Supplementary Information for

Highly Efficient and Selective Photocatalytic Hydroamination of Alkynes by Supported Gold Nanoparticles Using Visible Light at Ambient Temperature

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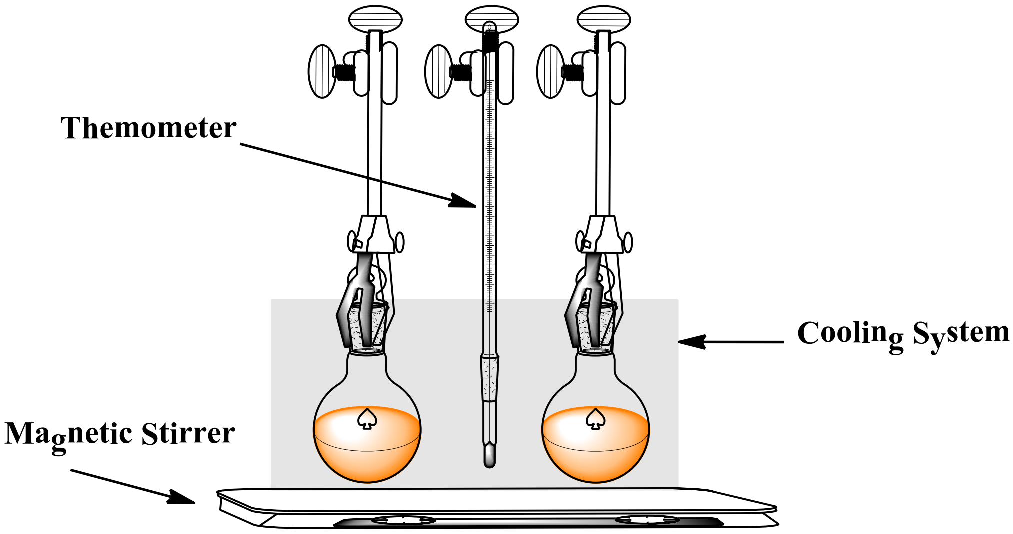
Experimental Details

Supports preparation: All chemicals were used as purchased from Sigma Aldrich (except P25 that was from Degussa, Germany) without further purification. Supports such as CeO_2 (50 nm BET), ZrO_2 (< 100 nm TEM), Fe_2O_3 (< 5 micron), Al_2O_3 (~100 mesh) were used as purchased from Sigma Aldrich. The nanofibre supports of TiO_2 based materials including TiO_2(B), TiO_2(anatase), and nitrogen doped TiO_2(B) nanofibres were synthesized through various post treatment of hydrogen titanate ($H_2Ti_3O_7$) fibers. Generally, 6 g of anatase particles (~325 mesh from Aldrich) was mixed with 80 mL of 10 M NaOH. The suspensions were sonicated in an ultrasonic bath for 0.5 h and then transferred into an autoclave with a PTFE container inside. The autoclave was maintained at hydrothermal temperature of 180 °C for 48 h. The precipitate (sodium titanate nanofibres) was recovered, washed with distilled water (to remove excess NaOH), exchanged with H^+ (using a 0.1 M HCl solution) to produce $H_2Ti_3O_7$ nanofibres, and washed again in with distilled water until pH~7 was reached. The $H_2Ti_3O_7$ nanofibre product was dried at 80 ^oC for 12 h. TiO_2(B) nanofibres was obtained by calcining the hydrogen titanate fibres at 723 K for 3 h. TiO_2(anatase) nanofibres support was synthesized by the hydrothermal reaction of H-titanate with dilute (0.05 M) HNO_3 solution for 62 h and then calcining at 723 K for 3 h. Nitrogen doped TiO_2(B) nanofibres (with trace amount of anatase) were obtained by calcining H-titanate nanofibres at 550 ^oC in ammonia gas flow for 3 h, and denoted as TiO_{2}-N or TiO_2(B)-N.

Photocatalysts preparation: A reduction method was used to load AuNPs on to the different supports. Briefly, 2.5 g of support powder was dispersed into 100 mL of a given concentration of $HAuCl_4$ solution. 20 mL of 0.53 M lysine was added under magnetic stirring and the stirring continued for 30 min. To this suspension, 10 mL of 0.35 M $NaBH_4$ solution was then slowly added. Following this, 10 mL of 0.3 M hydrochloric acid was added and the mixture was allowed to stand for 24 h. Finally, the solid formed was separated, washed with deionized water and ethanol, and dried at 70 °C. The prepared AuNPs on different supports were denoted as Au/TiO_2(anatase), Au/CeO_2, Au/Al_2O_3, etc.

