Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Role of Au–Sn Bonding for Stabilizing Gold Nanocatalyst: A Reinvestigation of Purple of Cassius

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Computational details

The Au(111) surface was cleaved as a slab model containing 48 Au atoms. During the simulation, the top two layers of the surface were fully relaxed, while the bottom layer was fixed. Periodic boundary condition was employed to represent the surface structure of Au nanoparticles. A vaccum gap of 16 Å was inserted to avoid the interaction between adjacent slabs. Density functional theory (DFT) with the exchange-correlation functional proposed by Perdew, Burke and Ernzerhof (PBE) (Phys. Rev. Lett. 1996, 77, 3865-3868.) with the spin-polarization scheme was used for the electronic structure calculations. The core electrons was treated by the projector augmented wave (PAW) method (*Phys. Rev. B* **1999**, *59*, 1758-1775.), and the valence orbitals were described with a plane-wave basis set with a cutoff energy of 400 eV. Electronic energies were calculated using a self-consistent-field (SCF) with the tolerance of 10^{-4} eV. The surface was fully equilibrated until the total energy of the system converged to within 10^{-3} eV. The Brillouin zone integration was treated with a 2 × 2× 1 Monkhorst–Pack *k*-point mesh. (*Phys. Rev. B* **1976**, *13*, 5188-5192.) All calculations were performed using the Vienna ab initio simulation package (VASP). (*Phys. Rev. B* **1996**, *54*, 11169-11186.)

X-ray absorption spectroscopy (XAS) analysis.

XAS measurements were performed in Beijing Synchrotron Radiation Facility (BSRF, station 1W1B). The fluorescence mode was employed for the benefit of improved elemental sensitivity. Au foil was measured for reference. The XAS processing and fitting were performed using the WinXAS 3.1 software and FEFF8.2 computer code. A *k*-range of 3 to 12 Å^{-1} was used for the Fourier transformation of all *k*-space data to R-space. And a range from 1.5 to 3.5 Å in R-space was fitted by Au-Au shell and Au-Sn shell. The former shell was generated from FEFF code using a first coordination shell of Au atom from Au foil. And the second shell was generated from a Au-Sn bimetallic complex.

d-hole count

The absorption edge E_0=11921 eV is for all samples. The bonding induced charge transfer was estimated from the increased white line area. The specific steps are as follows: 1, Au L_3 spectra of Au foil and Au@Sn-2 were shifted to a coincidence of E_0; 2, the Au foil spectrum was subtracted from that of Au@Sn-2; 3, integrate the area of the difference spectrum to the first zero crossing or the minimum. The result in unit of eV can be changed to transferred electron by using a rough calibration of 3 eV for one electron.

A theoretical model of Au nanoparticle

The model shown in Figure S6 is generated by using a software Diamond. It has a shape of cuboctahedron with a diagonal of about 2.3 nm. Such a size is very close to that of Au@Sn-2 (2.4 nm). Thus a rough comparison of the physical parameters extracted from EXAFS fitting with the model can be made. In this model, there are 309 Au atoms, between which 1491 Au–Au bonds are formed. Thus, the average coordination number (**CN**) of Au–Au shell should be (1490×2÷309)=9.65. There are 162 surface Au atoms in this model. If each of them is coordinated with one Sn ligand, there will be 162 Au–Sn bonds. Then the average **CN** of Au–Sn is 162÷309=0.52. These values are discussed in manuscript.

