Supporting Information

Smart Nanocatalysts with Streamline Shapes

Guowu Zhan and Hua Chun Zeng*

Department of Chemical and Biomolecular Engineering, Faculty of Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

*Email: chezhc@nus.edu.sg

Table of Contents

Experimental Section
Experimental Details .............................................................. 4

Supporting Tables

Table S1. Comparison of specific surface areas of different geometrical bodies .................................................. 10
Table S2. Summary of the templates and catalysts prepared in this work ......................................................... 11
Table S3. Investigated combinations of M_A and M_B in M_A@TCOS@M_B catalysts in this work ..................... 12
Table S4. Catalytic oxidation of aromatic alcohols catalyzed by M_A@TCOS@M_B ........................................... 59
Table S5. Catalytic oxidation of benzyl alcohol by M_A@TCOS@M_B catalysts .................................................. 60
Table S6. Catalytic oxidation of 4-methoxybenzyl alcohol .............................................................................. 60
Table S7. Catalytic oxidation of 4-nitrobenzyl alcohol ....................................................................................... 60
Table S8. Catalytic oxidation of 4-methylbenzyl alcohol .................................................................................... 61
Table S9. Catalytic oxidation of cinnamyl alcohol .............................................................................................. 61
Table S10. Catalytic oxidation of 1-phenylethanol ............................................................................................ 61
Table S11. Catalytic oxidation of 3-phenyl-1-propanol ....................................................................................... 61

Supporting Figures

Figure S1. Velocity vector plots and pressure fields of catalyst objects with various geometric shapes. ......................... 7
Figure S2. Velocity vector plots (a-b and d-e) and pressure fields (c and f) of streamline catalyst objects with different directions of the fluid motion. (a-c) the fluid motion is from left to right; and (d-f) the fluid motion is from right to left ......................................................... 8
Figure S3. Wall shear stress fields of catalyst objects with (a) sphere and (b) streamline structure. Color-code in the figures is used to indicate the strength of the wall shear stress, and the unit is Pascal .............................................................. 9
Figure S4. Location illustration of the M_A and M_B components in the catalyst structures ................................ 13
Figure S5. (a-f) TEM images of spherical Cu_2O nanoparticles at different magnifications ............................. 14
Figure S6. (a-d) TEM images of Cu$_2$O@Au at different magnifications, (e) size distribution and statistical mean particle size of Cu$_2$O spheres, and (f) size distribution and statistical mean particle size of Au nanoparticles on the external surface of Cu$_2$O spheres........14
Figure S7. EDX elemental maps of core–satellite structure of Cu$_2$O@Au sample.........................15
Figure S8. (a-i) STEM dark field micrographs of Au@TCOS sample at different magnifications...16
Figure S9. (a-f) SEM images of Au@TCOS sample at different magnifications.......................17
Figure S10. (a-f) AFM images of Au@TCOS sample. ..........................................................18
Figure S11. EDX elemental maps of Au@TCOS sample......................................................19
Figure S12. EDX elemental maps of Au@TCOS sample......................................................19
Figure S13. EDX elemental maps of Au@TCOS sample..........................................................20
Figure S14. EDX elemental line scans on the head portion of a single Au@TCOS particle. The image is obtained by high-angle annular dark-field scanning TEM (HAADF-STEM). ............20
Figure S15. EDX spectrum taken on Au@TCOS sample..........................................................21
Figure S16. (a-c) The effect of MPTMS concentration on the product morphology of Au@TCOS. 22
Figure S17. (a-i) The effect of reaction temperature on the product morphology of Au@TCOS.....23
Figure S18. (a-f) The effect of reaction durations on the product morphology of Au@TCOS.........23
Figure S19. (a,b) XRD patterns of TCOS (i.e., Au@TCOS) and its comparative samples, and (c) schematic illustration of the bilayer structures of organosilica and COS (or TCOS), where copper ions are shown as small green beads, d indicates the nearest interlayer spacing in the bilayer structure, and x indicates alkylthiol or alkylthiolate chain packing distance within the layer.................................................................24
Figure S20. XPS of S 2p core levels for organosilica (left) and TCOS or COS (right)..................25
Figure S21. XPS (a) Au 4f, (b) Cu 2p, (c) Si 2p, and (d) S 2p core-level spectra of TCOS sample..26
Figure S22. XPS (a) Si 2p, and (b) S 2p core-level spectra of MPTMS.................................26
Figure S23. XPS (a) Cu 2p, (b) Au 4f, and (c) O 1s core-level spectra of Cu$_2$O@Au sample.....27
Figure S24. XPS (a) Cu 2p, (b) Si 2p, and (c) S 2p core-level spectra of COS...........................28
Figure S25. XPS (a) Si 2p, (b) O 1s, and (c) S 2p core-level spectra of the conventional organosilica. .........................................................................................................................29
Figure S26. (a-c) TEM and HRTEM (d-f) images of the head portion of TCOS at different magnifications.................................................................30
Figure S27. FTIR spectra of Cu$_2$O@Au template (1), TCOS (2), COS (3) and organosilica (4). ...31
Figure S28. $^{29}$Si MAS NMR spectra of different samples. Chemical shifts are given relative to tetramethylsilane at 0 ppm. .................................................................32
Figure S29. TG-differential thermal analysis (TG-DTA) curves for TCOS sample and 3D-FTIR spectra of the evolved gases during the thermogravimetry analysis.................................33
Figure S30. N$_2$ physisorption isotherms of different samples investigated in this work............34
Figure S31. Pore size distribution of TCOS sample based on nitrogen desorption isotherm.....34
Figure S32. (a-f) TEM images of Au@TCOS sample after hydrothermal treatment at 160°C for 24 h. .................................................................35
Figure S33. (a-f) TEM images of Au@TCOS sample after calcination treatment under static laboratory air at 500°C for 6 h.................................................................35
Figure S34. (a-f) TEM images of COS at different magnification. Bottom panel: a digital color photograph of COS sample.................................................................36
Figure S35. EDX elemental maps and EDX spectrum of COS sample....................................37
Figure S36. (a-f) TEM images of the conventional organosilica at different magnifications. Bottom panel: a digital color photograph of the conventional organosilica sample........................................38
Figure S37. EDX elemental maps and EDX spectrum of the conventional organosilica............39
Figure S38. (a-f) TEM images of cubic Cu$_2$O@Au (single-crystalline Cu$_2$O nanocubes with exclusively exposed {100} surface planes) at different magnifications.

Figure S39. (a-f) TEM images of Cu$_2$O@Au@organosilica composite at different magnifications.

Figure S40. (a-f) Typical TEM images of Cu$_2$O@Pd nanoparticles at different magnifications.

Figure S41. EDX elemental maps and EDX spectrum of Cu$_2$O@Pd nanoparticles.

Figure S42. (a-i) Typical TEM images of Cu$_2$O@Pt nanoparticles at different magnifications.

Figure S43. EDX elemental maps and EDX spectrum of the Cu$_2$O@Pt nanoparticles.

Figure S44. (a-f) TEM images of TCOS material prepared by using Cu$_2$O@Pd as a template.

Figure S45. HAADF-STEM image and EDX elemental maps of TCOS material prepared by using Cu$_2$O@Pd as a template/precursor.

Figure S46. (a-c) TEM and HAADF-STEM (d-f) images of TCOS, prepared by using Cu$_2$O@Pt as a template/precursor.

Figure S47. HAADF-STEM image and EDX elemental maps of TCOS prepared by using Cu$_2$O@Pt as a template/precursor.

Figure S48. (a-c) Time-dependent UV–Vis spectra of the reaction mixture of reduction of 4-nitrophenol, and (d) comparison of the reaction rates of different catalysts.

Figure S49. (a-c) Representative TEM images of the tail portion of Au@TCOS support.

Figure S50. (a-f) Characterizations of Au@TCOS@Au catalyst.

Figure S51. (a-f) Typical high resolution TEM images of Au@TCOS@Au catalyst.

Figure S52. (a-f) Characterizations of Au@TCOS@Pd catalyst.

Figure S53. (a-f) Characterizations of Au@TCOS@Ag catalyst.

Figure S54. (a-f) Characterizations of Au@TCOS@Pt catalyst.

Figure S55. (a-f) TEM images of Au@TCOS@Pd catalyst with a relatively high Pd loading amount.

Figure S56. HAADF-STEM image and EDX elemental maps of Au@TCOS@Pd catalyst with larger sized Pd nanoclusters.

Figure S57. EDX spectrum taken on Au@TCOS@Pd catalyst with a high metal loading of Pd.

Figure S58. XPS S 2p core-level spectrum of Au@TCOS@Au catalyst.

Figure S59. XPS (a) Au 4f, (b) Pd 3d, (c) Ag 3d, and (d) Pt 4f core-level spectra of M$_A$@TCOS@M$_B$ catalysts (herein, M$_A$ = Au, and M$_B$ = Au, Pd, Ag or Pt).

Figure S60. TEM images and the corresponding EDX spectrum of M$_A$@TCOS@M$_B$ (M$_A$ = Au, and M$_B$ = Au + Pd) catalyst.

Figure S61. HAADF-STEM image and EDX elemental maps of binary Au/Pd nanoclusters loaded on TCOS support.

Figure S62. TEM images and the corresponding EDX spectrum of M$_A$@TCOS@M$_B$ (M$_A$ = Au, and M$_B$ = Au + Pd + Ag) catalyst.

Figure S63. HAADF-STEM image and EDX elemental maps of ternary Au/Pd/Ag nanoclusters loaded on TCOS support.

Figure S64. TEM images and the corresponding EDX spectrum of M$_A$@TCOS@M$_B$ (M$_A$ = Au, and M$_B$ = Au + Pd + Ag + Pt) catalyst.

