Gold nanoparticles stabilized by an amphiphilic pillar[5]arene: preparation, self-assembly into composite microtubes in water, and application in green catalysis

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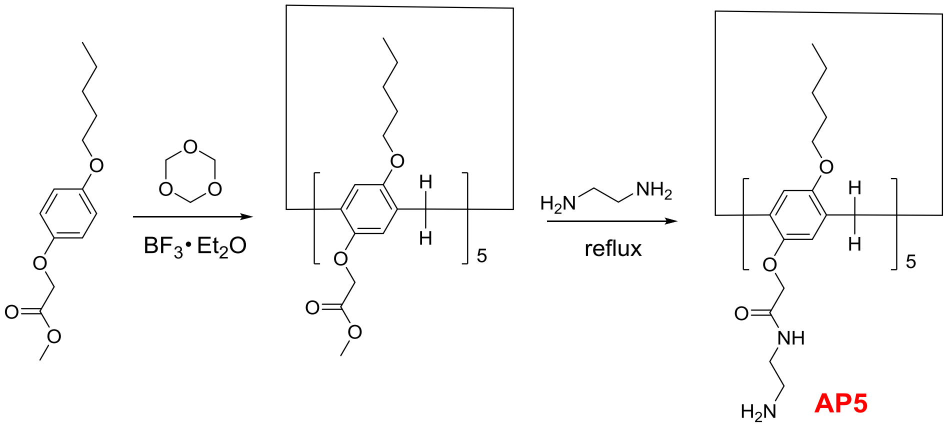
Electronic Supplementary Information

1. Materials and methods

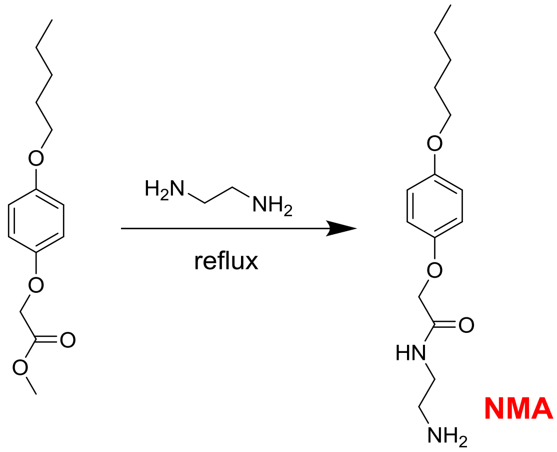
Hydroquinone, methyl chloroacetate, bromopentane, boron trifluoride diethyl etherate, ethanediamine, 1,2-dichloroethane, $HAuCl_4$, and ascorbic acid were reagent grade and used as received. Solvents were either employed as purchased or dried according to procedures described in the literature. **AP5** was reported previously.[S1] UV–Vis spectroscopy was measured on a Shimadzu UV-2501 PC UV–Vis spectrometer. The spectral background absorption was subtracted by means of the UV–Vis spectrum of water. Thermal gravimetric analysis (TGA) was recorded on a PerkinElmer Pyris 1 instrument. FT-IR spectra were taken with potassium bromide pellets on a TENSOR 27 spectrometer. The TEM images were obtained using a JEM-1200EX instrument with an accelerating voltage of 80 kV. The ultrathin section of microtube was placed on copper grids coated with formavar. SEM was applied to investigate the morphology, which was carried out with a Hitachi S-4800 field emission scanning electron microscopy. The SEM samples were prepared on clean Si substrates. Each sample solution was deposited onto a Si substrate, placed in a refrigerator for 30 min, and freeze-dried in a freeze-drying machine at −20 °C under reduced pressure. XRD data were obtained with a graphite monochromatic device and Cu Kα radiation (λ = 0.15406 nm) on the D8 Advance superspeed powder diffractometer (Bruker), operated in the θ:2θ mode primarily in the 20–85 ° (2θ) range and step-scan of 2θ = 0.04 °. The tube voltage was 80 kV, and the tube current was 200 mA.

*2. Syntheses of **AP5** and **NMA***[S1]

Scheme S1. Synthetic route to amphiphilic pillar[5]arene **AP5**



Scheme S2. Synthetic route to noncyclic monomeric analog **NMA**.