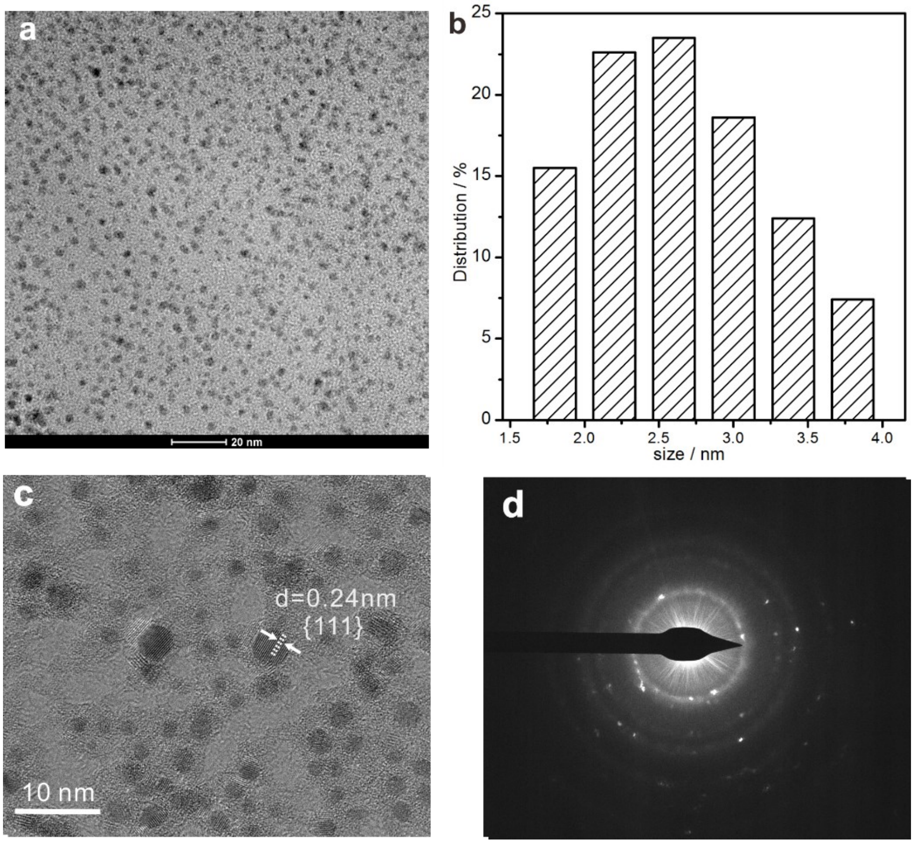

Figure S1. a) TEM image of Au@Sn-1. The scale bar is 20 nm. b) the size distribution histogram. c) The high-resolution TEM. d) Selective area electron diffraction image.

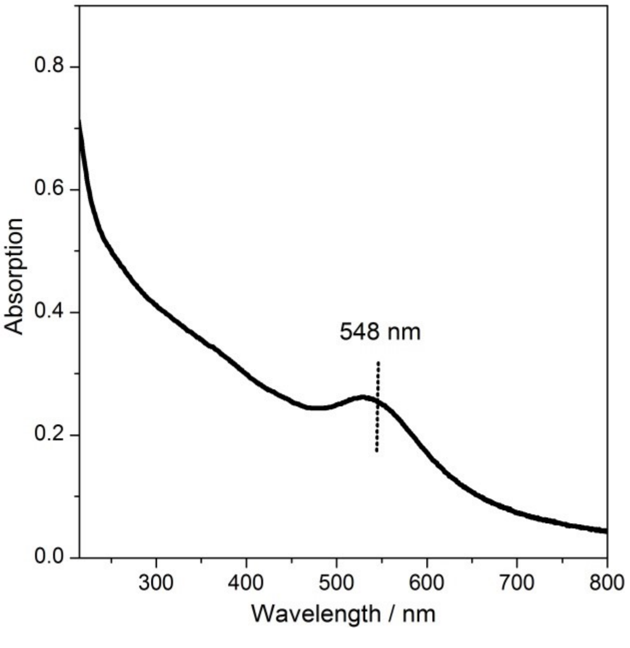

Figure S2. A typical UV-Vis spectrum of Au@Sn.

