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Highly efficient and selective photocatalytic hydroamination of alkynes by supported gold nanoparticles using visible light at ambient temperature[†]

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The direct hydroamination of alkynes driven by visible light can be achieved in high yield and selectivity at ambient temperature using supported gold nanoparticles (AuNPs) as photocatalysts. Aniline molecules interact with visible light activated AuNPs meanwhile alkynes could be activated at active sites on the support. The findings reveal a new green approach for synthesis of fine organic compounds and provide insight into catalyst design for the activation of $C \equiv C$ triple bonds and amines.

Hydroamination of alkynes, or the direct addition of an N-H bond to a $C \equiv C$ bond, is of great significance in synthetic chemistry. This reaction can offer an atom-economical route to various organic nitrogen molecules and provide a convenient route for the synthesis of numerous important fine chemicals and synthetic intermediates.¹ Developing efficient and green systems for this addition has attracted significant interest, particularly for the intermolecular process. A gold-based complex has also been identified as an active catalyst for this process.² Recently, supported AuNPs were found to be active for the hydroamination of alkynes.²ⁱ High conversions and a moderate selectivity for imines (55%) could be achieved after 22 h reaction at 100 °C.

Hydroamination of alkynes involves nucleophilic attack to $C \equiv C$ by amines, the activation energy of which is very high due to the electrostatic repulsion between the N lone pair and the π system of alkynes.³ Intermolecular hydroamination is most challenging as it is even more kinetically and thermodynamically problematic than the intramolecular process. Higher temperatures (generally above 100 °C) are typically necessary to achieve high yields. However, at high temperatures the reaction equilibrium shifts towards lower conversions as the reaction entropy ΔS_0 of the amine addition is negative,³ which creates a dilemma.

Recently, we found that the organic molecules adsorbed on the surface of AuNPs can be activated under the irradiation of visible light due to the Surface Plasmon Resonance (SPR) effect.⁴ As a result, the energy of the incident light is absorbed by the conducting electrons that exist at the surface of AuNPs. The resulting high energy surface may facilitate the reaction of organic molecules adsorbed on it. It is known that aniline and derivatives can weakly bind to gold surfaces through the nitrogen lone pair.5 Thus, we hypothesized that such amines might also be activated by visible light irradiation when bound to AuNPs. If the surface of AuNPs, or the support to which the NPs are bound, also activates the $C \equiv C$ bond of alkynes at the same time,⁶ then the intermolecular hydroamination of alkynes might be realized at ambient temperature. This approach would be of considerable interest as an environmentally benign alternative to the traditional synthetic route.

To verify our hypothesis, the addition of the N-H bond across $C \equiv C$ triple bonds was first investigated with the photocatalyst AuNPs on nitrogen doped TiO₂(B) nanofibres, labelled as Au/TiO₂-N (Table 1). The highest conversion was achieved for 4-phenyl-1-butyne (90%) with a selectivity of 91% to the target product, imine (entry 1). The results in Table 1 illustrate the excellent performance of the AuNP photocatalyst for this synthetic process. When electron withdrawing or donating groups are bonded to the aromatic ring of the reactants (entries 5-11), high conversion and selectivity were still achieved. Amines with electron withdrawing groups in the aromatic ring (entries 8 and 9) achieved significantly higher yields than those with electron donating groups (entries 10 and 11). This was also observed by Tanaka and co-workers in thermo-catalysis,^{2h} who suggested that it was more probable for the amine to coordinate with the cationic gold(1) species before the C-N formation. Very poor conversion for the aliphatic aminohexane was examined (entry 12). This may be attributed to the increased basicity of aliphatic amines, which can deactivate the catalysts.^{2i,7} The reaction with a secondary amine was shown to be possible (entry 15). For the alkynes, however, terminal alkynes gave the highest yields (entries 1-3) while there is almost no reaction for non-terminal triple bonds (entries 13 and 14), most likely because of the increased steric hindrance by the groups attached to the C \equiv C bond.^{2h,7}

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Table 1 Photocatalytic hydroamination of alkynes with amines on Au/TiO_2–N (under visible light)^a