3. *Preparation of **AP5**-stabilized gold nanoparticles*

In a typical experiment, 0.10 mL of 1.0 × 10^{-4} M $HAuCl_4$ and 6.0 mL of **AP5** aqueous solution (the values of [**AP5**]/[$HAuCl_4$] were 0.100, 0.500, 2.00, 10.0, and 100) were mixed in a 10 mL bottle. Then 0.20 mL of 1.0 × 10^{-2} M ascorbic acid was added into the above solution. The reaction mixture was allowed to proceed at 80 °C for 1 h, and the **AP5**-stabilized gold nanoparticles were obtained.

4. *FT-IR spectra of **AP5**-stabilized gold nanoparticles and pure **AP5***

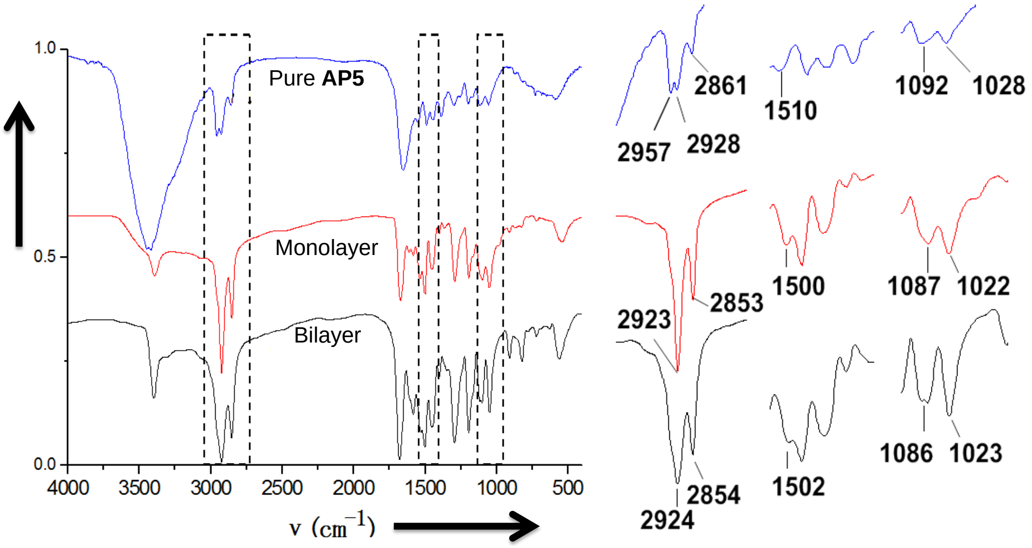


Fig. S1 FT-IR spectra of pure **AP5**, monolayer **AP5**-stabilized GNPs, and bilayer **AP5**-stabilized GNPs.

Water-soluble gold nanoparticles (GNPs), choloform-soluble GNPs and pure **AP5** were dried under vacuum and then taken with potassium bromide pellets on a TENSOR 27 spectrometer. The features of pure **AP5**'s spectrum in the region of 3000–2800 cm^{-1} are similar to that of surface-bound **AP5** molecules on GNPs. However, in the case of surface-bound molecules, for either water-soluble or chloroform-soluble GNPs, the peak positions shifted slightly to lower frequencies.

5. *TGA study of* ***AP5****-stabilizied gold nanoparticles*

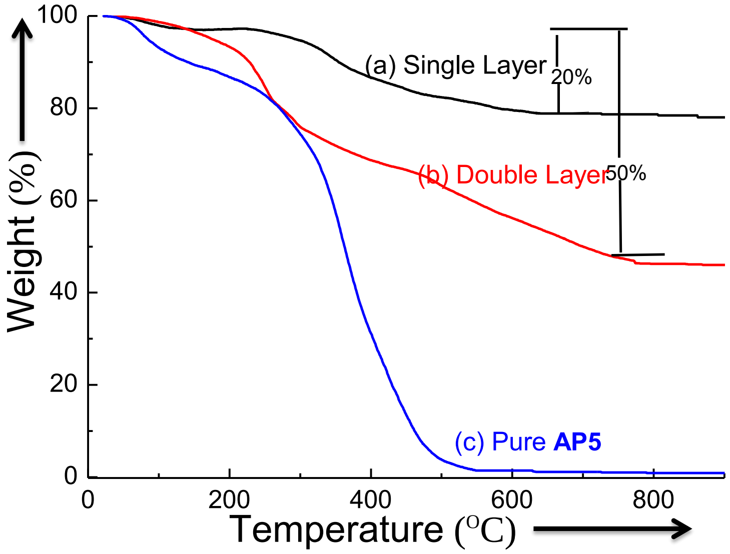


Fig. S2 TGA spectra of **AP5**-stabilizied gold nanoparticles and pure **AP5**.