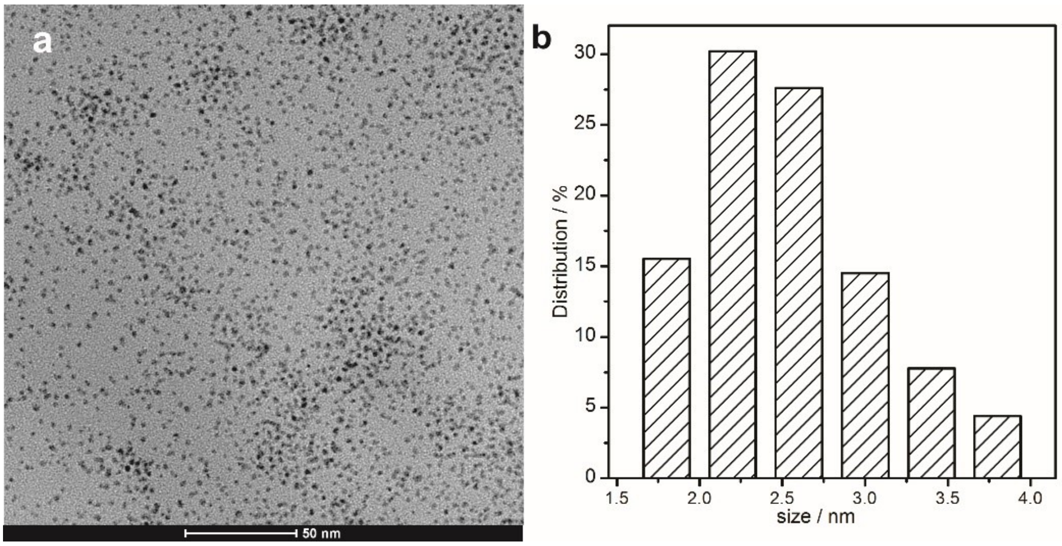

Figure S3. a) TEM image of Au@Sn-2 and b) the size distribution histogram. The scale bar is 50 nm.

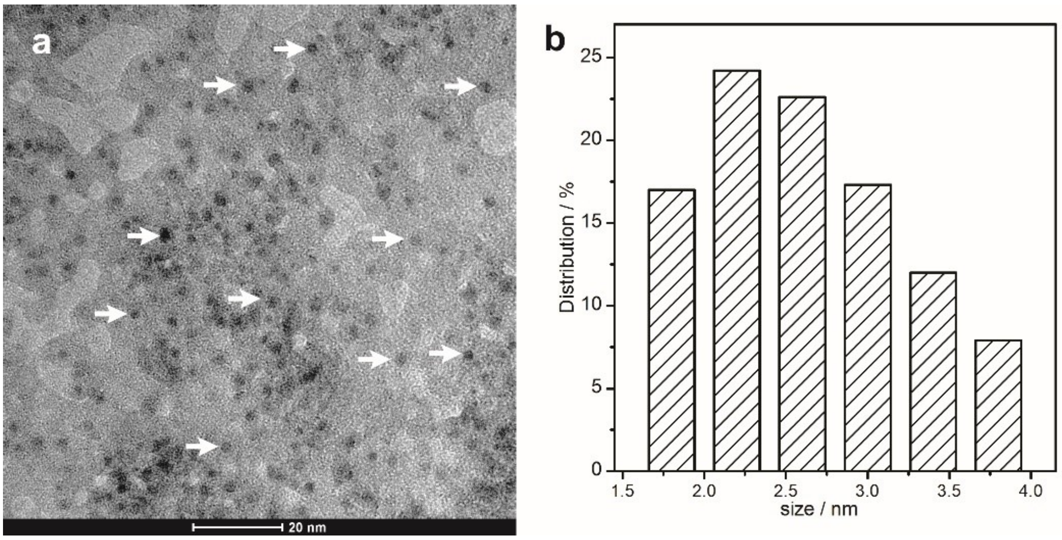

Figure S4. a) TEM image of Au@Sn synthesized in H_2O (Au:Sn =1:3). The scale bar is 20 nm. Arrows indicate Au nanoparticles. b) Size statistics (average diameter is 2.9 nm). The poor resolution is caused by the presence of $Sn(OH)_x$ from Sn^{2+} hydrolysis.

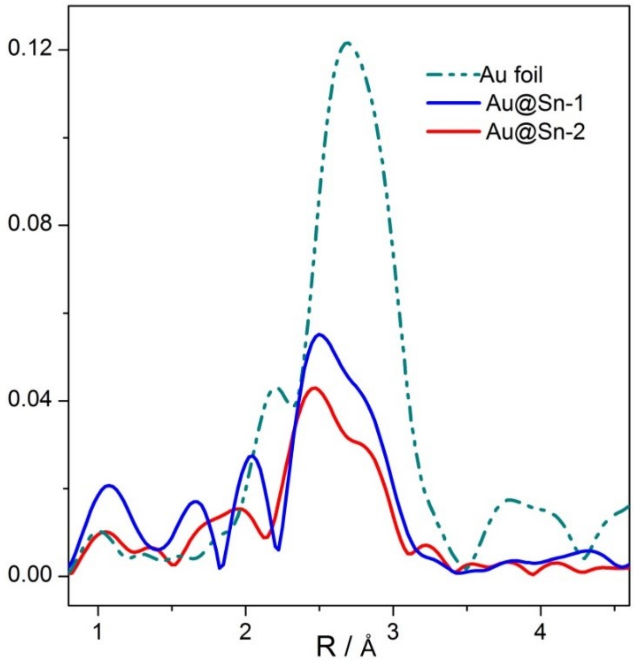

Figure S5. An amplitude comparison of EAXFS spectra of Au foil, Au@Sn-1 and Au@Sn-2.