Figure S65. HAADF-STEM image and EDX elemental maps of the quaternary Au/Pd/Ag/Pt nanoclusters loaded on TCOS support.

Figure S66. Catalytic stability of Au@TCOS@Pd (for Suzuki–Miyaura coupling of iodobenzene and phenylboronic acid) and Au@TCOS@Pt (for hydrogenation of n-hexene), respectively.

Figure S67. TEM images of TCOS supported catalyst after five consecutive runs of Suzuki–Miyaura coupling reaction between iodobenzene and phenylboronic acid.
Experimental Details

Materials. The following chemicals were used as received without further purification: (3-mercaptopropyl)trimethoxysilane (MPTMS, Aldrich, 95%), tetraethylorthosilicate (TEOS, Sigma-Aldrich, 99%), gold (III) chloride trihydrate (Sigma-Aldrich, 99.9%), palladium (II) chloride (Sigma-Aldrich, 99.9%), potassium tetrachloroplatinate (II) (Sigma-Aldrich, 98%), chloroplatinic acid hydrate (Sigma-Aldrich, 99.9%), silver nitrate (Merck, 99.0%), copper (II) nitrate trihydrate (Merck, 99.5%), triethylamine (TEA, Fisher, 99%), cetyltrimethylammonium chloride (CTAC, Sigma-Aldrich, 25%), polyvinylpyrrolidone (PVP, Aldrich, K-30), hydrogen peroxide (Merck, 30%), lactic acid (Merck, 90%), potassium hydroxide (SINO chemical, 85%), sodium borohydride (NaBH₄, Aldrich, 99.99%), diethylene glycol (DEG, Sigma-Aldrich, 99%), iodobenzene (Sigma-Aldrich, 98%), phenylboronic acid (Alfa Aesar, 98+%), n-hexane (Sigma-Aldrich, 97%), n-dodecane (Alfa Aesar, 99%), potassium carbonate (Merck, 99%), 4-nitrophenol (Fluka, 99.5%), ethyl acetate (Merck, 99.5%), acetone (Fisher, 99.5%), and ethanol (Fisher, 99.99%). Seven kinds of aromatic alcohols were bought from Sigma-Aldrich. Deionized water was used for all experiments.

Synthesis of Cu₃O. The colloidal Cu₃O nanospheres were prepared according to our previous reported method. In a typical synthesis, 121 mg of Cu(NO₃)₂, 1.0 g of PVP and 20 mL of DEG were poured into a two-necked flask. The mixture was then heated at 45 °C for 1 h to fully dissolve the solutes. Afterward, the starting solution was heated from 45 °C to 192 °C within 19 min, during which the solution color turned from blue to gray-orange gradually. The product was then cooled in a fume hood, washed with acetone and ethanol for two times. Finally, the washed product was redispersed in 10 mL of ethanol for future use.

Synthesis of Cu₃O@Au. Firstly, 50 μL of HAuCl₄ (50 mM) was diluted into 30 mL of water to give a concentration of 0.083 mM. The pH of the solution was then adjusted to 4 by using 0.2 M KOH aqueous solution. Then 2 mL of the obtained Cu₃O colloid (dispersed in ethanol) was added and the mixture was well stirred at room temperature for 15 s. After that, the product was immediately recovered by centrifugation and washed with ethanol (20 mL) for two times. Finally, the washed Cu₃O@Au was redispersed into 4 mL of ethanol for future use.

Synthesis of Cu₃O@Pd. Firstly, 76 μL of H₂PdCl₄ (112.7 mM) was diluted into 60 mL of water to give a concentration of 0.143 mM. The pH of the solution was then adjusted to 3.2 by using 0.2 M HCl aqueous solution. Then 5 mL of the obtained Cu₃O colloid (dispersed in ethanol) was added and the mixture was well stirred at room temperature for 2 min. The product was immediately recovered by centrifugation and washed with ethanol (20 mL) for two times. Finally, the washed Cu₃O@Pd was redispersed into 10 mL of ethanol for future use.

Synthesis of Cu₃O@Pt. Firstly, 90 μL of K₂PtCl₄ (71 mM) was diluted into 60 mL of water to give a concentration of 0.143 mM. The pH of the solution was then adjusted to 3.8 by adding 17 μL of lactic acid (dilute 5 times, dissolved into water). Then 5 mL of the obtained Cu₃O colloid (dispersed in ethanol) was added and the mixture and well stirred at room temperature for 2 min. The product was immediately recovered by centrifugation and washed with ethanol (20 mL) for two times. Finally, the washed Cu₃O@Pt was redispersed in 10 mL of ethanol for future use.

Synthesis of TCOS and COS. Herein, TCOS was made from Cu₃O@Au, thus the product was called as Au@TCOS. For the preparation of Pd@TCOS and Pt@TCOS, please refer to Figures S44, 46 (vide
Typically, a mixture of 10 mL of Cu$_2$O@Au ethanolic suspension, 12.5 mL of water was heated at 55°C for 2 min, to which 45 µL of (3-mercaptopropyl)trimethoxysilane (MPTMS) was then added and stirred again at 55°C for 15 h. The polymerization of MPTMS is shown in the following reaction. During the reaction, the solution color turned from brown to red gradually. The product was washed with ethanol for two times. Finally, the washed TCOS was dispersed in 10 mL of ethanol for future use. Instead of using Cu$_2$O@Au as template/precursor, bare Cu$_2$O was used for the preparation of COS.

Note: The above reaction scheme is the polymerization of (3-mercaptopropyl)trimethoxysilane (MPTMS). The catalysts used in this work include Cu$_2$O nanoparticles, Cu$_2$O@M$_A$ (M$_A$ = Au, Pd, or Pt) and TEA (triethylamine).

Synthesis of conventional organosilica spheres. In a typical synthesis, 45 µL of MPTMS was added into a mix-solvent of ethanol (10 mL) and water (12.5 mL). Then, the solution was heated to 55°C. After 10 min, TEA (20 µL) was quickly added and the mixture was stirred again for 18 h. Finally, the product was washed with ethanol for two times.

Synthesis of TCOS/metal catalysts (i.e., M$_A$@TCOS@M$_B$, in these cases, M$_A$ = Au). Firstly, 10 mL of the obtained TCOS ethanolic suspension (i.e., Au@TCOS, ~20 mg) was mixed with 50 mL of water. To this solution, a specific amount of metal precursors (e.g., 116 µL of AgNO$_3$ (118 mM), or 105 µL of HAuCl$_4$ (130 mM), or 120 µL of PdCl$_2$ (113 mM), or 600 µL of H$_2$PtCl$_6$ (22 mM)) was added and the mixture was stirred for 15 min at 70°C. The metal precursor can be in-situ reduced by NaBH$_4$. Upon the addition of 2.7 mL of NaBH$_4$ (1.6 M), the mixture changes to a black color within a few seconds. Then, the solution was continuously stirred for 15 min. Finally, the product was washed with ethanol for two times.

Catalytic reduction of 4-nitrophenol: To assess the catalytic activity in 4-nitrophenol reduction, typically, 2.5 mL of 4-nitrophenol (0.2 mM) was mixed with a tested catalyst (containing 0.305 µg of Au nanoparticles; see Figure S48 for more experimental details). Then 0.2 mL of NaBH$_4$ (100 mM) was added to the reaction system. The mixture (under stirring) was immediately measured at 25°C for their UV–Vis absorption spectra in order to monitor the changes of the reaction mixture.

Catalytic oxidation of alcohol: The oxidation of aromatic alcohols was carried out in a magnetically stirred glass reactor (capacity: 50 mL) by dispersing 30 mg of catalysts in 10 mL of aqueous medium composed of a specific aromatic alcohol (1.0 mmol) and H$_2$O$_2$ (4.4 mmol). The reaction was conducted at 85°C. At a specific time, the samples were extracted with ethyl acetate and centrifuged to separate the catalysts from the reaction mixture. The extracts were analyzed with a gas chromatography machine (GC, Agilent, HP-5 capillary column, FID detector) and GC-mass spectrometry (GC: HP 6890 and mass...
selective detector: HP 5973). Activities of different catalysts were compared based on turn over frequency (TOF). In all cases, the TOF values were determined after the first 0.5 h of the reaction.

**Catalytic hydrogenation of n-hexene:**\(^2\) \(n\)-hexene (1.0 mmol, 0.125 mL), \(n\)-dodecane (0.44 mmol (0.1 mL), as the internal standard) and 15 mg of catalyst (Au@TCOS@Pt) were mixed with 15 mL of ethyl acetate. Then, the mixture was placed in a static hydrogen atmosphere. The reaction was carried out at 35°C for 5 h. After the reaction, the catalyst powder was removed by centrifugation (6000 rpm for 10 min) and the liquid phase was analyzed with a gas chromatography machine (Agilent, HP-5 capillary column, FID detector). The separated catalyst was washed with ethanol and water, respectively, dried, and reused.

**Suzuki–Miyaura coupling reaction.** Firstly, 15 mg of catalyst powder was dispersed in 5 mL of ethanol by sonication for 15 min. Then, the suspension together with iodobenzene (0.9 mmol, 0.1 mL), phenylboronic acid (1.8 mmol, 0.22 g), \(n\)-dodecane (0.1 mL, as the internal standard), \(\text{K}_2\text{CO}_3\) (0.276 g), and 10 mL of ethanol were placed in a 50 mL of glass reactor. The resulting mixture was stirred (500 rpm) at 80°C in an ambient atmosphere for 2 h. After the reaction, the catalyst solid was separated via centrifugation, and the liquid phase was analyzed with a gas chromatography machine (Agilent, HP-5 capillary column, FID detector). The separated catalyst was washed with ethanol and water, respectively, dried, and reused in consecutive experiments.