6. ***NMA*-stabilizied gold nanoparticles**

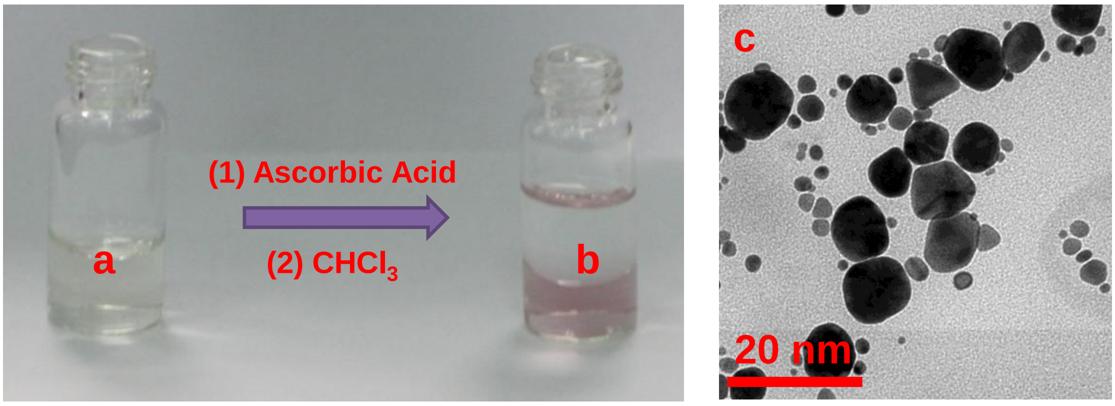


Fig. S3. Photograph showing the **NMA**-stabilized gold nanoparticles transferred into the chloroform phase: (a) the aqueous solution of **NMA** and $HAuCl_4$; (b) gold nanoparticles transferred into the chloroform phase. (c) TEM image of **NMA**-stabilized gold nanoparticles.

7. *Self-assembly of colloidal molecules*

Fig. S4 Photographs showing the colloidal molecules adsorbed on the surfaces of **AP5**-based microtubes: (a) the **AP5**-based microtubes were immersed into a solution of water-soluble gold nanoparticles; (b) two weeks after the microtubes were immersed.

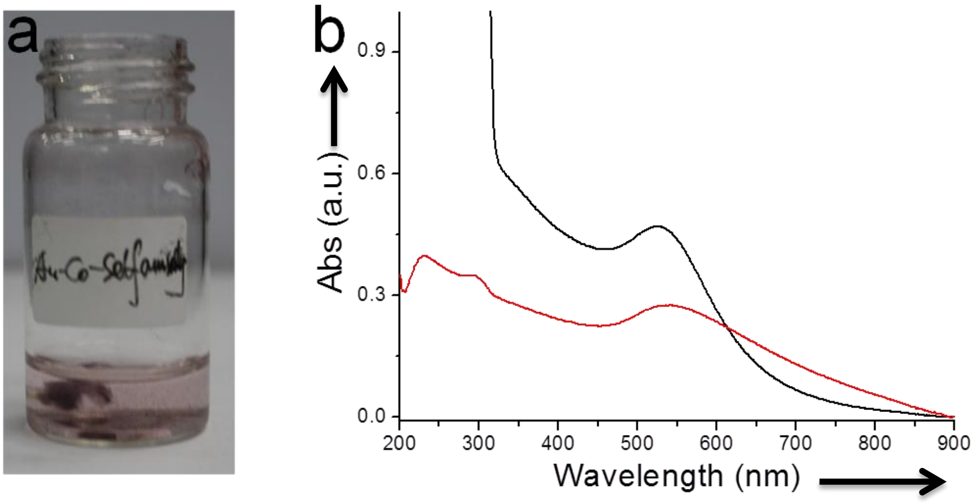


Fig. S5 (a) Optical picture of the self-assembled composite floccules (2 months after preparation); (b) UV–Vis spectra of the **AP5**-stabilized gold nanoparticles before (black line) and after (red line) self-assembly in water. The UV–Vis absorption intensity decrease indicated the decrease of free gold nanoparticles in water after self-assembly.

