A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
International Edition
www.angewandte.org

Accepted Article

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201904452
Angew. Chem. 10.1002/ange.201904452

Link to VoR: http://dx.doi.org/10.1002/anie.201904452
http://dx.doi.org/10.1002/ange.201904452

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Plasmonic Switching of Reaction Pathway: Visible-Light Irradiation Varies Reactant Concentration at the Solid-Solution Interface of a Gold-Cobalt Catalyst

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Abstract: Product selectivity of alkyne hydroamination over catalyst Au_2Co alloy nanoparticles (NPs) can be made switchable by a light-on, light-off process, yielding imine (cross-coupling product of aniline and alkyne) under visible-light irradiation, but 1,4-diphenylbutadiyne in the dark. The low-flux light irradiation concentrates aniline on the catalyst, accelerating the catalytic cross-coupling by several orders even at a very low overall aniline concentration (1.0×10^{-3} mol/L). A tentative mechanism is that Au_2Co NPs absorb light, generating an intense fringing electromagnetic field and hot electrons. The sharp field-gradient (plasmonic optical force) can selectively enhance adsorption of light-polarizable aniline molecules on the catalyst. The light irradiation thereby alters the aniline/alkyne ratio at the NPs surface, switching product selectivity. This represents a new paradigm to modify a catalysis process by light.

Controllable product selectivity is of equal importance to efficient reactant conversion in chemical synthesis.[1,2] Recently, we found that alloying small amounts of Cu into Au NPs can alter the reaction pathway of the catalytic reduction of nitro-aromatics under visible-light irradiation, directly transforming them into anilines in a highly selective manner.[2] Using a monometallic Au NP photocatalyst instead generates azobenzene as the final product, indicating the reaction pathway changes, due to the alloy effect in this case. If light irradiation applied in photocatalytic selective synthesis could determine the reaction pathways with the same catalyst material, it could prove useful to addressing the challenge of product selectivity control in catalysis generally.

Previously we have found that Au NPs supported on ZrO_2 can catalyse the hydroamination of alkyne with aniline when irradiated by visible-light at ambient temperature.[3] This reaction provides an atom-economical route for the synthesis of various organic nitrogen molecules that are important fine chemicals and synthetic intermediates.[4] In the present study we conduct screening test of various alloy NPs of gold with a transition metal for alkyne hydroamination reaction and observe an interesting photo-switchable product selectivity on Au_2Co alloy NPs. As illustrated in Figure 1 product selectivity of the reaction can be readily switched by a light-on or light-off process, yielding imine under low-flux (~0.5 W/cm^2), visible-light irradiation (Figure 1A), and 1,4-diphenylbutadiyne (homo-coupling product of alkyne) in the dark (Figure 1B). We have found that visible-light irradiation can change this reaction's pathway and reaction kinetics by inducing selective adsorption of reactant molecules on the catalyst surface. This finding is of fundamental significance to photocatalysis.

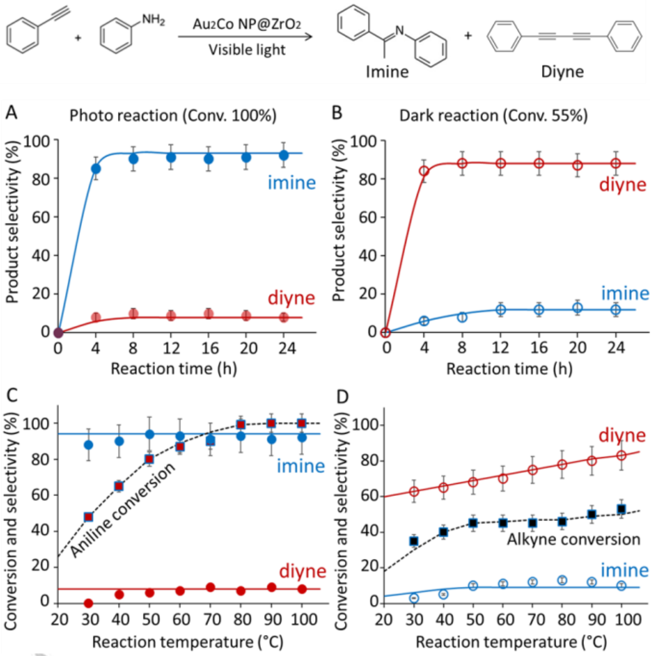

Figure 1. Product selectivity of alkyne hydroamination reaction. (A) The reaction catalysed by Au_2Co/ZrO_2 under visible-light irradiation and (B) in the dark. (C) The influence of temperature under visible-light irradiation and (D) in the dark.