Photocatalytic reduction test: Hydroamination of alkynes was undertaken in argon atmosphere at 40 °C unless otherwise specified. In a typical reaction, 2 mmol alkyne and 2 mmol amine were dissolved into 2 mL toluene, into which 0.10 g photocatalyst was added. The flask was then filled with argon for 1 min to eliminate the air. After that, the reaction mixture was illuminated with visible light (500 W Halogen Lamp, light intensity was tested to be 0.43 W/cm^2) for 25 h under magnetic stirring. Due to the low energy consumption of LEDs, the photocatalytic hydroamination of 4-phenyl-1-butyne for Au/TiO_2(B) was also conducted using LED as light source while keeping other reaction conditions unchanged (The conversion achieved 45% after the reaction of 6 h). Fans or an air conditioner were used to keep the temperature during the reaction to be 40 °C. The liquid products were filtered and analyzed using an Agilent HP-6890 GC with a HP-5 column.



The irradiating light source coming from Halogen lamp put in the front of reaction systems, behind the reaction systems is the cooling system (fans or/and air conditioner). Thermometer was used to monitor the reaction temperature during the reaction. The cooling system was adjusted to maintain the temperature at 40 °C and the reaction flasks were put into the system after the temperature kept stable.

Characterization: Transmission electron microscopic (TEM) images were taken with a Philips CM200 Transmission electron microscope employing an accelerating voltage of 200 kV. The UV-Vis diffuse reflectance spectra of the samples were recorded on a Cary 5000 UV-Vis-NIR

Spectrophotometer. The Raman spectra of the samples were measured on inVia Renishaw microscope Raman, the excitation source was He-Ne laser (785 nm). FT-IR measurements were conducted on NEXUS 870 FT-IR (SMART ENDURANCE), Thermo Nicolet, and the IES measurements on a Digilab FTS-60A spectrometer equipped with a TGS detector, which was modified by replacing the IR source with an emission cell.

Table S1. Photocatalytic hydroamination of 4-phenyl-1-butyne by different gold contents on TiO_{2}-N

Sample	Conv. (%)[a]	d. (nm)[b]	S_{Au}. (m^2/g)[c]	S_{Au}. (m^2)[d]
1wt%Au/TiO_2-N	67	4.6	73	0.7
2wt%Au/TiO_2-N	71	5.0	68	1.4
3wt%Au/TiO_2-N	90	5.1	66	2.0

[a] Conversion of 4-phenyl-1-butyne determined by GC analysis. [b] Average diameter of AuNPs, estimated from more than 200 AuNPs in the transmission electron microscopy (TEM) analysis. [c] Specific surface area of AuNPs. [d] Total surface area of AuNPs per gram of Au/TiO_2-N is calculated from the specific surface area of AuNPs.

The specific surface area of AuNPs is calculated according to S_{Au} (m^2/g) = $C_1S_1+C_2S_2+\ldots C_nS_n$. S_n was obtained from following equation:

$$S_n = \frac{A_n}{m_n} = \frac{4\pi\left(\frac{d_n}{2}\right)^2}{\rho V_n} = \frac{\pi d_n^{\,2}}{\rho\cdot\frac{4}{3}\pi\left(\frac{d_n}{2}\right)^3} = \frac{6}{\rho d_n}$$

where C_n is the ratio of AuNPs with the diameter of dn, ρ is the density of gold, 19.30 g•cm^{-3}, d_n is the diameter of AuNPs in certain range, μm.

Reference

1. Janz, A., Köockritz, A., Yao, L. & Martin, A. Fundamental calculations on the surface area determination of supported gold nanoparticles by alkanethiol adsorption. Langmuir 26, 6783-6789 (2010).

Table S2. Photocatalytic hydroamination of 4-phenyl-1-butyne with aniline by AuNPs on different supports[a]

Entry	Photocatalysts	Conv. (%)[b]	$S_{I.}$ (%)[c]	$S_{K.}$ (%)[d]
1	Au/TiO_2(B)	76	94	2
2	Au/TiO_2(B)-N	90	91	1
3	Au/TiO_2(anatase)	59	90	5
4	Au/P25	70	95	4
5	Au/ZrO_2	35	95	2
6	Au/CeO_2	0.4	100	-

[a] Reaction conditions: 0.015 mmol of AuNPs, 4-phenyl-1-butyne (2 mmol), aniline (2 mmol), 2 ml of toluene as solvent, reacted under visible light at 40 °C for 25 h, argon atmosphere. [b] Determined by GC analysis. [c] Selectivity to imine. [d] Selectivity to ketone.