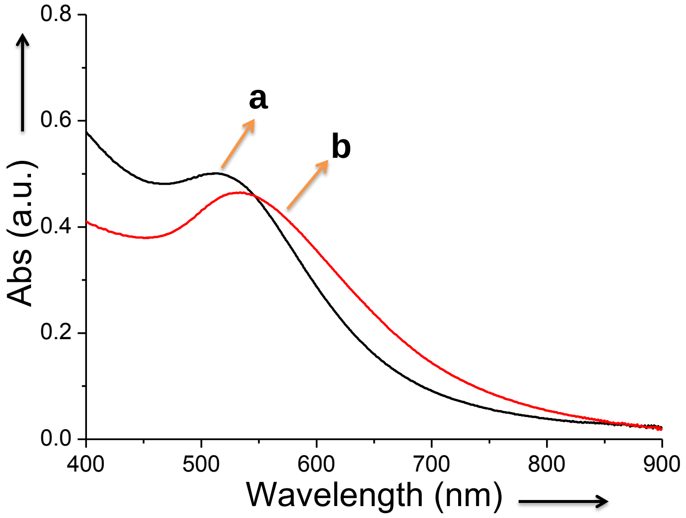


Fig. S6 UV–Vis spectra: (a) self-assembled composite microtubes; (b) gold nanoparticles.

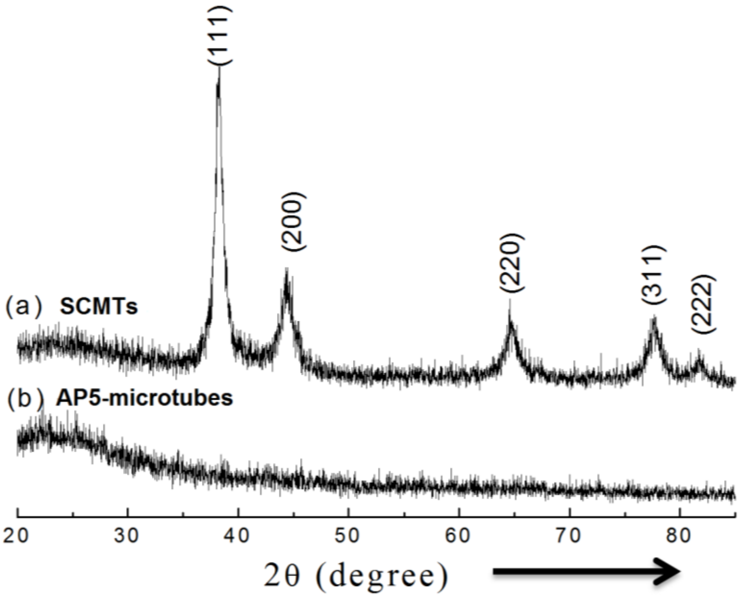


Fig. S7 Powder XRD pattern of self-assembled composite microtubes and **AP5-microtubes**.

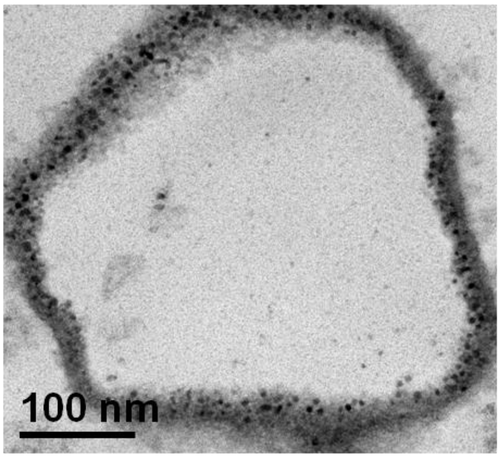


Fig. S8 TEM image of the cross-section of a single self-assembled composite microtube.