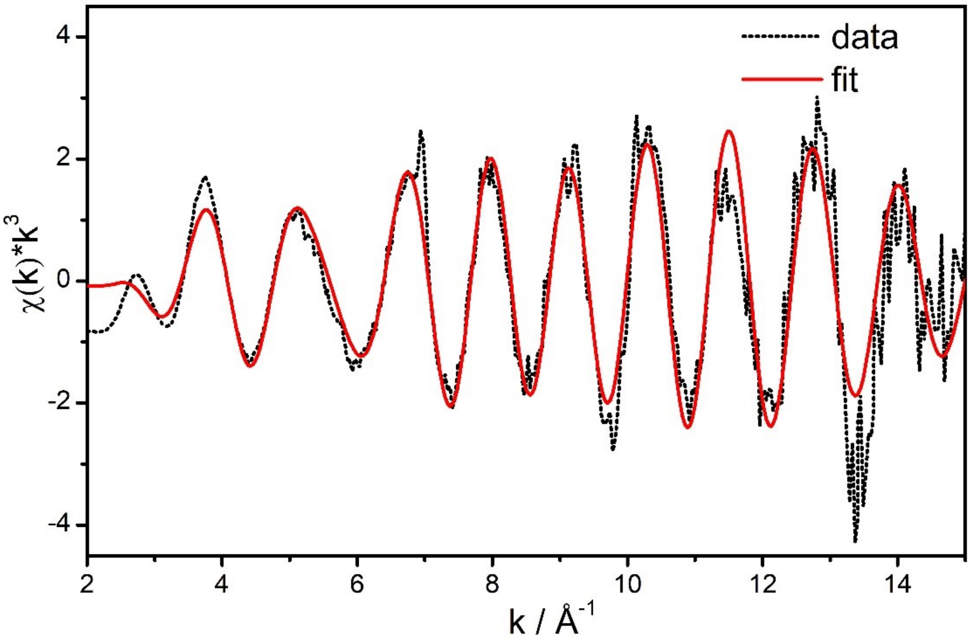

Figure S6. Two-shell fitting of Au@Sn-2 in k-space.

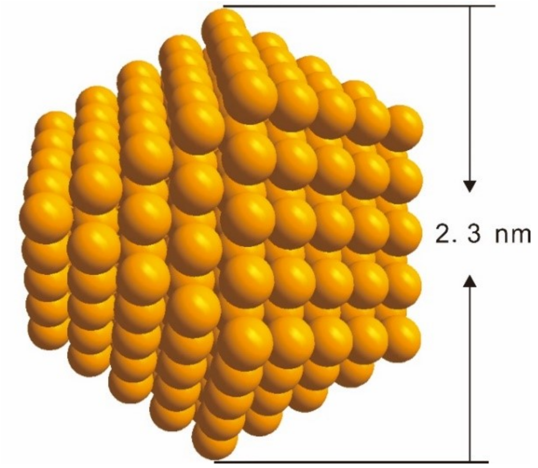

Figure S7. A model of a cuboctahedron Au nanoparticle which has 309 atoms. The analysis on it is in the above section “A theoretical model of Au nanoparticle”.