**Materials characterizations.** The crystallographic information of the samples was collected through powder X-ray diffraction (XRD, Bruker D8 Advance). Morphological investigations were carried out with the field-emission scanning electron microscopy (FESEM, JSM-6700F), transmission electron microscopy (TEM, JEM-2010), and atomic force microscopy (AFM, Bruker Dimension Icon). Elementary mapping and line scanning were conducted on the EDX microanalysis (EDX/JEM-2100F). Fourier transform infrared (FTIR, Bio-Rad) spectroscopy was used to obtain the chemical bonding information. Surface analysis for samples was performed by using X-ray photoelectron spectroscopy (XPS, AXIS-HSi, Kratos Analytical). Porosity of the samples was determined by using \(\text{N}_2\) adsorption/desorption isotherms at 77 K (Quantachrome NOVA-3000 system). Solid state \(^2\text{9Si}\) MAS NMR spectra were recorded on a Bruker Avance 400 spectrometer (DRX400). The contact angles of water droplets on the samples were measured using a contact angle meter (Kyoritsu Interfacial Science Japan, CA-D). Metal loading in the catalyst samples was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 7300DV, Perkin Elmer, USA).

**A general note:** In the main text as well as the Supporting Information hereafter, the shorthand notation TCOS is equivalent to Au@TCOS unless otherwise specified.
Catalyst Shapes

Figure S1. Velocity vector plots and pressure fields of catalyst objects with various geometric shapes.

Comment: (a) The alignment of streamline catalyst particles in the presence of a circular solvent flow. (b-f) velocity vector plots of catalyst objects with various shapes. (g) is the magnified diagram of (f), and the red arrow in (g) indicates the narrow-elongated wake region (downstream), where the fluid separates from the particle. (h-l) pressure fields of catalyst objects with various shapes. Herein, five different geometrical shapes were analyzed, including streamline body, cube, circular cone, rectangular flat plate, and sphere, which share the same projected frontal area. Color-code in these figures is used to express the strength of the flow velocity and pressure. Other computing conditions: flow rate = 0.1 m·s⁻¹ (water) and temperature = 25°C. The Computational Fluid Dynamics (CFD) simulation was performed with FLUENT 15.0 software (ANSYS).
Comment: As shown above, if a streamline particle is at rest, the flowing fluid will run over the particle from the head part to the tail part. Under this condition, if the active catalytic centers are immobilized in the head of the streamline particles, the reactants will diffuse more easily from the solution to the surface of the catalysts and the mass exchange rate is faster than those in other conditions.

If the catalyst objects are at rest, while the fluid is in motion, it is observed that the fluid flow rate is fastest at the bulk and slowest close to the catalyst surface. Then, the friction creates a tangential force exerted by the flowing fluid and is referred to as the “wall shear stress”. The developed wall shear stress will drive the moving of the catalyst object in the fluid.

The wall shear stress, $\tau_w$, is given by:

$$\tau_w = \mu \left( \frac{\partial u}{\partial y} \right)_{y=0}$$

where $\mu$ is the dynamic viscosity, $u$ is the flow velocity parallel to the wall, and $y$ is the distance to the wall. The SI unit of wall shear stress is Pascal. See Figure S3.
Figure S3. Wall shear stress fields of catalyst objects with (a) sphere and (b) streamline structure. Color-code in the figures is used to indicate the strength of the wall shear stress, and the unit is Pascal.

Comment: It is clearly indicated that the streamline body experiences less wall shear stress, compared to the case of sphere, which implies that the relative movement between the fluid and the catalyst is greater and thus mass exchange is easier for the case of streamlined body.

The surface-area-to-volume ratio ($S_A:V$) is the amount of surface area per unit volume of an object. In chemical reactions involving a solid material, the surface area to volume ratio is an important factor for the reactivity, that is, the rate at which the chemical reaction will proceed. See Table S1 for a comparison among different geometries.
### Table S1. Comparison of specific surface areas of different geometrical bodies.

| shape                      | flat plate (i) | cube (ii) | sphere | circular cone (iii) | streamline body (iv) |
|----------------------------|----------------|-----------|--------|---------------------|----------------------|
|                            | ![flat plate](image1) | ![cube](image2) | ![sphere](image3) | ![circular cone](image4) | ![streamline body](image5) |
| dimension definition       | $a, b = a/5, c = a/10$ | $a = b = c$ | $r$ (radius) | $h = 4r$ | $l = 4r$ |
| equal volume               | 1000           | 1000      | 1000   | 1000                | 1000                 |
| characteristic length      | $a = 36.8$     | $a = b = c = 10$ | $r = 6.2$ | $r = 6.2, h = 24.8$ | $r = 5.4, l = 21.6$ |
| surface area               | 867            | 600       | 483.3  | 618.7               | 560.9                |
| $S_A/V$ ratio              | 0.867          | 0.600     | 0.483  | 0.619               | 0.561                |
| $S_A/V$ ratio              | $32/a$         | $6/a$     | $3/r$  | $3.84/r$            | $3.06/r$             |

(i) $a$ is the plate length (axial direction), $b$ is the width of the plate, and $c$ is the height of the plate.

(ii) $a = b = c$, where $a$, $b$ and $c$ are the side lengths of the cube.

(iii) $r$ is the radius of the bottom circle, and $h$ is the height of the cone.

(iv) $r$ is the radius in the head part, and $l$ is the length of the tail part. For simplicity in this estimation, the streamline body is built from connecting a hemisphere (the head part) to a cone (the tail part) with equal diameter.

**Reynolds number (Re) formula is given by**

$$Re = \frac{\rho \cdot v \cdot L}{\mu}$$

where $v$ is the mean velocity of the object relative to the fluid (SI units: m/s); $L$ is a characteristic linear dimension (m), $\mu$ is the dynamic viscosity of the fluid (Pa·s or N·s/m² or kg/m·s), and $\rho$ is the density of the fluid (kg/m³).
Nomenclature of the Catalysts in This Work

Table S2. Summary of the templates and catalysts prepared in this work.

| Sample name | Templates/catalysts prepared in this work |
|-------------|------------------------------------------|
| Cu$_2$O@M$_A$ | ![Cu$_2$O@M$_A$](image1) M$_A$ = Au | ![Cu$_2$O@M$_A$](image2) M$_A$ = Pd | ![Cu$_2$O@M$_A$](image3) M$_A$ = Pt |
| M$_A$@TCOS | ![M$_A$@TCOS](image4) M$_A$ = Au | ![M$_A$@TCOS](image5) M$_A$ = Pd | ![M$_A$@TCOS](image6) M$_A$ = Pt |
| M$_A$@TCOS@M$_B$ | ![M$_A$@TCOS@M$_B$](image7) M$_A$ = Au, M$_B$ = Au | ![M$_A$@TCOS@M$_B$](image8) M$_A$ = Au, M$_B$ = Pd | ![M$_A$@TCOS@M$_B$](image9) M$_A$ = Au, M$_B$ = Pt |
| M$_A$@TCOS@M$_B$ | ![M$_A$@TCOS@M$_B$](image10) M$_A$ = Au, M$_B$ = Ag | ![M$_A$@TCOS@M$_B$](image11) M$_A$ = Au, M$_B$ = Au + Pd |
| M$_A$@TCOS@M$_B$ | ![M$_A$@TCOS@M$_B$](image12) M$_A$ = Au, M$_B$ = Au + Pd + Ag | ![M$_A$@TCOS@M$_B$](image13) M$_A$ = Au, M$_B$ = Au + Pd + Ag + Pt |

**Note:** Regarding the type of M$_A$@TCOS@M$_B$ catalysts in our work, M$_A$ can be exploited as Au, Pd or Pt nanoparticles, and at the same time, M$_B$ can be realized as mono-metals Au, Pd, Pt, Ag nanoparticles, or their binary, ternary, and even quaternary combinations. Therefore, ideally, there are 48 kinds of different combinations between the inner metals (M$_A$) and the metals distributed in the shell (M$_B$), as shown in the table below (Table S3).
**Table S3.** Investigated combinations of M\textsubscript{A} and M\textsubscript{B} in M\textsubscript{A}@TCOS@M\textsubscript{B} catalysts in this work.

| Entry | Metals | Entry | Metals |
|-------|--------|-------|--------|
|       | M\textsubscript{A} | M\textsubscript{B} |       | M\textsubscript{A} | M\textsubscript{B} |
| 1     | Au     | Au    | 25    | Pt     | Au + Pt     |
| 2     | Au     | Pd    | 26    | Pt     | Ag + Pd    |
| 3     | Au     | Ag    | 27    | Pt     | Au + Ag + Pt |
| 4     | Au     | Pt    | 28    | Pt     | Ag + Pt + Pd |
| 5     | Au     | Au + Pd | 29 | Pt     | Au + Ag + Pd |
| 6     | Au     | Ag + Pd | 30 | Pt     | Au + Pd + Pt |
| 7     | Au     | Pd + Pt | 31  | Pt     | Au + Ag + Pd + Pt |
| 8     | Au     | Au + Ag | 32  | Pt     | nil         |
| 9     | Au     | Au + Pt | 33  | Pd     | Au          |
| 10    | Au     | Ag + Pd | 34  | Pd     | Pd          |
| 11    | Au     | Au + Ag + Pt | 35 | Pd     | Ag          |
| 12    | Au     | Ag + Pt + Pd | 36 | Pd     | Pt          |
| 13    | Au     | Au + Ag + Pd | 37 | Pd     | Au + Pd     |
| 14    | Au     | Au + Pd + Pt | 38 | Pd     | Ag + Pd     |
| 15    | Au     | Au + Ag + Pd + Pt | 39 | Pd     | Pd + Pt     |
| 16    | Au     | nil   | 40    | Pd     | Au + Ag     |
| 17    | Pt     | Au    | 41    | Pd     | Au + Pt     |
| 18    | Pt     | Pd    | 42    | Pd     | Ag + Pd     |
| 19    | Pt     | Ag    | 43    | Pd     | Au + Ag + Pt |
| 20    | Pt     | Pt    | 44    | Pd     | Ag + Pt + Pd |
| 21    | Pt     | Au + Pd | 45  | Pd     | Au + Ag + Pd |
| 22    | Pt     | Ag + Pd | 46  | Pd     | Au + Pd + Pt |
| 23    | Pt     | Pd + Pt | 47  | Pd     | Au + Ag + Pd + Pt |
| 24    | Pt     | Au + Ag | 48  | Pd     | nil         |
Figure S4. Location illustration of the $M_A$ and $M_B$ components in the catalyst structures.