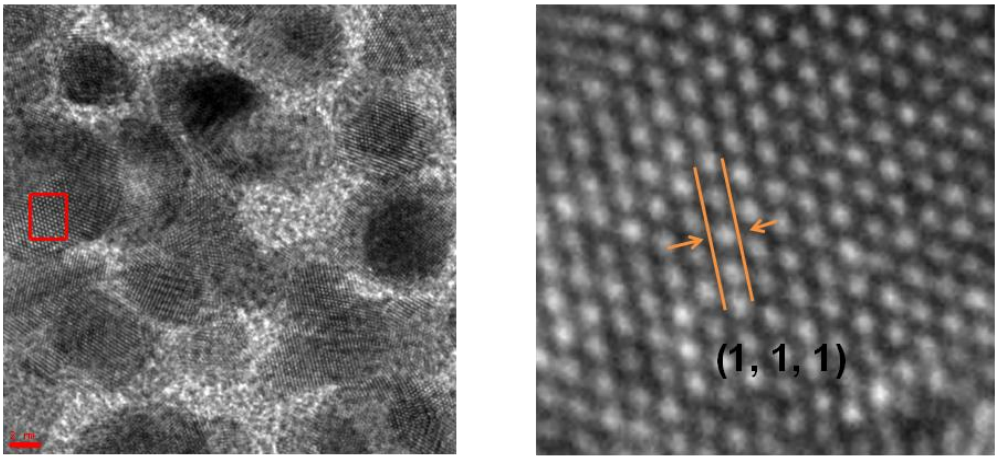


Fig. S9 High-resolution TEM image of gold nanoparticles stabilized by **AP5** on the surfaces of the self-assembled composite microtubes. The marked inter-planar d spacing is 0.235 nm, which are consistent with the inter-planar distance of (111) plane.[S2]

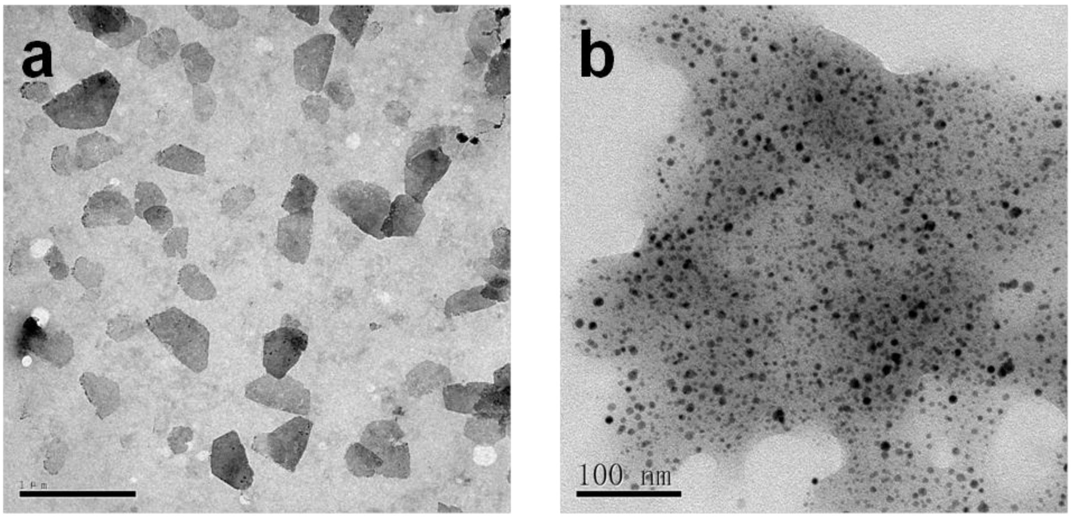


Fig. S10. (a) TEM image of sheet-like structures prepared from self-assembly of water-soluble gold nanoparticles in water; (b) enlarged image of a.