	R₁────H	+ H ₂ N—R ₂	Au/TiO ₂₋ N hv F	$R_1 \sim CH_3$	
Entries	Alkynes (R ₁)	Amines (R ₂)	$\operatorname{Conv.}^{b}(\%)$	Sel. ^c (%)	$\operatorname{TON}^{d}(\%)$
1	$Ph-(CH_2)_2$	Ph	90	91	118
2	Ph-CH ₂	Ph	86	91	113
3	Ph	Ph	79	98	104
4	$CH_3(CH_2)_5$	Ph	50	99	66
5	Br–Ph	Ph	80	98	105
6	CH ₃ O-Ph	Ph	56	97	74
7	CH ₃ -Ph	Ph	55	98	72
8	Ph	Cl–Ph	93	97	122
9	Ph	Br–Ph	84	98	111
10	Ph	CH ₃ -Ph	71	98	93
11	Ph	CH ₃ O-Ph	47	96	62
12	Ph	$C_{6}H_{11}$	0.5	50	1
13^e	$Ph-C \equiv C-CH_3$	Ph	5	71	7
14^e	Ph-C=C-Ph	Ph	0	0	0
15^e	Ph	Ph-NH-CH ₃	32	84	42

^{*a*} Reaction conditions: 0.38×10^{-2} mmol of AuNPs, 0.5 mmol alkynes, 0.5 mmol anilines, 0.5 ml of toluene as solvent, reacted under visible light at 40 °C for 25 h in an argon atmosphere. ^{*b*} Determined by GC analysis. ^{*c*} The selectivity of imine was estimated from GC results. ^{*d*} Turnover number (TON) was calculated using mole content of gold. ^{*e*} Internal alkynes or amines.

Control experiments showed that very low conversion of alkynes was achieved in the dark at 40 °C. Given that the reaction under light illumination was maintained at the same temperature as the reaction in the dark, visible light contributes most for this reaction in the system. The heat produced by the light irradiated AuNPs¹² is minor as described in the ESI.[†] When the light intensity was reduced from 0.49 W cm² to 0.43 W cm² and 0.30 W cm², while all the other experimental conditions remained unchanged, the conversion of 4-phenyl-1-butyne for 10 h decreased from 61% to 47% and 5%, respectively. These results further confirm that the reduction reactions were driven by visible light.

In the absence of the AuNPs (using supports only as catalysts), no reaction occurred. This demonstrated that the AuNPs are essential for the reaction. It is thus logical to assume that the properties of AuNPs can influence the photocatalyst performance. Catalysts with different Au contents and TiO₂–N support were prepared and the specific surface area of the AuNPs in 1 g of the photocatalysts was estimated (by assuming that the AuNPs are spheres) and the results are provided in Table S1 (ESI†). As the content of AuNPs in Au/TiO₂–N increased from 1% to 3%, the specific surface area of the AuNPs are of the AuNPs in Au/TiO₂–N increased from 0.7 m² to 2.0 m², and the conversion of 4-phenyl-1-butyne increased from 67% to 90%. The fact that higher conversion is observed on AuNPs with a larger specific surface area implies that the AuNPs activated at least one reactant.

To explore the role of the supports in this novel photocatalytic process, reactions were examined using AuNPs loaded on a range of different inorganic support materials. A very interesting finding is that supports have much more important impact on the catalyst activity than the size of AuNPs, sufficient to make the photocatalyst active or inactive (Table S2 and Fig. S1, ESI⁺). Generally, TiO₂ supports exhibit superior performance to other supports (entries 1–4 in Table S2, ESI⁺). The highest activity was obtained



Fig. 1 (A) UV-Vis spectra of TiO₂(B) (black line), Au/TiO₂(B) (green line), 4-phenyl-1-butyne adsorbed on TiO₂(B) (red line) and Au/TiO₂(B) (blue line), and free liquid 4-phenyl-1-butyne (cyan line). (B) FT-IR spectra of phenylacetylene (0.1 g) adsorbed on TiO₂-N (0.02 g) after drying at 60 °C under vacuum (a), TiO₂-N (b), free liquid phenylacetylene (c, the intensity was divided by 4). Fig. S4 (ESI†) shows the spectra in the wavenumber range from 600 to 4000 cm⁻¹. The bands at 1650–1330 cm⁻¹ arise from the characteristic vibrational modes ν (C-C) of the mono-substituted phenyl ring as well as the phenyl ring.

by the AuNP photocatalyst on the nitrogen doped TiO2. It is known that the oxidation state of Ti4+ can be reduced during nitrogen doping.⁸ It would be expected that the Ti³⁺ sites on the support surface would interact with the reactant much more strongly than the Ti⁴⁺ sites. Indeed Ti³⁺, within such a defected structure, has previously been found to be more able to adsorb and interact with alkynes.9 Thus, the presence of Ti3+ in N-doped samples would likely enhance the conversion without sacrificing selectivity. The significant visible light absorption after adsorbing alkynes in UV-Vis spectra (Fig. 1A and Fig. S2 and S3, ESI⁺), the shift of the peaks and disappearance of the peak for \equiv C-H in FT-IR spectra (Fig. 1B and Fig. S4, ESI⁺) imply that the adsorption of alkynes on the support surface affects the triple bond significantly, which may lead to the activation of the triple bond for reaction on the support surface. Indeed, Infrared Emission Spectroscopy (IES) analysis indicates that the interaction of alkynes with the surface of N-doped TiO₂ is much stronger than that with the undoped surface (Fig. S5a and S5b, ESI[†]). Furthermore, aniline adsorption on undoped (Fig. S5c, ESI⁺) and N-doped TiO₂ surfaces (Fig. S5d, ESI⁺) is negligible, compared with the adsorption of phenylacetylene. Therefore, the mechanism of the reaction is unlikely to involve aniline activation on the surface of the support materials and is more likely to involve gold surface binding.

