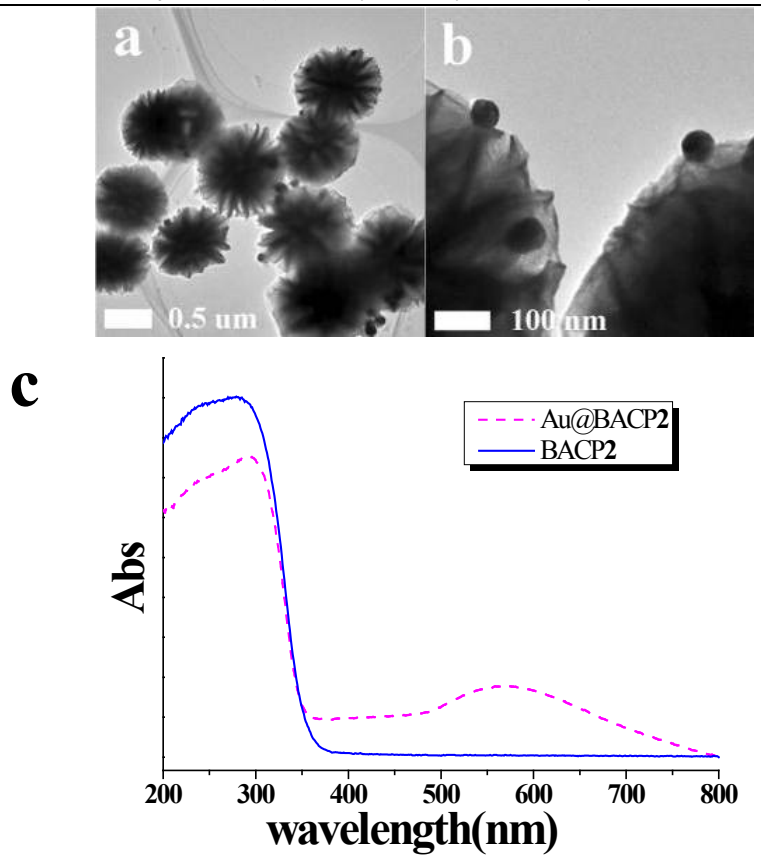
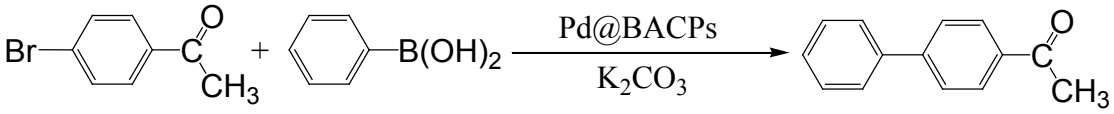


Figure S12. (a and b) TEM images of BACP-2 decorated by gold nanoparticles Au@BACP-2, (c) UV-vis spectra of BACP-2 and Au modified BACP-2

Figure S13. (a) Pd 3d XPS spectra of 1%Pd@BACP-2, (b), Au4f XPS spectra of 1%Au@BACP-2. The peaks at 83.7 eV ($Au4f_{7/2}$) and 87.4 eV ($Au4f_{5/2}$) were assigned to Au^0, which were due to the auto-reduction of $AuCl_4^-$ in the presence of BACP-2**.** The shoulder at 84.9 eV ($Au4f_{7/2}$) and 88.5 eV ($Au4f_{5/2}$) were ascribed to the Au^{3+}.

Table S3. The Suzuki reactions via the 1%Pd@BACPs in the solvent mixture of H_2O and EtOH (2:3 by volume)



Catalyst	T/°C	Time/h	Yield(%)
BACP-2	80	1	0
Pd@BACP-2	30	1	0
Pd@BACP-1	80	1	95
Pd@BACP-2	80	1	100
Pd@BACP-3	80	1	96

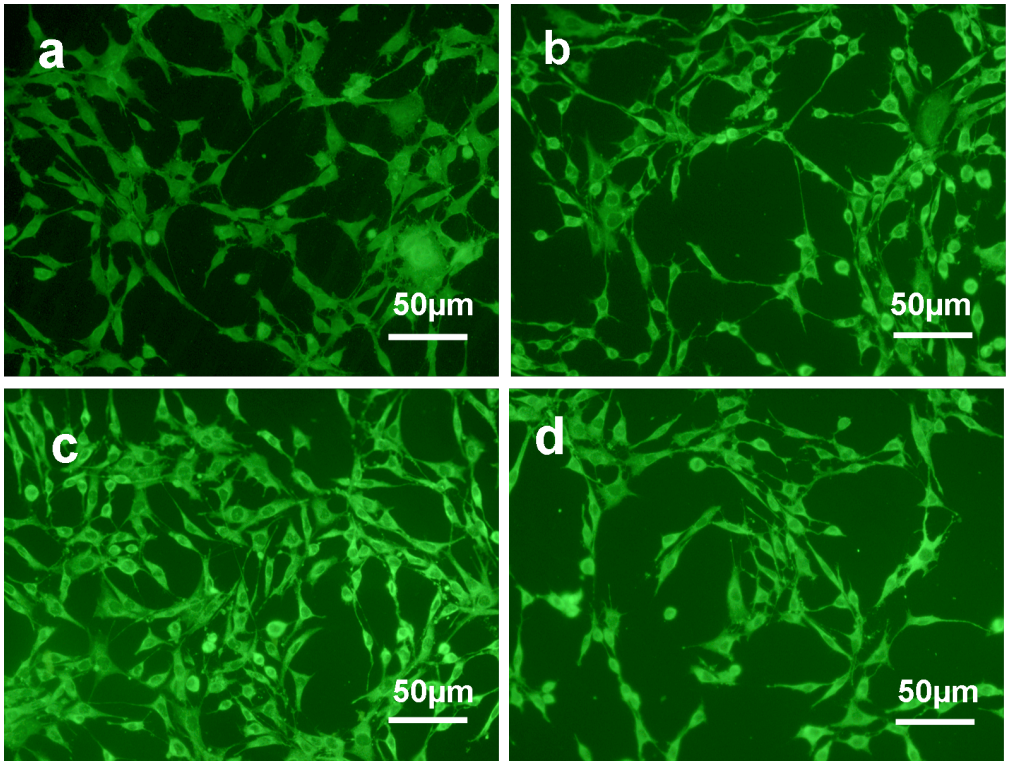


Fig.S14. Morphology of the cells after incubating with different concentrations of asparagine for 24 h, as observed by DiO staining. (a) control, (b) 50 μg/mL, (c) 100 μg/mL and (d), 200 μg/mL asparagine.