8. Study of the stability of the two types of composite microtubes

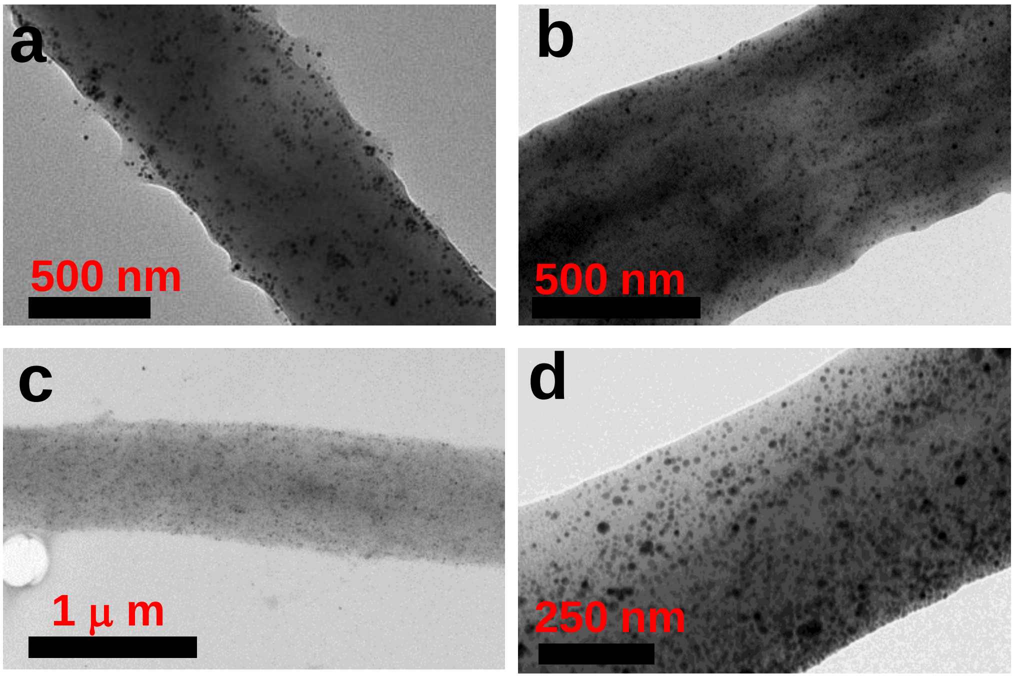


Fig. S11 TEM images of a single self-assembled composite microtube treated (a) at high temperature (> 100 °C), (b) with strong acid (pH < 1), (c) with base (pH > 14), and (d) under sonication more than 1 hour.

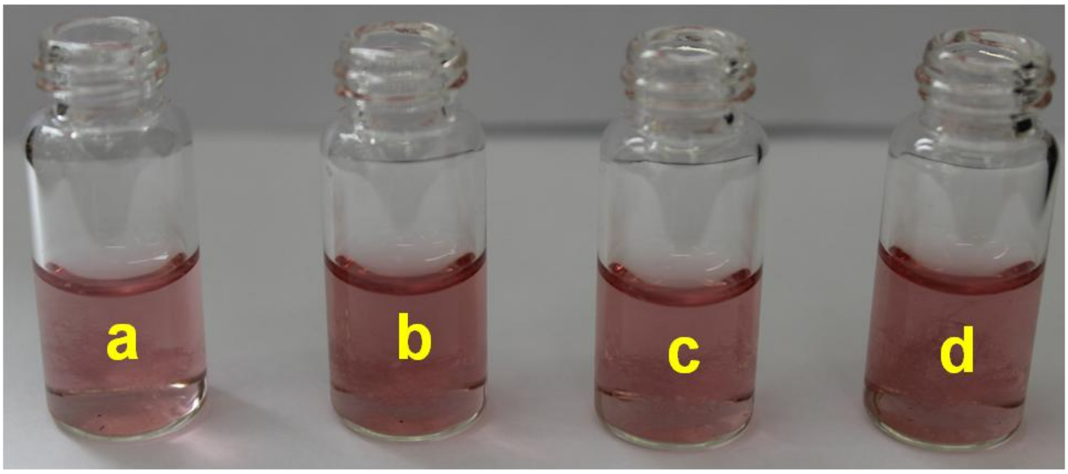
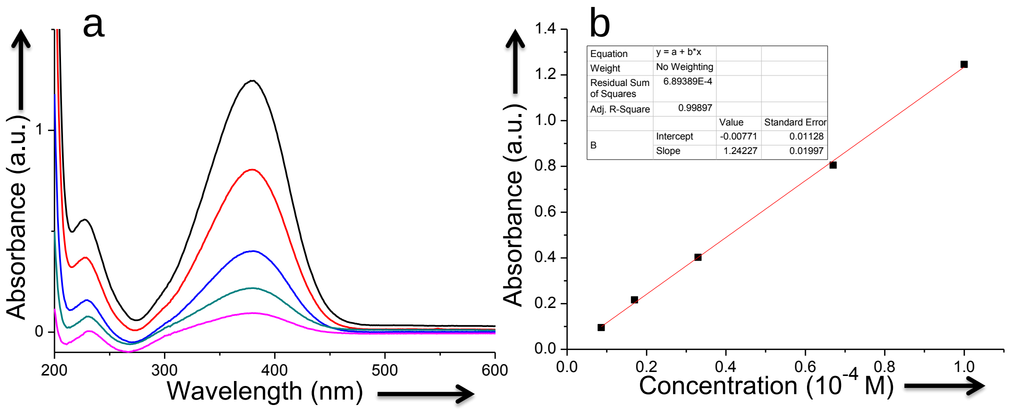