The gold content according to analysis of energy dispersion X-ray spectroscopy (EDX) and particle size distribution (TEM analysis) on the different supports were similar.

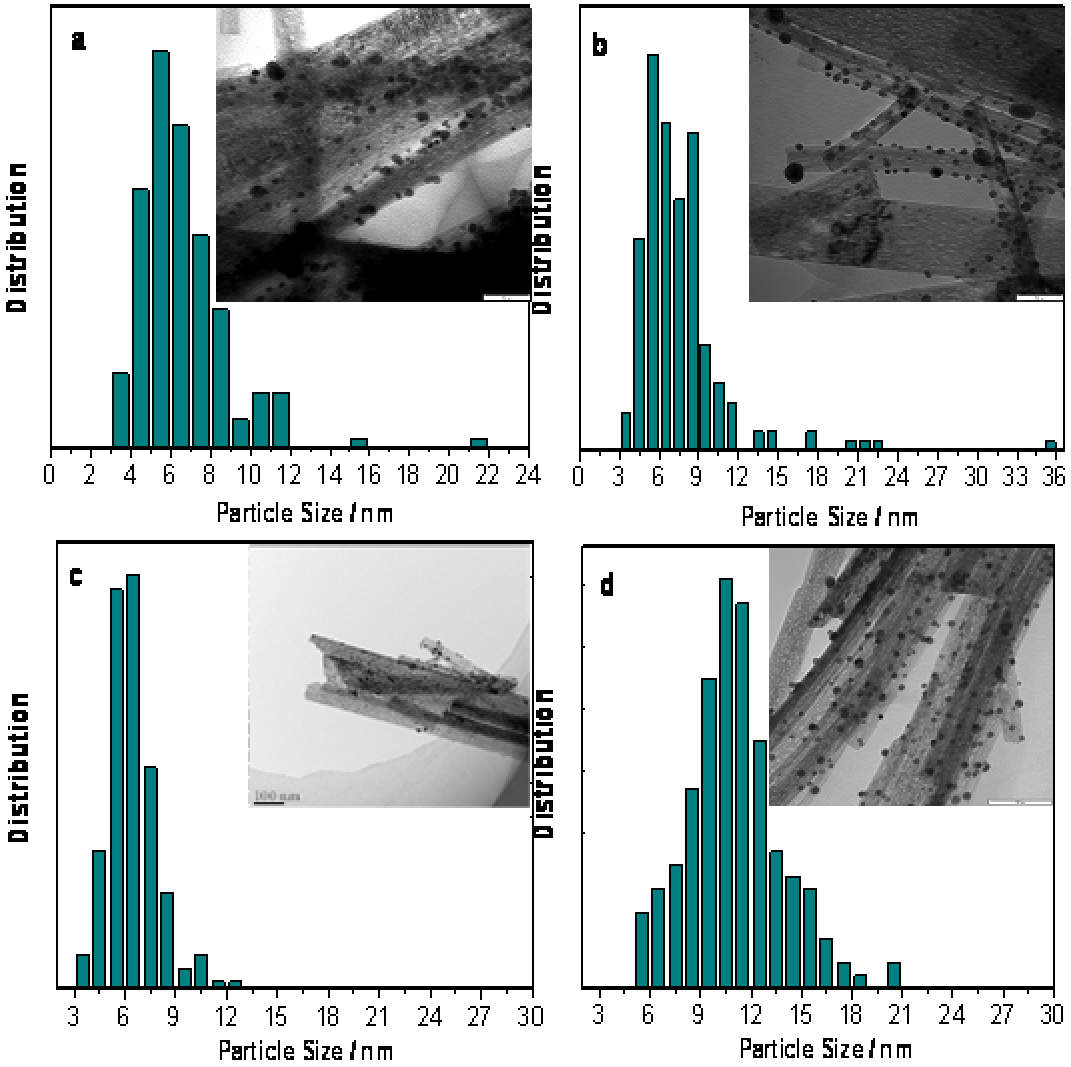


Figure S1. The size distribution of AuNPs on TiO_2(B) according to TEM analysis. [a] 2wt% Au/TiO_2(B), 50 nm scale; [b] 2wt% Au/TiO_2(B) calcined at 300 ℃ for 3 h, 50 nm scale; [c] 3wt% Au/TiO_2(B), 100 nm scale; [d] 3wt% Au/TiO_2(B) calcined at 400 ℃ for 12 h, 100 nm scale.