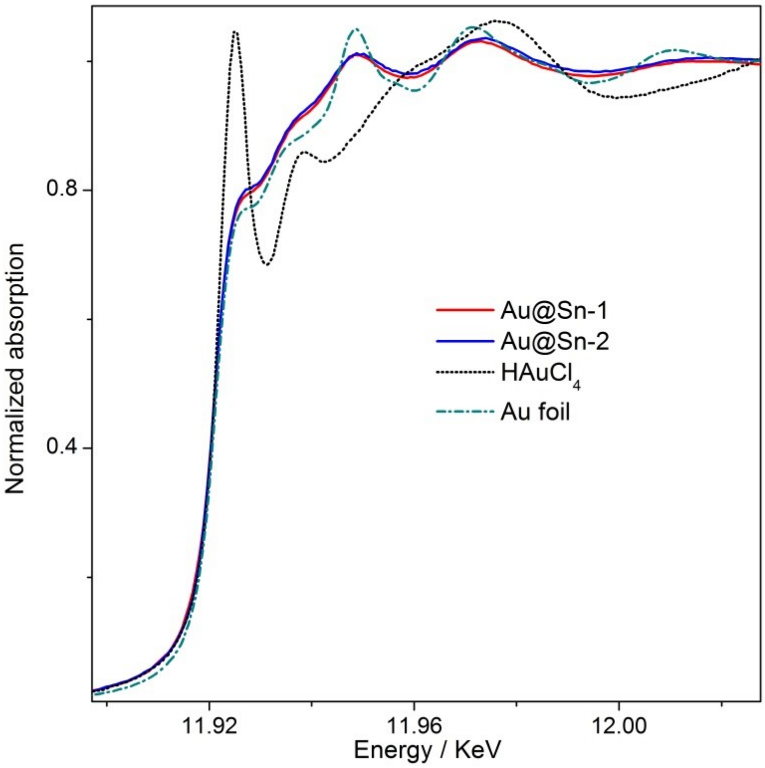

Figure S8. XANES spectra of HAuC$_{l4}$, Au foil, Au@Sn-1 and Au@Sn-2.

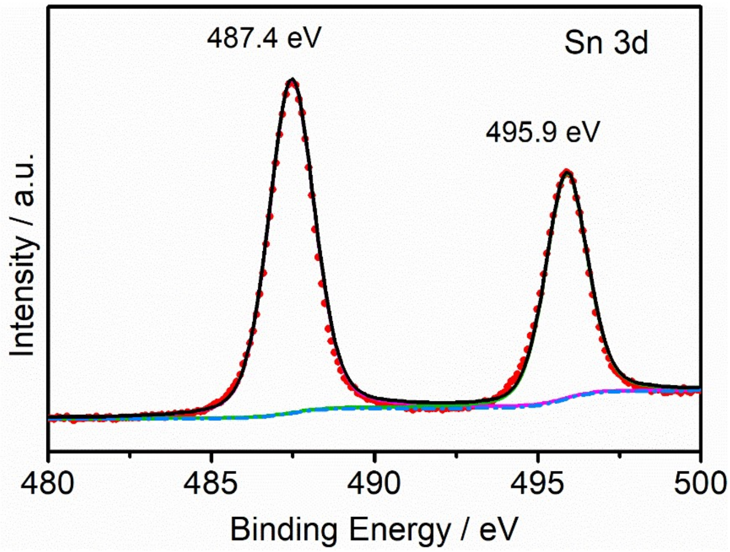

Figure S9. The high-resolution Sn 3d XPS spectrum.

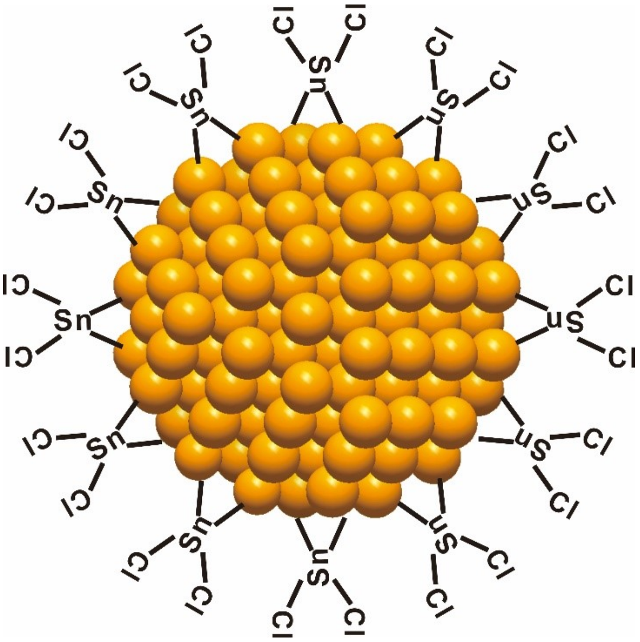

Figure S10. A proposed model of Au@Sn.