The interaction between gold and the nitrogen atom of aniline was investigated using Raman spectroscopy (Fig. 2). No characteristic Raman peaks of pure aniline liquid are observed for an aqueous solution of 7.7 mM aniline (spectrum f). When the aqueous solution was adsorbed on AuNP photocatalysts, most of the characteristic bands (spectrum b) can be observed. However, these bands cannot be detected (spectrum d) when the aqueous solution was adsorbed on the support without the AuNPs. Thus, the AuNPs are necessary to provide enhancement of the Raman bands. Such a surface enhancement effect is well known in Raman spectroscopy (the so-called SERS effect). The SERS effect observed may also be associated with the enhanced reactivity of aniline, as the enhancement in Raman signals arises from charge transfer.^{10a} Comparing with spectrum d, a new band at 317 cm⁻¹ is observed (in spectrum b), which can be attributed to the Au-N stretching mode.^{10a} The shift of the C-N stretching mode from 1279 cm⁻¹ in spectrum a to 1267 cm⁻¹ in



Fig. 2 Raman spectra of pure aniline liquid (a), aniline adsorbed on Au/TiO₂–N (b), and TiO₂–N (d) from 7.7 mM aniline aqueous solution. The spectra of pure Au/TiO₂–N (c), pure TiO₂–N (e), and the 7.7 mM aniline aqueous solution (f) are also provided for comparison. The bands at 317 cm⁻¹ and 1267 cm⁻¹ are, respectively, attributed to the stretching modes of Au–N and C–N.



Fig. 3 The proposed mechanism for the photocatalytic hydroamination c alkynes on supported AuNPs. The interpretation is given in the text.

spectrum b further confirms that the chemical mechanism for the charge transfer is dominant for this reaction system, where the charge transfer is from aniline to metal atoms.^{10b} Therefore, it is concluded that amines are most likely to be activated on AuNPs *via* the interaction between the nitrogen atoms and AuNPs, while the alkynes would be adsorbed on the support material. The combined effect is that the catalyst is able to activate the two reactants simultaneously. Thus, we propose a tentative mechanism for the photocatalytic hydroamination of alkynes on the AuNP photocatalysts as illustrated in Fig. 3.

The AuNPs absorb visible light due to the SPR effect. The conducting electrons of the AuNPs gain the energy of light and can migrate to the conduction band of the support, which would result in the formation of positively charged AuNPs.¹¹ The nucleophilic aniline could interact with the positively charged AuNPs forming N-centred radical cations, which would lead to its activation for the electrophilic attack to the electron rich sites of alkynes (*e.g.* the C atom at the position of \equiv C-Ph). Meanwhile, alkynes could be activated *via* the interaction of the C-H bond of the terminal alkynes with active Ti sites in the support, preferably the electron rich sites with a lower oxidation state, such as Ti³⁺ sites. The next step would most likely entail the addition of the two activated reactants: the N atom links to the C atom of the phenyl ring meanwhile a H atom is added onto the

terminal C atom of $C \equiv C$. Ti^{3+} sites formed due to the N doping have higher coordination ability than Ti^{4+} sites, which may also make the terminal C atom more favourable for the H addition. The final step would be desorption of the product molecules from the support surface. This desorption process proceeds because the adsorption of C=C on the surface is weaker than $C \equiv C$.¹³ Subsequently, the activated sites on the photocatalyst return to the state needed to re-start the process (Fig. 3).

In conclusion, the hydroamination of alkynes with amines can be driven with visible light using photocatalysts generated from AuNPs supported on inorganic materials, with excellent yields achievable at ambient temperature. During this photocatalytic process, both AuNPs and the supports contribute to the activation of reactants, which may lead to the discovery of new reaction pathways for the hydroamination reactions. This approach reveals a new class of useful catalytic processes with the potential to utilize solar energy for cleaner, lower environmental impact synthesis of fine chemicals for organic chemistry.

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