The difference between Au/CeO_2 and other catalysts in Table S2 is sufficient to make a catalyst active or unactive while supported Au NPs with small difference (2 nm) cannot make a catalyst active or unactive. For example, conversion difference is only 3% for 2wt% Au/TiO_2(B) and 2wt% Au/TiO_2(B) calcined at 300 ℃ (size difference of AuNPs 1-2 nm), while 20% for Au/TiO_2(B) and Au/TiO_2(B) calcined at 400 ℃ (size difference of AuNPs $\geqslant$ 5 nm).

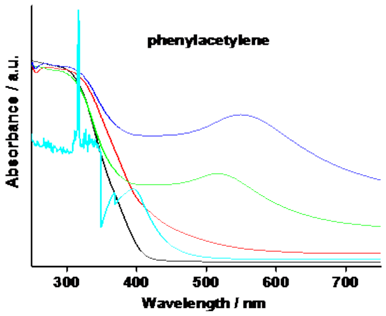


Figure S2. UV-Vis spectra of TiO_2(B) (black line), Au/TiO_2(B) (green line), alkynes adsorbed on TiO_2(B) (red line) and Au/TiO_2(B) (blue line), and free liquid alkynes (cyan line).

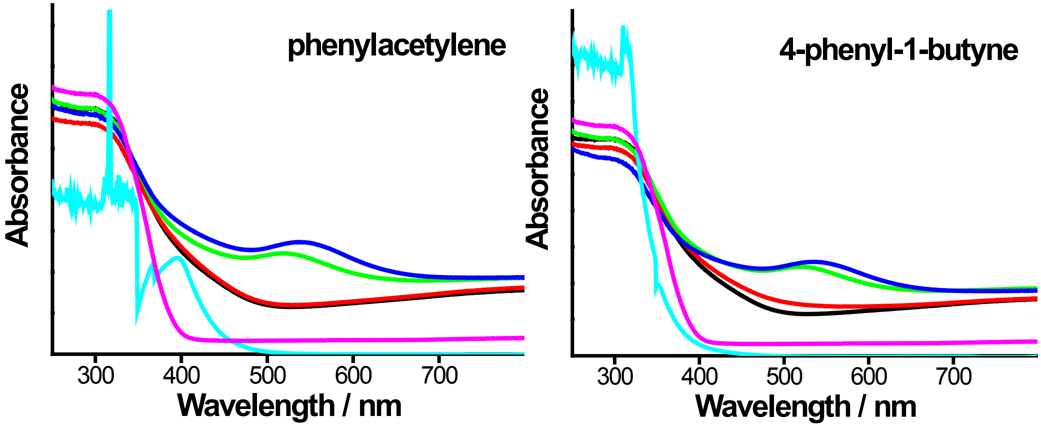


Figure S3. UV-Vis spectra of TiO_2(B) (Magenta), TiO_{2}-N (black line), Au/TiO_{2}-N (green line), alkynes adsorbed on TiO_{2}-N (red line) and Au/TiO_{2}-N (blue line), and free liquid alkynes (cyan line).

The nitrogen doped TiO_2 systems absorb visible light, and thus the contribution from the adsorbed alkyne cannot be demonstrated clearly in their UV-Vis spectra.

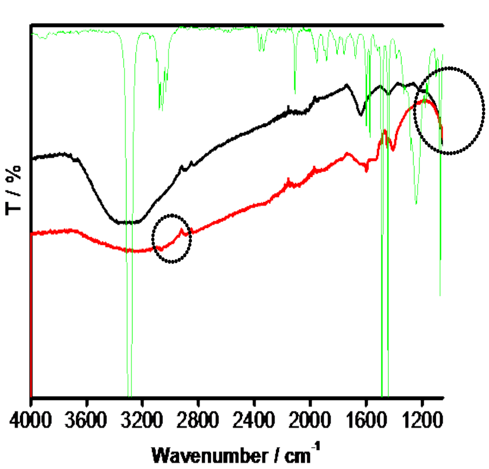


Figure S4. FT-IR of free liquid phenylacetylene (green line), TiO_{2}-N (black line), phenylacetylene (0.1 g) adsorbed on TiO_{2}-N (0.02 g) after dried at 60 ℃ under vacuum (red line). The bands in the range of 3300-3200 cm^{-1} are attributed to C-H stretching vibration of ≡C-H.

The experiment using only alkynes as reactant under the same reaction conditions was conducted. No polymerization or even no coupling product was observed (GC-MS method with HP-5 column). Therefore, the disappearance of the alkyne signals is not due to the polymerization of alkynes.