**Comment:** We can imagine such a scene that those tadpole-shaped catalyst particles would move easily in the reactor looking like many swimming tadpoles. The fast movement benefits a fast mass exchange, which may have a strong impact on catalytic performance. Note: The above photo of a real tadpole is adopted from an online source:

[https://jeremybiggs.wordpress.com/2010/08/29/frogs-spawn-in-spring-and-tadpoles-emerge-in-summer-but-not-always/](https://jeremybiggs.wordpress.com/2010/08/29/frogs-spawn-in-spring-and-tadpoles-emerge-in-summer-but-not-always/)
Characterizations of Cu$_2$O and Cu$_2$O@Au

Figure S5. (a-f) TEM images of spherical Cu$_2$O nanoparticles at different magnifications.

Figure S6. (a-d) TEM images of Cu$_2$O@Au at different magnifications, (e) size distribution and statistical mean particle size of Cu$_2$O spheres, and (f) size distribution and statistical mean particle size of Au nanoparticles on the external surface of Cu$_2$O spheres.
Figure S7. EDX elemental maps of core–satellite structure of Cu$_2$O@Au sample.

Comment: Three elements were found in the sample: copper, gold and oxygen. One can see that the Cu$_2$O is seated in the core and the small Au nanoparticles are deposited on the external surface of Cu$_2$O, forming a “shell” of Au nanoparticles. Thus, this resultant structure is called as core–satellite structure in the main text.
STEM Characterization of Au@TCOS

**Figure S8.** (a-i) STEM dark field micrographs of Au@TCOS sample at different magnifications.

**Comment:** Herein, the TCOS sample was prepared by using Cu$_2$O@Au as a template/precursor. (a-d) Particle 1, (e,f) Particle 2, and (g-i) Particle 3. Particles 1 to 3 are randomly chosen in different places on a TEM copper grid. The white dots (brighter contrast) in the head portion of the tadpole-like structure are Au nanoparticles. Actually, these Au nanoparticles are covered by a porous layer of copper organosilicate; refer to the following XPS characterization (Figure S21) and TEM characterization (Figure S26).
SEM Characterization of Au@TCOS

Figure S9. (a-f) SEM images of Au@TCOS sample at different magnifications.

Comment: Herein, the TCOS sample was prepared by using Cu₂O@Au as a template/precursor. As shown, the morphological yield of product with a tadpole shape is about 100%.
AFM Characterization of Au@TCOS

**Figure S10.** (a-f) AFM images of Au@TCOS sample.

**Comment:** Herein, the TCOS sample was prepared by using Cu$_2$O@Au as a template/precursor. In the above figures, (a,c,e) are the 2D height mode images, and (b,d,f) are the corresponding phase mode images.
EDX Characterization of Au@TCOS

Description: The information in this section includes the EDX elemental maps, EDX elemental line scans, and EDX spectra of Au@TCOS samples. Note: Au@TCOS samples were prepared in several different (independent) experiments.

Figure S11. EDX elemental maps of Au@TCOS sample.

Figure S12. EDX elemental maps of Au@TCOS sample.
Figure S13. EDX elemental maps of Au@TCOS sample.

Figure S14. EDX elemental line scans on the head portion of a single Au@TCOS particle. The image is obtained by high-angle annular dark-field scanning TEM (HAADF-STEM).
Figure S15. EDX spectrum taken on Au@TCOS sample.

Comment: The Ni element signal originated from the EDX sample holder (Ni grid). There are mainly six elements which are present in the Au@TCOS sample: C, O, S, Si, Cu, and Au. The inset is the corresponding weight percentages and atomic percentages of these elements. Note: C element content was not shown due to the effect of carbon film on the TEM sample grid (made from Ni).
Investigation on Preparation Conditions of Au@TCOS

Figure S16. (a-c) The effect of MPTMS concentration on the product morphology of Au@TCOS.

Comment: Herein, the TCOS sample was prepared by using Cu$_2$O@Au as a template/precursor. The tail length of TCOS material could be increased when increasing the concentration of MPTMS. For example, (a) TCOS with an average tail length of 0.30 μm was obtained by using the initial MPTMS concentration of 0.0057 mmol L$^{-1}$, (b) TCOS with an average tail length of 0.54 μm was obtained by using the initial MPTMS concentration of 0.0079 mmol L$^{-1}$, and (c) TCOS with an average tail length of 1.25 μm was obtained by using the initial MPTMS concentration of 0.0102 mmol L$^{-1}$. Therefore, the tail length of TCOS material can be tuned simply by varying the starting concentration of MPTMS.
**Figure S17.** (a-i) The effect of reaction temperature on the product morphology of Au@TCOS.

**Comment:** The above samples were prepared at (a-c) 25 °C, (d-f) 45 °C, and (g-i) 55 °C, respectively. As shown, at low temperature, the hydrolysis and condensation of MPTMS is quite slow, which cannot form a complete tadpole shape. From the images of (a-c), we can clearly see the formation of surface breaches on the particles, due to the etching of Cu₂O (refer to the discussion in the main text).

**Figure S18.** (a-f) The effect of reaction durations on the product morphology of Au@TCOS.

**Comment:** (a-c) 3 h, and (d-f) 6 h. As shown, the formation of TCOS can be finished within 6 h.
**XRD Characterization**

**Figure S19.** (a,b) XRD patterns of TCOS (i.e., Au@TCOS) and its comparative samples, and (c) schematic illustration of the bilayer structures of organosilica and COS (or TCOS), where copper ions are shown as small green beads, $d$ indicates the nearest interlayer spacing in the bilayer structure, and $x$ indicates alkylthiol or alkylthiolate chain packing distance within the layer.

**Comment:** Herein, TCOS was prepared by using Cu$_2$O@Au as template/precursor, and thus TCOS also represents Au@TCOS (that is, $M_A=\text{Au}$, unless otherwise specified). In comparison with Cu$_2$O@Au template, all the Cu$_2$O phase was absent in TCOS product, except that the Au phase was preserved. The formation of layered structures in these materials can be clearly confirmed by the XRD patterns, which displays discernible broad, clay-based reflections. In the case of TCOS and COS, the peaks at 16.2, 8.1, 2.7 and 1.9 Å provide information regarding the layer distance value of the lamellar structure, suggesting that different diffraction orders can be identified (e.g., (001), (002), etc. reflections), although the exact peak position for higher order reflections is much more difficult to locate. However, the $d$-spacing determined to be 1.62 nm (or $d_{001}$) is interpreted as the sum of the tetrahedral siloxane layer thickness plus the interlayer distance created by the alkylthiol or alkylthiolate spacers (refer to the structural models in the figure, where the organic chains are in bilayer arrangements). On the other hand, the periodicity at 4.2 Å can be attributed to alkylthiol or alkylthiolate chain packing within the layer (via van der Waals interactions, labeled as “$x$” in Figure S19). The observed reflection peaks in the XRD patterns are quite broad, suggesting some degree of intra-layer disorder/defects due to the sorption of
copper ions. The \( d \)-spacing value (1.62 nm) of the lamellar solid in both TCOS and COS is larger than that of the conventional organosilica prepared by MPTMS (1.12 nm), due to the incorporation of copper ions in the organic bilayer in the gallery space. It is worth noting that the increased value is very close to double of the theoretical distance \( S^{-}\text{Cu} \) (2.2 Å). The enlargement of the interlayer spacing will also affect the porosity of the materials, which will be determined later by \( \text{N}_2 \) physisorption experiments. However, the periodicities due to alkylthiol or alkylthiolate chain packing (labeled as “x” in Figure S19) maintain the same (i.e., 4.2 Å) in all the three materials.

XPS Characterization

All binding energies (B.E.) of the peaks were referenced to the C 1s of alkyl chains or adventitious carbon at 284.6 eV. The S 2p peaks were fitted using a Gaussian function with provision for the 1.18 eV spin–orbit splitting of the 2\( \text{p}_{1/2} \) and 2\( \text{p}_{3/2} \); the 1:2 intensity ratio of this splitting was maintained in the fitting. For the noble metal (i.e., Au, and Pt) 4f peaks; the 3:4 intensity ratio of splitting of the 4f\( \text{5/2} \) and 4f\( \text{7/2} \) was maintained in the fitting. In the cases of Pd 3d and Ag 3d peaks; the 2:3 intensity ratio of splitting of the 3d\( \text{3/2} \) and 3d\( \text{5/2} \) was maintained in the fitting.