Fig. S12 Optical picture of the template composite microtubes treated (a) at high temperature (> 100 °C), (b) with strong acid (pH < 1), (c) with base (pH > 14), and (d) under sonication more than 1 hour. The wine color of the solutions indicated that gold nanoparticles originally decorating the surfaces of template composite microtubes left the microtube templates.

9. *Applications of composite microtubes*



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	6.89389E-4		
Adj. R-Square	0.99897		
		Value	Standard Error
B	Intercept	-0.00771	0.01128
	Slope	1.24227	0.01997

Fig. S13 (a) Successive UV–Vis spectra of *p*-nitroaniline at different concentrations in water and (b) plot of the characteristic absorption of *p*-nitroaniline against concentration. A = 1.2423 C – 0.0077 (A is absorbance and C is the concentration).

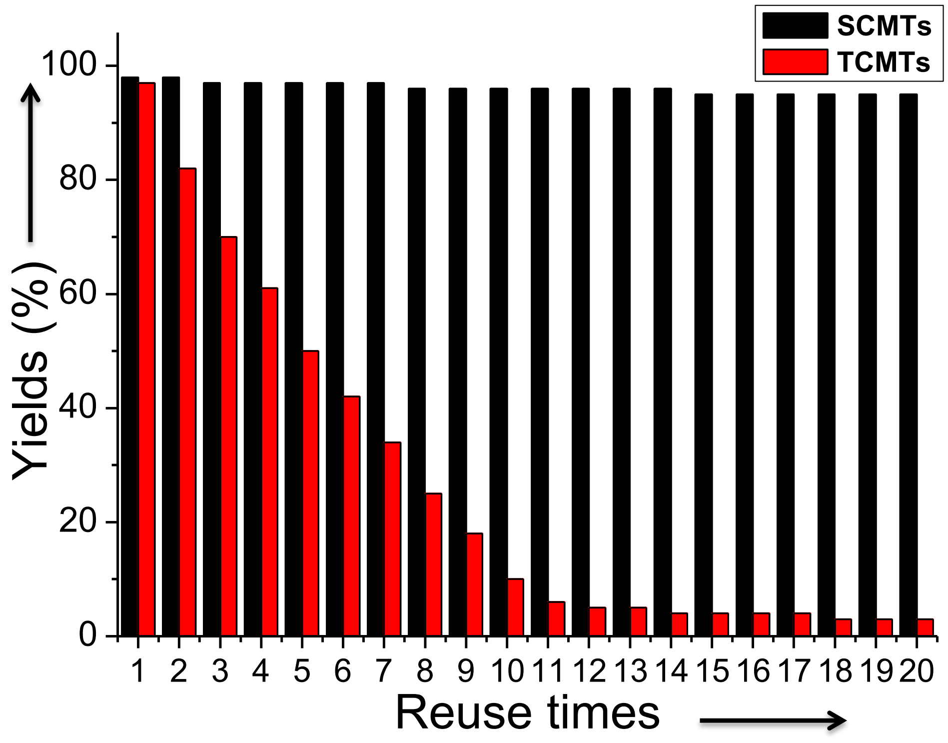


Fig. S14 Catalytic yields of **TCMTs** and **SCMTs** against reuse times.