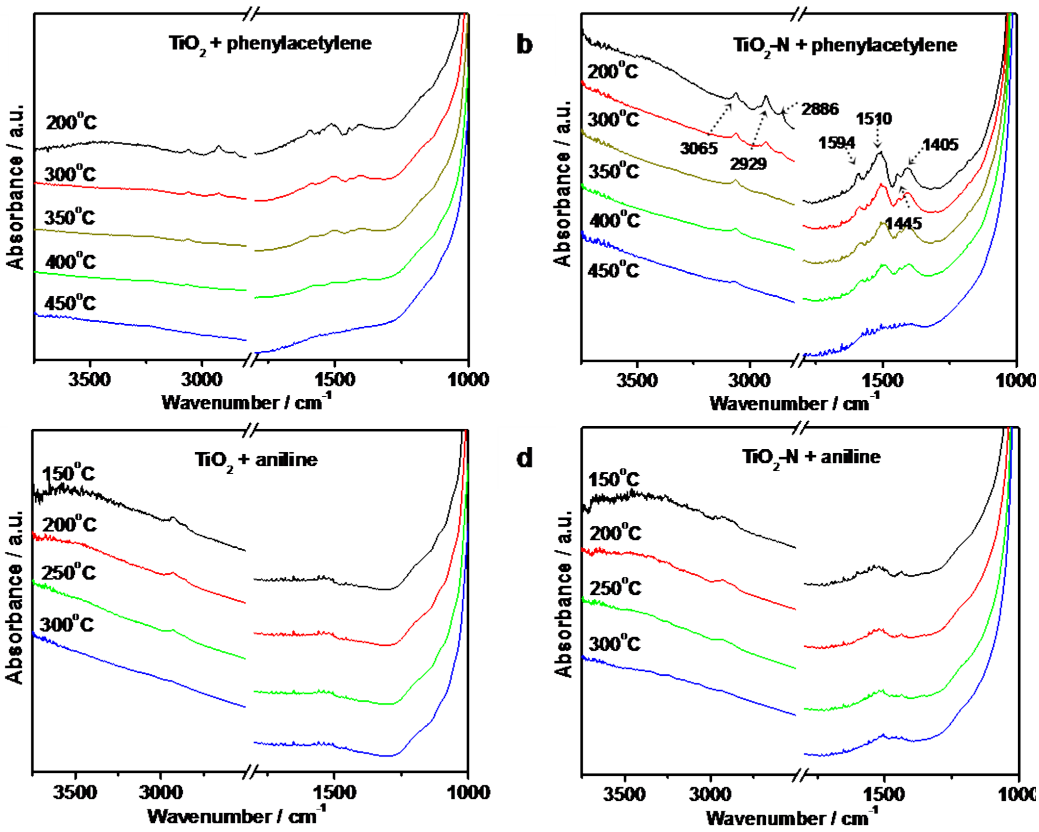


Figure S5. IES spectra of phenylacetylene (a and b) and aniline (c and d) adsorbed on different catalysts. Experiment condition: phenylacetylene or aniline (0.1 g) was added onto the prepared catalyst (0.02 g), then dried at 60 °C under vacuum.

At 400 °C, the peaks from phenylacetylene adsorbed on the surface of N doped TiO_2 are still obvious (Figure S5b), whereas these peaks cannot be observed from the sample with undoped TiO_2 (Figure S5a). This indicates that at this temperature phenylacetylene is not adsorbed on to undoped TiO_2, and the surface of N-doped TiO_2 has a stronger ability to adsorb and thereby activate phenylacetylene than undoped TiO_2. Such activation contributes to the higher photocatalytic activity for this catalyst. Furthermore, aniline adsorption on undoped (Figure S5c) and N-doped TiO_2 surface (Figure S5d) is negligible, compared with the adsorption of phenylacetylene as almost all the adsorbed aniline desorbed at 250 °C.

The reaction was conducted in the dark at several temperatures. When we increased the reaction temperature from 40 ^{o}C to 50 ^{o}C, the increase of the conversion (< 40%) is much lower than the increase induced by the visible light irradiation (> 60%). In our system, the AuNPs account for only 3 wt% of the catalyst mass. Namely, each reaction cycle we use only 3 mg of AuNPs (in 2 ml toluene as solvent), the heat produced by the AuNPs should have very limited impact. Moreover, the temperature of the reaction mixture was carefully controlled and maintained at 40 ±1°C in the reaction irradiated with light. Thus, the temperature increase caused by the heat produced by the AuNPs under the visible light irradiation should be much less than 10 ^{o}C. Therefore, the contribution from the heat is much less than that from light irradiation. The most contribution comes from the electron transfer rather than the heat produced by AuNPs.