Comment: It was documented that copper cations can be coordinated with the organic ligands in the lamellar solid. Here, evidence for the copper coordination with thiol group through forming a covalent Cu–S bond is provided by XPS characterizations. As shown in the following figures, the S 2\( \text{p}_{3/2} \) and S 2\( \text{p}_{1/2} \) were fitted with a fixed binding energy (B.E.) difference of 1.18 eV and an intensity ratio of 2:1, which displays two different energy levels in both samples of TCOS and COS, but reflects only one energy level in organosilica. The fitted S 2\( \text{p}_{3/2} \) B.E. of free thiol is 163.5 eV and for sulfur bound to Cu, the S 2\( \text{p}_{3/2} \) B.E. is 162.3 eV.5 And the oxidation of \( \text{S}^{-}\text{H} \) to \( \text{SO}_3\text{H} \) was not observed. The fitted S 2p of organosilica is similar to the one in MPTMS, again confirming that the difference is caused by copper sorption. Likewise, the Cu 2\( \text{p}_{3/2} \) curve-fitted values at lower B.E. of 932.6 eV is assigned to Cu\(^+\) while the value at higher B.E. of 933.9 eV is assigned to Cu\(^2+\), implying that most surface copper atoms involved in Cu–S bonding exist as Cu(I), and a small part of Cu\(^+\) was oxidized to Cu\(^2+\) at 55°C (probably due to the oxidation during preparation or sample storage). In contrast, no XPS signal due to Au was observed in the TCOS sample, indicating that Au nanoparticles were totally buried under the organosilicate layer, as also evidenced from the corresponding high-magnification TEM images (\textit{vide infra}).

![Figure S20. XPS of S 2p core levels for organosilica (left) and TCOS or COS (right).](image-url)
Comment: Herein, the TCOS sample was prepared by using Cu$_2$O@Au as a template/precursor. As shown, there is no obvious signal in the Au 4$f$ region, indicating that there was no gold present on the external surface (note: XPS technique only detects the surface information), consisting with the results of TEM images (displayed in Figure S26), which shows that Au nanoparticles were totally covered by a thin layer of organosilica. The Cu 2$p_{3/2}$ spectrum can be deconvoluted into two distinct peaks at B.E. of 932.6 eV and 933.9 eV, which are assigned to Cu(I) and Cu(II), respectively. The shake-up satellite peaks due to Cu(II) are slightly distinguishable. The Si 2$p$ spectrum is fitted at B.E. of 102.5 eV. The deconvolution of S 2$p_{3/2}$ provides two different contributions with their maxima at B.E. of 162.3 eV (peak 1) and 163.5 eV (peak 2). The corresponding S 2$p_{1/2}$ can be deconvoluted into at B.E. of 163.5 eV (peak 1) and 164.7 eV (peak 2), respectively. The former peak (i.e., peak 1) is assigned to alkylthiolate group (S–Cu), while the latter one (i.e., peak 2) is attributed to the free alkylthiol group (RS–H).
Comment: As shown, the Si 2p spectrum is fitted at B.E. of 102.3 eV. And the S 2p<sub>3/2</sub> and 2p<sub>1/2</sub> spectra are fitted at B.E. of 163.4 eV and 164.6 eV, respectively, which is ascribed to the free alkylthiol group (RS–H). Therefore, in this work, the values of the B.E. of 163.4 eV and 164.6 eV were used as referred data for S 2p<sub>3/2</sub> and 2p<sub>1/2</sub> in alkylthiol group.

Figure S23. XPS (a) Cu 2p<sub>3/2</sub>, (b) Au 4f, and (c) O 1s core-level spectra of Cu<sub>2</sub>O@Au sample.

Comment: As shown, the Cu 2p<sub>3/2</sub> spectrum of the sample could be deconvoluted into two components centered at B.E. of 932.1 and 934.3 eV, which could be assigned to Cu(I) and Cu(II), respectively. The presence of two shake-up satellite peaks at B.E. of 943.8 eV and 941.4 eV also indicates the presence of Cu(II) species. The result indicates that the surface Cu<sub>2</sub>O in the Cu<sub>2</sub>O@Au sample is partially oxidized, due to the reduction of HAuCl<sub>4</sub> via spontaneous galvanic replacement. Similarly, the Au 4f<sub>7/2</sub> spectrum could be deconvoluted into two components centered at B.E. of 84.0 and 84.7 eV, which could be assigned to Au(0) (∼64%) and Au(I) (∼36%), respectively. Likewise, the O 1s could both be deconvoluted into two chemically distinct peaks at B.E. of 531.6 and 532.2 eV, corresponding to two types of lattice oxygen in the metal oxides.
Figure S24. XPS (a) Cu 2p, (b) Si 2p, and (c) S 2p core-level spectra of COS.

Comment: As shown, the Cu 2p$_3/2$ spectrum is fitted at B.E. of 932.8 eV, which is assigned to Cu(I). The Si 2p spectrum is centered at B.E. of 102.3 eV. The deconvolution of the S 2p$_3/2$ provides two different contributions with their maxima at 162.8 eV (peak 1) and 163.6 eV (peak 2). The corresponding S 2p$_1/2$ peaks can be deconvoluted into B.E. of 164.0 eV (peak 1) and 164.8 eV (peak 2), respectively. The former peak (i.e., peak 1) is assigned to alkylthiolate group (S–Cu), whereas the latter one (i.e., peak 2) is attributed to the alkylthiol group (RS–H).
Figure S25. XPS (a) Si 2p, (b) O 1s, and (c) S 2p core-level spectra of the conventional organosilica.

Comment: As shown, the Si 2p spectrum is fitted at B.E. of 102.2 eV and O 1s spectrum is fitted at B.E. of 531.9 eV. And S 2p_{3/2} and 2p_{1/2} spectra are fitted at B.E. of 163.3 eV and 164.5 eV, respectively, which can be ascribed to the alkylthiol group (RS–H), similarly to those found in the original MPTMS monomer.
TEM Characterization

Figure S26. (a-c) TEM and HRTEM (d-f) images of the head portion of TCOS at different magnifications.

**Comment:** Herein, the TCOS sample was prepared by using Cu$_2$O@Au as a template/precursor. The results show that Au nanoparticles exist mostly at the head portion of the tadpole during the fabrication process. However, the Au nanoparticles are covered by a thin layer of copper organosilicate in the tadpole-like structure, which is also the reason why the above XPS characterization cannot detect the signal of Au on TCOS sample.
FTIR Characterization

**Figure S27.** FTIR spectra of Cu$_2$O@Au template (1), TCOS (2), COS (3) and organosilica (4).

**Comment:** Herein, the TCOS sample was prepared by using Cu$_2$O@Au as a template/precursor. FTIR spectra of the TCOS show that the Cu(I)–O vibrational band (at 630 cm$^{-1}$, from Cu$_2$O template)$^{15}$ disappeared and a new organosilicate phase formed, consistent with conclusions derived from XRD. Specifically, the FTIR spectra show the general features of alkylsiloxane network: Si–O–Si stretching vibrations (1100 and 1030 cm$^{-1}$), O–H stretching and bending vibrations (3430 and 1635 cm$^{-1}$, respectively), silanol groups stretching vibration (910 cm$^{-1}$), O–Si–O bending vibration (470 cm$^{-1}$). Abundant methylene units originated from mercaptopropyl groups give rise to four distinct peaks at 2930, 1450, 1242, and 736 cm$^{-1}$ (corresponding to symmetric stretching, scissoring, twisting, and rocking modes, respectively).$^7$ The COS sample exhibits similar FTIR characters as TCOS. In contrast, for the conventional organosilica, the silanol and hydroxyl groups are much weaker as indicated with the lower intensities, which might contribute to the highly hydrophobic surface of the organosilica. Moreover, compared with the conventional organosilica, the thiol groups (S–H stretching vibrations, 2557 cm$^{-1}$)$^{16-17}$ in the bulk TCOS and COS samples are missing, again supporting the coordination between thiol group to copper.$^5$ Although free thiol groups on the surface of TCOS and COS were found by the above XPS investigations, they were mostly bonding to copper ions in the bulk phase of the materials.
Solid-State $^{29}$Si MAS NMR Characterization

![Solid-state $^{29}$Si MAS NMR spectra of different samples](image)

**Figure S28.** $^{29}$Si MAS NMR spectra of different samples. Chemical shifts are given relative to tetramethylsilane at 0 ppm.

**Comment:** Herein, the TCOS sample was prepared by using Cu$_2$O@Au as a template. As shown, solid-state $^{29}$Si MAS NMR spectra confirm the presence of organosiloxane units ($T_m = R Si(OSi)_m(OH)_{3-m}$) in the TCOS, COS and the conventional organosilica, which exhibits two distinct resonances: the two peaks at −67 and −58 ppm can be assigned to the fully condensed T$_3$ and the partially condensed T$_2$ species, respectively. The result also indicates that Si–C bonds were not cleaved during the reaction. The relative abundance of T$_2$ and T$_3$ species in TCOS was quantified as 1:1.1 from the integrated peak area ratios, which is the same as the value of COS, but quite different from the value of conventional organosilica ($T_2/T_3 = 1:9.5$). In addition, all these organosilica/organosilicates samples are distinctly different from the Stöber silica, which exhibits the Q$_3$ and Q$_4$ species ($Q_n = Si(OSi)_n(OH)_{4-n}$, relative intensity of $Q_3/Q_4 = 1:0.7$). Therefore, the aforesaid hydrophilic property of TCOS might be built in the presence of a higher amount of hydrophilic silanol groups, probably also owing to the presence of hydrophilic Au nanoparticles.
Thermogravimetry Coupled with FTIR Characterization

Figure S29. TG-differential thermal analysis (TG-DTA) curves for TCOS sample and 3D-FTIR spectra of the evolved gases during the thermogravimetry analysis.