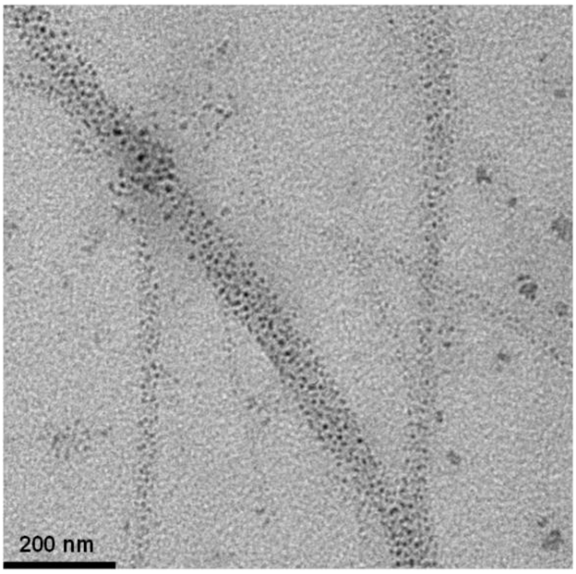


Fig. S15 TEM image of the self-assembled composite microtubes after reuse for 20 times.

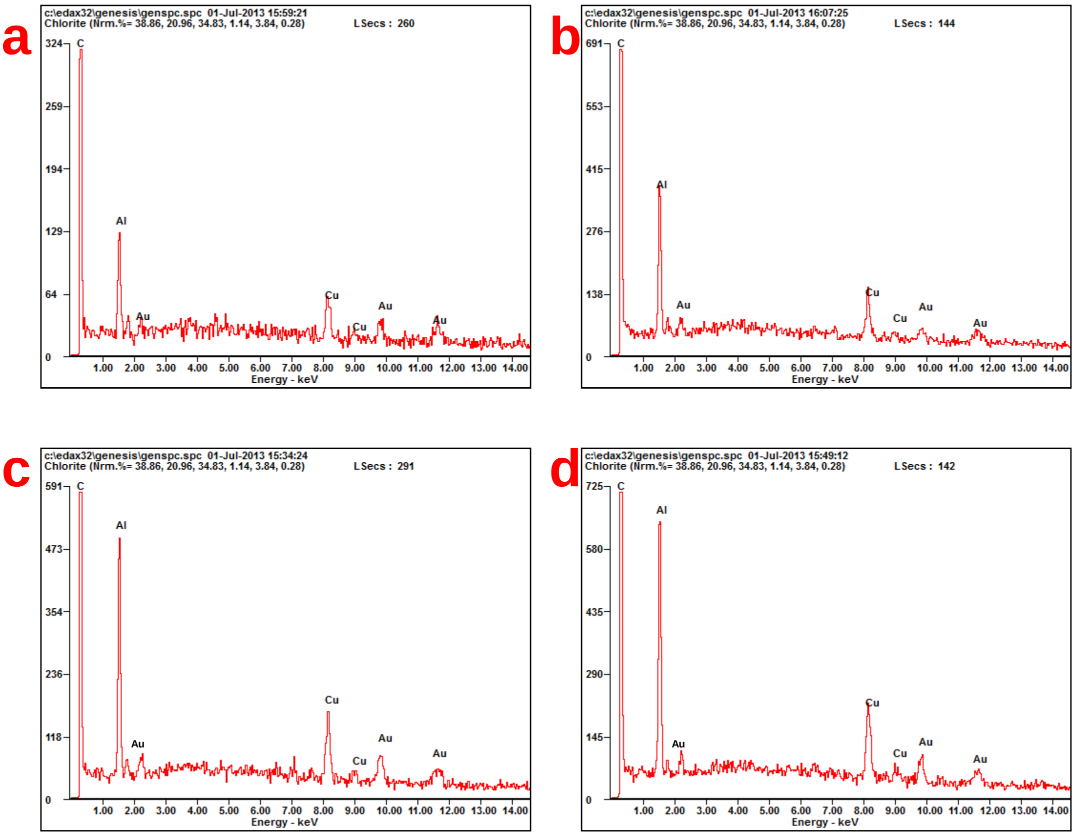


Fig. S16 EDS studies of the self-assembled composite microtubes treated (a) at high temperature (> 100 °C), (b) with strong acid (pH < 1), (c) with base (pH > 14), and (d) under sonication more than 1 hour. Cu and C are from copper grids and Al is from the sample holder.

References:

S1. Y. Yao, M. Xue, J. Chen, M. Zhang and F. Huang, *J. Am. Chem. Soc.* 2012, **134**, 15712.

S2. Y. Yao, M. Xue, X. Chi, Y. Ma, J. He, Z. Abliz and F. Huang, *Chem. Commun.* 2012, **48**, 6505.