The photo-switchable reaction pathway was not observed with supported monometallic catalysts of either Au/ZrO_2 or Co/ZrO_2, respectively (Figure S1 in Supporting information). The hydroamination reaction rate over Au_2Co/ZrO_2 catalyst was increased, compared with the rate over Au/ZrO_2 catalyst. The catalytic performances of other Au alloy catalysts (e.g. Au-Ni, Au-Cu alloy) for the hydroamination were investigated under visible-light irradiation and in the dark as well. In terms of the reactant conversion and selectivity towards the cross-coupling imine product, the Au_2Co/ZrO_2 catalyst exhibited a superior photocatalytic performance compared to other alloy catalysts (Table S1) and to AuCo alloy catalysts with other Au:Co ratios (Figure S2). Light irradiation of Au/ZrO_2 catalyst and other gold alloy catalysts did not result in substantial change in product selectivity. Further investigation revealed that the Au_2Co/ZrO_2 catalyst maintained the optical-switching capability at elevated temperatures as illustrated in Figure 1C and 1D. Notably, the product selectivity abruptly changed upon light irradiation even at low light intensity (0.1 Wcm^{-2}), demonstrating a reaction pathway switch due to light irradiation (Figure S3).

The scope of the photo-switchable product selectivity was explored by using various anilines and alkynes as the reactants. The results in Table 1 clearly show that the optical switch of product-selectivity occurs when the reactants have different

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Supporting information for this article is given via a link at the end of the document substituent groups. We were pleased to see that the optical switch-effect was observed for a wide range of reactants, where cross-coupling pathway prevails under light irradiation, while homo-coupling does in the dark. The optimal reaction conditions are given Table S2.

Table 1. Substrate scope for the hydroamination of alkyne

Entry	R1	R2	Cross coupling % Photo	Cross coupling % Dark	Homo coupling % Photo	Homo coupling % Dark
1	Ph	Ph	95	25	≤5	75
2	Ph-CH2	Ph	84	40	16	60
3	Ph-C2H4	Ph	80	29	20	71
4	Ph-Br	Ph	95	13	≤5	87
5	Ph-I	Ph	96	11	≤4	89
6	Ph-OCH3	Ph	91	15	9	85
7	Ph-CH3	Ph	93	13	7	87
8	Ph	Ph-Cl	96	21	4	79
9	Ph	Ph-Br	94	20	6	80
10	Ph	Ph-OCH3	90	19	10	81
11	Ph	Ph-CH3	88	15	12	85
12	C3H7	Ph	80	30	20	70

50 mg of catalyst, 1 mmol alkyne, 1.2 mmol amine, 1.0 ml toluene as solvent, 0.5 W/cm^2 light intensity, 24 h, argon atmosphere, 80 °C temperature.

Structure analysis of the catalyst is shown in Figure 2 and Figure S4. The Au_2Co alloy NPs with a mean particle size of 7 nm were dispersed on a ZrO_2 support (Figure 2A, S4A and 4B), slightly larger than the Au/ZrO_2 (5 nm in average, Figure S4C). The actual Au:Co mass ratio is 2:0.84 (Figure S5 and Table S3), very close to the designed ratio 2:1. Energy dispersive X-ray spectroscopy line scan analysis indicates that both Au and Co coexist in the particle (Figure 2B), confirming the formation of alloy NPs. X-ray photon spectra (XPS) analysis indicates that Au is in metallic state, while both metallic Co^0 and oxidized Co^{2+} coexist in the catalyst (Figure S4D).

The catalyst of Co NPs on ZrO_2 support, Co/ZrO_2(3 wt%), exhibited limited activity with a 20% conversion under light (Table S4, entry 7). The Co^{2+} species alone have no catalytic activity to this reaction. This conclusion is corroborated by the results of the experiment to further clarify the contribution of the metallic Co in the Au_2Co/ZrO_2 catalyst (Table S4).

The Au_2Co/ZrO_2 catalyst absorbed visible-light over a broad range with a peak at 520 nm, similar to the absorption of Au/ZrO_2 (Figure 2C). The Au NPs can efficiently absorb visible-light due to the localized surface plasmon resonance (LSPR) effect and conduction electrons are rapidly excited to higher energy levels.[1d,5] These excited, energetic electrons (hot electrons) can activate reactant molecules to induce chemical reactions.[1d,2,3] Silica coated $Au_2Co@ZrO_2$ catalysts (TEM images are provided Figure S6), did not exhibit catalytic activity. The SiO_2 layer presents an impermeable barrier to reactant molecules, preventing the interaction between the light-excited electrons and reactant and, thus, the reactions. However, the hot electron mechanism cannot explain the photo-switchable product selectivity phenomenon.