Comment: Herein, the TCOS sample was prepared by using Cu$_2$O@Au as a template/precursor. TGA was carried out under a flowing air atmosphere (50 mL min$^{-1}$) at a heating rate of 10°C min$^{-1}$. The two endothermic peaks between 190 and 400°C in the DTA curve are due to the oxidation of the organic constituents in TCOS sample. There is no significant weight loss over 500°C. Thus, the total mass percentage of the organic constituents in TCOS is calculated to be ca. 35 wt%. As viewed from 3D-FTIR spectra, the evolved gases from this thermal process include water, CO$_2$ and SO$_2$. 
**BET Characterization**

![N2 physisorption isotherms](image)

**Figure S30.** N$_2$ physisorption isotherms of different samples investigated in this work.

![Pore size distribution](image)

**Figure S31.** Pore size distribution of TCOS sample based on nitrogen desorption isotherm.

**Comment:** Herein, the TCOS sample was prepared by using Cu$_2$O@Au as a template/precursor. The mesoporosity of TCOS was confirmed by the N$_2$ physisorption experiment. As shown, the nitrogen sorption isotherms exhibit representative type IV curves, which indicate that TCOS material has a large BET surface area of 234 m$^2$g$^{-1}$, a total pore volume of 0.42 mLg$^{-1}$, and well-defined mesopores with an average pore size of 3.7 nm (Barret–Joyner–Halenda (BJH) method). BET results suggest that TCOS material is more porous as compared with the COS (BET surface area of 58 m$^2$g$^{-1}$), the conventional organosilica (3 m$^2$g$^{-1}$), and the Stöber silica beads (16 m$^2$g$^{-1}$).
Hydrothermal and Thermal Treatments of Au@TCOS

Figure S32. (a-f) TEM images of Au@TCOS sample after hydrothermal treatment at 160°C for 24 h.

Figure S33. (a-f) TEM images of Au@TCOS sample after calcination treatment under static laboratory air at 500°C for 6 h. Note that the organic part of this sample has been removed (Figure S29).
Characterizations of COS

Figure S34. (a-f) TEM images of COS at different magnification. Bottom panel: a digital color photograph of COS sample.

Comment: The color photograph is a COS powder sample held in a mortar (light green color), which is quite different from the color of TCOS sample prepared by using Cu₂O@Au as a precursor (pale red color).
Figure S35. EDX elemental maps and EDX spectrum of COS sample.

**Comment:** In the EDX spectrum, the Ni signal originated from the Ni sample grid used for loading COS sample in EDX measurement.
Characterizations of Conventional Organosilica

Figure S36. (a-f) TEM images of the conventional organosilica at different magnifications. Bottom panel: a digital color photograph of the conventional organosilica sample.

Comment: The conventional organosilica was prepared from the hydrolysis and polycondensation of MPTMS by using a modified Stöber method under triethylamine (TEA)-catalyzed conditions. As shown, the average particles size of the conventional organosilica was determined as 829 ± 38 nm by counting more than 100 particles. The photograph is the conventional organosilica powder sample (held in a mortar), showing the white color of the solid.
Figure S37. EDX elemental maps and EDX spectrum of the conventional organosilica.

Comment: In the EDX spectrum, the Cu signal originated from the Cu grid which was used for loading sample in the EDX measurement.
Investigation with Single Crystal Cu$_2$O

Figure S38. (a-f) TEM images of cubic Cu$_2$O@Au (single-crystalline Cu$_2$O nanocubes with exclusively exposed {100} surface planes) at different magnifications.
Figure S39. (a-f) TEM images of Cu$_2$O@Au@organosilica composite at different magnifications.

**Comment:** As mentioned in Experimental Section, TCOS was prepared by using spherical Cu$_2$O@Au as a template/precursor. Herein, if we adopted the cubic Cu$_2$O decorated with Au nanoparticles, the products were not TCOS, as shown in the above TEM images. It can be seen that a uniform layer of organosilica was coated on the external surface of Cu$_2$O@Au cores. The products are named as Cu$_2$O@Au@organosilica. Because the Cu$_2$O nanocubes used here possess exclusively the {100} faces, their etching rate under mild acidic condition is slow (see the main text). Thus, the overall product morphology is still cube-like, but there are many central voids generated within, instead of forming the streamline structure of TCOS.
Cu₂O@Pd and Cu₂O@Pt

Figure S40. (a-f) Typical TEM images of Cu₂O@Pd nanoparticles at different magnifications.

Comment: Please refer the preparation conditions in Experimental Section. As shown, the size of Pd nanoparticles prepared by the galvanic replacement method is quite small (below 2 nm). The density of Pd nanoparticles on the external Cu₂O surface is quite high, as inferred from the above TEM images.

Figure S41. EDX elemental maps and EDX spectrum of Cu₂O@Pd nanoparticles.
Comment: The results show that Pd nanoparticles can be homogenously deposited on the external surface of Cu₂O particles by the galvanic replacement method. In the EDX spectrum, the Ni element signal originated from the EDX sample holder (viz., Ni grid).

**Figure S42.** (a-i) Typical TEM images of Cu₂O@Pt nanoparticles at different magnifications.

Comment: Please refer the preparation conditions in Experimental Section. As shown, the size of Pt nanoparticles prepared by the galvanic replacement method is quite small (below 2 nm).
Figure S43. EDX elemental maps and EDX spectrum of the Cu$_2$O@Pt nanoparticles.

Comment: As shown in the elemental maps, Pt nanoparticles were homogenously deposited on the external surface of Cu$_2$O particles by the galvanic replacement method. The Ni element signal in the EDX spectrum originated from the EDX sample holder (viz., Ni sample grid).
**TCOS Material Prepared with Cu$_2$O@Pd and Cu$_2$O@Pt**

Figure S44. (a-f) TEM images of TCOS material prepared by using Cu$_2$O@Pd as a template.

**Preparation condition:** 10 mL of Cu$_2$O@Pd ethanolic suspension and 12.5 mL of water were mixed and heated at 55 °C for 2 min, to which 45 μL of MPTMS was then added and the mixture was kept stirring at 55 °C for 14 h. After the reaction, solid product was collected by centrifugation, and washed with ethanol twice.

Figure S45. HAADF-STEM image and EDX elemental maps of TCOS material prepared by using Cu$_2$O@Pd as a template/precursor.

**Comment:** As shown above, the Pd nanoparticles are distributed on the head portion of the tadpole structure, similar to the distribution of Au nanoparticles in Au@TCOS sample.
Figure S46. (a-c) TEM and HAADF-STEM (d-f) images of TCOS, prepared by using Cu$_2$O@Pt as a template/precursor.

**Preparation conditions:** 10 mL of Cu$_2$O@Pt ethanolic suspension and 12.5 mL of water were mixed and heated at 55 °C for 2 min, to which 45 µL of MPTMS was then added and the mixture was kept stirring at 55 °C for 14 h. After the reaction, solid product was collected by centrifugation, and washed with ethanol twice.

Figure S47. HAADF-STEM image and EDX elemental maps of TCOS prepared by using Cu$_2$O@Pt as a template/precursor.

**Comment:** The digital photos show the original Cu$_2$O ethanolic suspension (1) and the TCOS aqueous suspensions prepared by using Cu$_2$O@Au (2), Cu$_2$O@Pt (3) and Cu$_2$O@Pd (4) as templates and precursors in this work.
Catalytic Reduction of 4-Nitrophenol

Figure S48. (a-c) Time-dependent UV–Vis spectra of the reaction mixture of reduction of 4-nitrophenol, and (d) comparison of the reaction rates of different catalysts.

Comment: In these reactions, we used NaBH₄ as a reducing agent and TCOS (long tail) (a), TCOS (short tail) (b), and spherical Cu₂O@Au@mSiO₂ (c) as catalysts. Figure S48(d) shows the linear relationship between \( \ln(C_t/C_0) \) and reaction time during the course of reaction in (a)-(c). The kinetic data without using catalysts were also depicted for comparison (see line (4) in (d)). Insets show the corresponding TEM images and structural models of the particles. Note that the Au weight percentages of TCOS (long tail), TCOS (short tail) and spherical Cu₂O@Au@mSiO₂ were 2.24, 2.39, and 5.66 wt%, respectively. For example, 3.4 mg of TCOS (long tail; (1)) catalyst was redispersed in 5 mL of water by sonication, and then 20 µL of the aqueous suspension was used for the reaction. Therefore, the amount of gold used for the reaction was 0.305 µg. The mass of other two catalysts ((2) and (3) in (d)) was also adjusted accordingly to give the same Au amount of 0.305 µg in all the reactions.
Characterizations of \( M_A@TCOS@M_B \)

In this section, we employed Au@TCOS as supports for the deposition of various noble metal nanoclusters (e.g., Au, Pt, Ag or Pd). The obtained catalysts were called as \( M_A@TCOS@M_B \) (\( M_A = \text{Au, Pd} \), \( M_B = \text{Au, Pt, Ag, or Pd} \)).

**Figure S49.** (a-c) Representative TEM images of the tail portion of Au@TCOS support.

**Comment:** As shown, there are essentially no metal nanoparticles existing on the surface. These TEM images were taken for a comparison with the samples reported in Figures S50-55 below.

**Figure S50.** (a-f) Characterizations of Au@TCOS@Au catalyst.

**Comment:** (a-e) Typical TEM images of Au nanoclusters loaded on the hybrid materials, and (f) statistic particle size distribution for the Au nanoclusters. As compared with Figure S49 (blank sample), it can be seen that Au nanoclusters were successfully loaded on the external surface of TCOS.
Figure S51. (a-f) Typical high resolution TEM images of Au@TCOS@Au catalyst.

**Comment:** Figures (a-f) were all taken at the tail portion of the tadpole structure, in order to achieve a high image contrast. As shown in (f), the basal spacing of the lattice is 0.23 nm, in agreement with the (111) lattice fringes of the Au crystals.

Figure S52. (a-f) Characterizations of Au@TCOS@Pd catalyst.