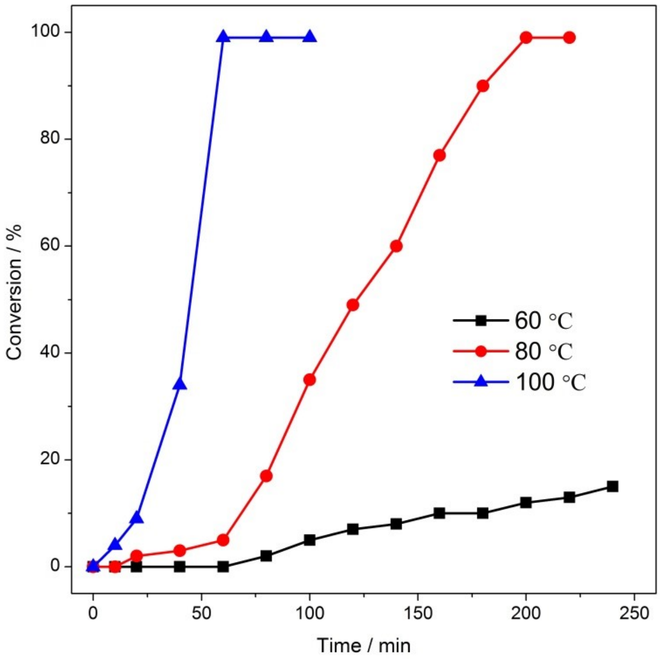

Figure S11. Conversion of phenylacetylene as a function of time and temperature. Reaction conditions: 5 mL methanol, catalyst Au@Sn-2, 0.05 mmol Au, 2.5 mmol phenylacetylene, 200 µL of H_2O.

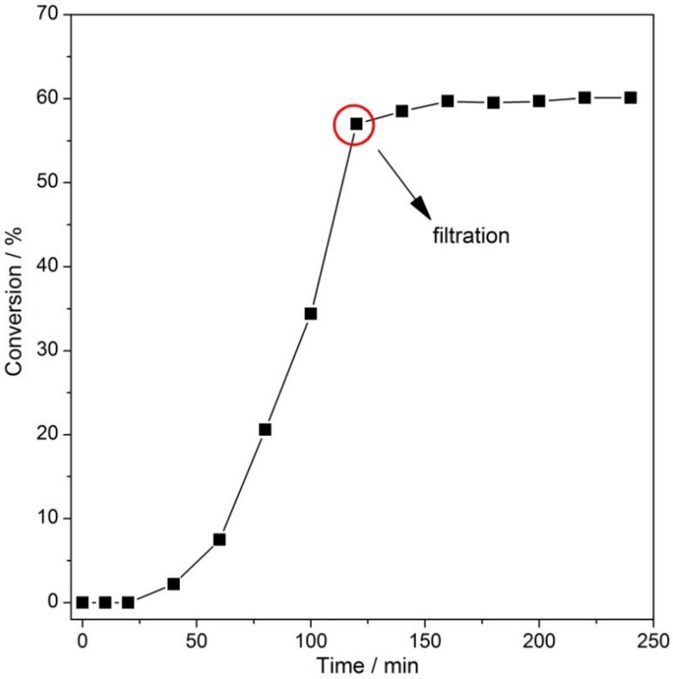

Figure S12. Hot-filtration experiment in Au@Sn-2 catalyzed hydration of phenylacetylene.

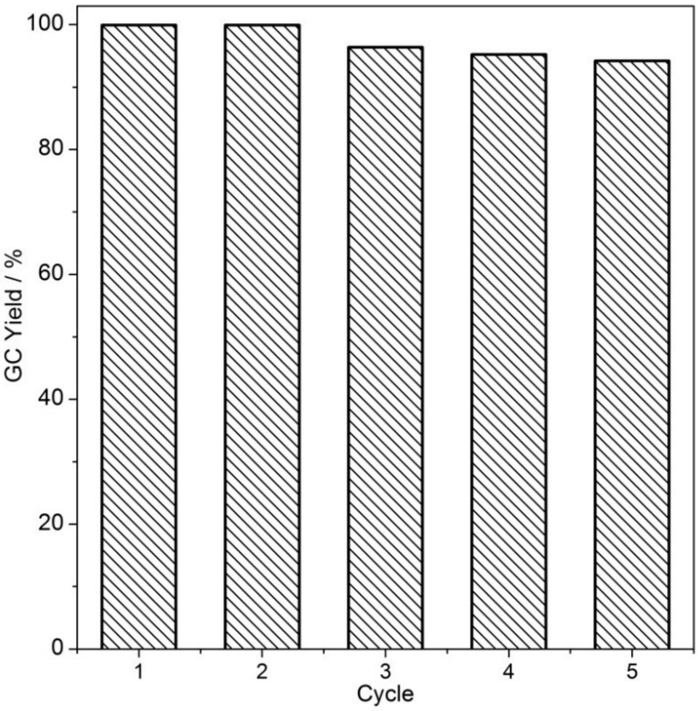

Figure S13. Recycling of Au@Sn-2 in hydration of phenylacetylene.

Figure S14. The setup for the alkyne hydration catalyzed by Au@Sn.