**Comment:** (a-e) Typical TEM images of Pd nanoclusters loaded on the hybrid materials, and (f) statistic particle size distribution for the Pd nanoclusters.
Figure S53. (a-f) Characterizations of Au@TCOS@Ag catalyst.

Comment: (a-e) Typical TEM images of Ag nanoclusters loaded on the hybrid materials, and (f) statistic particle size distribution for the Ag nanoclusters.

Figure S54. (a-f) Characterizations of Au@TCOS@Pt catalyst.

Comment: (a-e) Typical TEM images of Pt nanoclusters loaded on the hybrid materials, and (f) statistic particle size distribution for the Pt nanoclusters.
**Figure S55.** (a-f) TEM images of Au@TCOS@Pd catalyst with a relatively high Pd loading amount.

**Comment:** The catalyst shown above has a higher Pd loading amount as compared with the case shown in Figure S52. In the preparation solution, the metal precursor concentration was adjusted to 3 times of the amount in normal condition (referring to the Experimental Section). The result suggests that an increase of Pd content would lead to a larger size of Pd nanoclusters on TCOS external surface.

**Figure S56.** HAADF-STEM image and EDX elemental maps of Au@TCOS@Pd catalyst with larger sized Pd nanoclusters.
Figure S57. EDX spectrum taken on Au@TCOS@Pd catalyst with a high metal loading of Pd.

Comment: The Ni element signal originated from the EDX sample holder (viz., Ni grid). The inset is the corresponding weight percentages and atomic percentages of the elements in the tested sample. Herein, the higher Pd loading is compared with the sample shown in Figure S52.
XPS Characterization of $M_A@TCOS@M_B$

**Figure S58.** XPS $S\ 2p$ core-level spectrum of $Au@TCOS@Au$ catalyst.

**Comment:** $Au@TCOS@Au$ catalyst was prepared by deposition of Au nanoclusters on the $Au@TCOS$ support. As shown, after loading with Au nanoclusters, the peak area 1, which corresponds to $S–Cu$ (or newly formed $S–Au$), becomes larger than the peak area 2 which belongs to the pristine thiol group (i.e., $RS–H$). For a better comparison, refer to Figure S21(d) and related comment.

**Figure S59.** XPS (a) $Au\ 4f$, (b) $Pd\ 3d$, (c) $Ag\ 3d$, and (d) $Pt\ 4f$ core-level spectra of $M_A@TCOS@M_B$ catalysts (herein, $M_A = Au$, and $M_B = Au, Pd, Ag$ or $Pt$).
Comment: It should be noted that, there are no signals belonging to M₄ found in the XPS spectra of M₄@TCOS@M₅ catalysts, because of that M₄ is covered by a layer of copper organosilicate. For the Au 4f region, only one doublet at 84.2 eV and 87.9 eV was found, corresponding to Au(0) 4f½, and Au(0) 4f½. The slight shift in the Au(0) peak to higher B.E. than the reported value in literature is caused by two effects: (1) small particle size (there is a positive shift in the Fermi level edge and in the Au 4f core level B.E. which is related to an extrinsically final effect ²⁰), (2) strong interaction of Au–S bonds. For the Pd 3d region, only one doublet at 337 eV and 342.2 eV was found, corresponding to Pd(0) 3d₃/₂, and Pd(0) 3d₅/₂. For the Ag 3d region, only one doublet at 368.1 eV and 374.1 eV was found, corresponding to Ag(0) 3d₃/₂, and Ag(0) 3d₅/₂. For the Pt 4f region, only one doublet at 72.0 eV and 75.3 eV was found, corresponding to Pt(0) 4f½, and Pt(0) 4f½. ²¹ It should be noted that there is overlapping between Pt 4f½ peak and Cu 3p peak, which lead to a higher intensity of the measured Pt 4f½ peak. In all, the B.E. values of the fitting peaks might shift to higher values than those reported in literature, probably due to the small size of the metal clusters and the chemical bonding between thiols and metal clusters.
Binary, Ternary, and Quaternary Metals on TCOS

**Figure S60.** TEM images and the corresponding EDX spectrum of $M_A@TCOS@M_B$ ($M_A = Au$, and $M_B = Au + Pd$) catalyst.

**Comment:** As noted in the EDX spectrum, the Ni element signal originated from the EDX sample holder (viz., Ni grid).

**Figure S61.** HAADF-STEM image and EDX elemental maps of binary Au/Pd nanoclusters loaded on TCOS support.

**Comment:** As shown, both Au and Pd nanoclusters are evenly distributed in the entire TCOS support.
Figure S62. TEM images and the corresponding EDX spectrum of $M_A$@TCOS@$M_B$ ($M_A$ = Au, and $M_B$ = Au +Pd + Ag) catalyst.

**Comment:** As noted, in the EDX spectrum, the Ni element signal originated from the EDX sample holder (viz., Ni sample grid).

Figure S63. HAADF-STEM image and EDX elemental maps of ternary Au/Pd/Ag nanoclusters loaded on TCOS support.

**Comment:** As shown, all of the three nanoclusters (Au, Ag, and Pd) are evenly distributed in the entire TCOS support.
Figure S64. TEM images and the corresponding EDX spectrum of $M_A@TCOS@M_B$ ($M_A = Au$, and $M_B = Au + Pd + Ag + Pt$) catalyst.

Comment: As noted in the EDX spectrum, the Ni element signal originated from the EDX sample holder (viz., Ni grid).
Figure S65. HAADF-STEM image and EDX elemental maps of the quaternary Au/Pd/Ag/Pt nanoclusters loaded on TCOS support.

Comment: As shown, all of the four metal nanoclusters (Au, Ag, Pd and Pt) are evenly distributed in the entire TCOS support.
Catalytic Applications of $M_A@TCOS@M_B$

**Table S4.** Catalytic oxidation of aromatic alcohols catalyzed by $M_A@TCOS@M_B$.

| Catalyst $^a$ | Substrate | Product and selectivity (%) | t (h) | Conv. (%) | TOF $^b$ (h$^{-1}$) |
|---------------|-----------|----------------------------|-------|-----------|---------------------|
| 1 Au          |           | $\text{aryl-OH}$ $\rightarrow$ $\text{aryl-OR}$ | 1     | 92        | 115                 |
| 2 Pd          |           |                            | 1     | 16        | 22                  |
| 3 Pt          |           |                            | 1     | 2         | 0.2                 |
| 4 Ag          |           |                            | 1     | 86        | 127                 |
| 5 Au          |           |                            | 2     | 91        | 45                  |
| 6 Au          | $\text{aryl-OH}$ $\rightarrow$ $\text{aryl-OR}$ | 2     | 91        | 45                  |
| 7 Au          | $\text{aryl-OH}$ $\rightarrow$ $\text{aryl-OR}$ | 5     | 59        | 22                  |
| 8 Au          | $\text{aryl-OH}$ $\rightarrow$ $\text{aryl-OR}$ | 1     | 62        | 59                  |
| 9 Au          | $\text{aryl-OH}$ $\rightarrow$ $\text{aryl-OR}$ | 2     | 94        | 98                  |
| 10 Au         | $\text{aryl-OH}$ $\rightarrow$ $\text{aryl-OR}$ | 2     | 100       | 91                  |

$^a$ For the catalysts of $M_A@TCOS@M_B$ used, $M_A = Au, M_B$ was listed in this column.  
$^b$ TOF = \((\text{molar amount of reacted substrate})/(\text{total molar amount of metal})\times(\text{reaction time})\). The TOFs were measured after first 0.5 h of reaction.  
$^c$ Data was measured at the reaction time of 0.5 h. See more data in Tables S5-S11.
Table S5. Catalytic oxidation of benzyl alcohol by Mₐ@TCOS@M₈ catalysts.

| Catalyst  | Time (h) | Conversion (%) | Selectivity (%) | Selectivity (%) |
|-----------|----------|----------------|----------------|-----------------|
| Au@TCOS@Au | 0.5      | 68.3           | 79.3           | 20.7            |
|           | 1.0      | 92.0           | 66.9           | 33.1            |
| Au@TCOS@Pd | 0.5      | 12.7           | 100.0          | 0.0             |
|           | 1.0      | 16.1           | 100.0          | 0.0             |
| Au@TCOS@Pt | 0.5      | 1.5            | 100.0          | 0.0             |
|           | 1.0      | 1.8            | 100.0          | 0.0             |
| Au@TCOS@Ag | 0.5      | 62.6           | 68.9           | 31.1            |
|           | 1.0      | 86.2           | 69.4           | 30.6            |

*Reaction conditions: benzyl alcohol 1 mmol, hydrogen peroxide 4.4 mmol, water 10 mL, catalyst 30 mg, reaction temperature 85°C, stirring speed 500 rpm. Au loading on the TCOS external surface was 7.78 wt%. Pd loading on the TCOS external surface was 4.16 wt%. Pt loading on the TCOS external surface was 8.77 wt%. Ag loading on the TCOS external surface was 3.55 wt%. The data were calculated based on our ICP tests.

Table S6. Catalytic oxidation of 4-methoxybenzyl alcohol.

| Catalyst  | Time (h) | Conversion (%) | Selectivity (%) | Selectivity (%) |
|-----------|----------|----------------|----------------|-----------------|
| Au@TCOS@Au | 0.5      | 13.1           | 95.6           | 4.4             |
|           | 1.0      | 21.5           | 90.5           | 9.5             |
|           | 3.0      | 50.1           | 69.2           | 30.8            |
|           | 5.0      | 58.8           | 64.2           | 35.8            |

*Reaction conditions: 4-methoxybenzyl alcohol 1 mmol, hydrogen peroxide 4.4 mmol, water 10 mL, catalyst 30 mg, reaction temperature 85 °C, and stirring speed 500 rpm. Au loading on the TCOS external surface was 7.78 wt%.

Table S7. Catalytic oxidation of 4-nitrobenzyl alcohol.

| Catalyst  | Time (h) | Conversion (%) | Selectivity (%) | Selectivity (%) |
|-----------|----------|----------------|----------------|-----------------|
| Au@TCOS@Au | 0.5      | 35.0           | 100.0          | 0.0             |
|           | 1.0      | 62.1           | 100.0          | 0.0             |

*Reaction conditions: 4-nitrobenzyl alcohol 1 mmol, hydrogen peroxide 4.4 mmol, water 10 mL, catalyst 30 mg, reaction temperature 85°C, and stirring speed 500 rpm. Au loading on the TCOS external surface was 7.78 wt%.
### Table S8. Catalytic oxidation of 4-methylbenzyl alcohol.

| Catalyst               | Time (h) | Conversion (%) | Selectivity (%) |
|------------------------|----------|----------------|-----------------|
| Au@TCOS@Au            | 0.5      | 26.9           | 92.2            | 7.8             |
|                        | 1.0      | 50.7           | 80.5            | 19.5            |
|                        | 2.0      | 91.2           | 66.2            | 33.8            |

*a Reaction conditions: 4-methylbenzyl alcohol 1 mmol, hydrogen peroxide 4.4 mmol, water 10 mL, catalyst 30 mg, reaction temperature 85°C, and stirring speed 500 rpm. Au loading on the TCOS external surface was 7.78 wt%.

### Table S9. Catalytic oxidation of cinnamyl alcohol.

| Catalyst               | Time (h) | Conversion (%) | Selectivity (%) |
|------------------------|----------|----------------|-----------------|
| Au@TCOS@Au            | 0.5      | 53.8           | 34.0            | 58.2            | 7.8             |
|                        | 1.0      | 75.9           | 27.7            | 56.7            | 15.6            |
|                        | 2.0      | 100.0          | 10.2            | 63.0            | 26.8            |

*a Reaction conditions: cinnamyl alcohol 1 mmol, hydrogen peroxide 4.4 mmol, water 10 mL, catalyst 30 mg, reaction temperature 85°C, and stirring speed 500 rpm. Au loading on the TCOS external surface was 7.78 wt%.

### Table S10. Catalytic oxidation of 1-phenylethanol.

| Catalyst               | Time (h) | Conversion (%) | Selectivity (%) |
|------------------------|----------|----------------|-----------------|
| Au@TCOS@Au            | 0.5      | 58.1           | 100             |
|                        | 1.0      | 84.8           | 100             |
|                        | 2.0      | 93.9           | 100             |

*a Reaction conditions: 1-phenylethanol 1 mmol, hydrogen peroxide 4.4 mmol, water 10 mL, catalyst 30 mg, reaction temperature 85°C, and stirring speed 500 rpm. Au loading on the TCOS external surface was 7.78 wt%.

### Table S11. Catalytic oxidation of 3-phenyl-1-propanol.

| Catalyst               | Time (h) | Conversion (%) | Selectivity (%) |
|------------------------|----------|----------------|-----------------|
| Au@TCOS@Au            | 0.5      | 10.1           | 42.8            | 57.2            |
|                        | 1.0      | 24.4           | 32.4            | 67.6            |
|                        | 4.0      | 39.0           | 23.8            | 76.2            |
|                        | 5.0      | 42.2           | 16.3            | 83.7            |

*a Reaction conditions: 3-phenyl-1-propanol 1 mmol, hydrogen peroxide 4.4 mmol, water 10 mL, catalyst 30 mg, reaction temperature 85°C, and stirring speed 500 rpm. Au loading on the TCOS external surface was 7.78 wt%.
Figure S66. Catalytic stability of Au@TCOS@Pd (for Suzuki–Miyaura coupling of iodobenzene and phenylboronic acid) and Au@TCOS@Pt (for hydrogenation of \( n \)-hexene), respectively.

Figure S67. TEM images of TCOS supported catalyst after five consecutive runs of Suzuki–Miyaura coupling reaction between iodobenzene and phenylboronic acid.
References

(1) Xiong, S. L.; Zeng, H. C. Serial ionic exchange for the synthesis of multishelled copper sulfide hollow spheres. *Angewandte Chemie International Edition* 2012, 51, 949.

(2) Lu, G.; Li, S.; Guo, Z.; Farha, O. K.; Hauser, B. G.; Qi, X.; Wang, Y.; Wang, X.; Han, S.; Liu, X.; DuChene, J. S.; Zhang, H.; Zhang, Q.; Chen, X.; Ma, J.; Loo, S. C. J.; Wei, W. D.; Yang, Y.; Hupp, J. T.; Huo, F. Imparting functionality to a metal–organic framework material by controlled nanoparticle encapsulation. *Nature Chemistry* 2012, 4, 310.

(3) Daikopoulos, C.; Bourlinos, A. B.; Georgiou, Y.; Deligiannakis, Y.; Zboril, R.; Karakassides, M. A. A functionalized phosphonate-rich organosilica layered hybrid material (PSLM) fabricated through a mild process for heavy metal uptake. *Journal of Hazardous Materials* 2014, 270, 118.

(4) Ni, L.; Chemtob, A.; Croutxe-Barghorn, C.; Brendle, J.; Vidal, L.; Rigole, S. Photoinduced synthesis and ordering of lamellar n-alkylsiloxane films. *Journal of Materials Chemistry* 2012, 22, 643.

(5) Mateo Marti, E.; Methivier, C.; Pradier, C. M. (S)-Cysteine chemisorption on Cu(110), from the gas or liquid phase: An FT-RAIRS and XPS study. *Langmuir* 2004, 20, 10223.

(6) Shimojima, A.; Umeda, N.; Kuroda, K. Synthesis of layered inorganic–organic nanocomposite films from mono-, di-, and trimethoxy(alkyl)silane–tetramethoxysilane systems. *Chemistry of Materials* 2001, 13, 3610.

(7) Parikh, A. N.; Schivley, M. A.; Koo, E.; Seshadri, K.; Aurentz, D.; Mueller, K.; Allara, D. L. n-Alkylsiloxolanes: from single monolayers to layered crystals. The formation of crystalline polymers from the hydrolysis of n-octadecyltrichlorosilane. *Journal of the American Chemical Society* 1997, 119, 3135.

(8) Kaneko, Y.; Iyi, N.; Matsumoto, T.; Fujii, K.; Kurashima, K.; Fujita, T. Synthesis of ion-exchangeable layered polysiloxane by sol-gel reaction of aminoalkyltrialkoxysilane: a new preparation method for layered polysiloxane materials. *Journal of Materials Chemistry* 2003, 13, 2058.

(9) Walker, A. V.; Tighe, T. B.; Cabarcos, O. M.; Reinard, M. D.; Haynie, B. C.; Uppili, S.; Winograd, N.; Allara, D. L. The dynamics of noble metal atom penetration through methoxy-terminated alkanethiolate monolayers. *Journal of the American Chemical Society* 2004, 126, 3954.

(10) Bourg, M.-C.; Badia, A.; Lennox, R. B. Gold–sulfur bonding in 2D and 3D self-assembled monolayers: XPS characterization. *The Journal of Physical Chemistry B* 2000, 104, 6562.

(11) Yoshitake, H.; Nakajima, H.; Oumi, Y.; Sano, T. Control of spacing between aminoalkyl functions by mesostructural transition in a polysilsesquioxane lamellar assembly. *Journal of Materials Chemistry* 2010, 20, 2024.

(12) Brust, M.; Blass, P. M.; Bard, A. J. Self-assembly of photoluminescent copper(I)–dithiol multilayer thin films and bulk materials. *Langmuir* 1997, 13, 5602.

(13) Pang, M.; Wang, Q.; Zeng, H. C. Self-generated etchant for synthetic sculpturing of Cu2O-Au, Cu2O@Au, Au/Cu2O, and 3D-Au nanostructures. *Chemistry – A European Journal* 2012, 18, 14605.

(14) Biesinger, M. C.; Lau, L. W. M.; Gerson, A. R.; Smart, R. S. C. Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn. *Applied Surface Science* 2010, 257, 887.

(15) Nagase, K.; Zheng, Y.; Kodama, Y.; Kakuta, J. Dynamic study of the oxidation state of copper in the course of carbon monoxide oxidation over powdered CuO and Cu2O. *Journal of Catalysis* 1999, 187, 123.

(16) Iwata, T.; Tokutomi, S.; Kandori, H. Photoreaction of the cysteine S-H group in the LOV2 domain of adiantum phytochrome3. *Journal of the American Chemical Society* 2002, 124, 11840.

(17) Zhang, Y. X.; Zeng, H. C. Gold(I)-alkanethiolate nanotubes. *Advanced Materials* 2009, 21, 4962.

(18) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. Periodic mesoporous organosilicas with organic groups inside the channel walls. *Nature* 1999, 402, 867.

(19) Song, K. C.; Park, J. K.; Kang, H. U.; Kim, S. H. Synthesis of hydrophilic coating solution for polymer substrate using glycidoxypropyltrimethoxysilane. *Journal of Sol-Gel Science and Technology* 2003, 27, 53.
(20) Felten, A.; Bittencourt, C.; Pireaux, J. J. Gold clusters on oxygen plasma functionalized carbon nanotubes: XPS and TEM studies. *Nanotechnology* **2006**, *17*, 1954.

(21) Liu, Z.; Gan, L. M.; Hong, L.; Chen, W.; Lee, J. Y. Carbon-supported Pt nanoparticles as catalysts for proton exchange membrane fuel cells. *Journal of Power Sources* **2005**, *139*, 73.