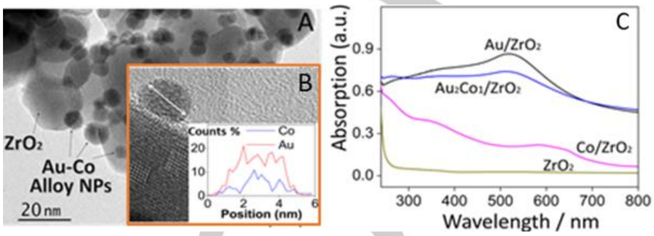

Figure 2. Characterization of the Au_2Co/ZrO_2 photocatalyst. (A) TEM image of the catalyst. (B) HR-TEM image of an Au_2Co alloy NP. The inset shows a line profile analysis providing information on Au/Co distribution of the NP (C) Diffuse reflectance ultraviolet-visible (DR-UV-Vis) spectra of samples.

Since the first step of all heterogeneous catalysis processes is reactant adsorption at the catalyst surface we investigated whether light irradiation induced changes in the reactant adsorption. As shown in Figure 3A, light irradiation on Au_2Co/ZrO_2 catalyst suspended in bulk liquid phase causes substantial changes to the concentration of aniline and phenylacetylene (denoted as alkyne). In dark conditions, the alkyne adsorption to the catalyst surface is observed as a 20% concentration decrease detected in the bulk liquid. With aniline, a 10% concentration decrease in the bulk liquid was observed. Upon visible-light irradiation, the measured aniline concentration in the bulk liquid decreased from 90% to 70% of the initial concentration, which could be explained if aniline was concentrated near the catalyst NPs, by visible-light irradiation.

In contrast, the measured alkyne concentration in the bulk liquid phase increased from 80% to 90% of the initial concentration under irradiation: the amount of the adsorbed alkyne decreased from 20% (in the dark) to 10% under the light irradiation. The irradiation weakened the alkyne adsorption on the catalyst. Moskovits and co-worker have observed similar photodesorption of molecule with a quinoline ring from plasmonic silver NPs.[6] Since light irradiation does not cause any obvious change in either reactant concentration in the presence of ZrO_2 alone (≤4%), it is concluded that aniline was attracted-to and alkyne was released-from the illuminated alloy NPs of the catalyst in solution. The concentration changes are reversible: when the light was switched off, the reactant concentration restored, the schematic illustration of concentration change is shown in Figure 3C. The light induced adsorption changes on Au/ZrO_2 and Co/ZrO_2 samples are provided in Figure S7 for comparison.

In the dark, alkyne adsorption on the alloy catalyst was twice that of aniline adsorption (Figure 3A), thus, most alkyne molecules adsorbed on the surface of the alloy NPs were activated to yield the diyne, homo-coupling product. The actual aniline/alkyne molar ratio at the catalyst surface determines the reaction pathway, but this ratio may be significantly different under conditions of visible-light irradiation. Under the same conditions in the dark the initial adsorption of the two reactants on Au/ZrO_2 catalyst were similar (Figure S7B), which is favouring the cross-coupling reaction in the dark. Visible-light irradiation did not switch the selectivity on Au/ZrO_2.

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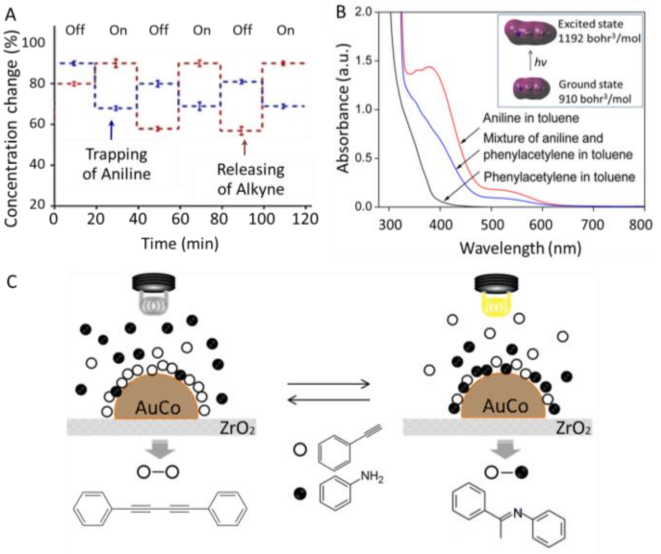

Figure 3. Results and schematic illustrations of selective trapping aniline to alloy NPs by irradiation of Au_2Co/ZrO_2 photocatalyst. (A) Visible-light irradiation induced reactant concentration change on Au_2Co alloy NPs in the light-on and light-off cycle process (which were measured by gas chromatography, GC). (B) The UV-Vis spectra of aniline and phenylacetylene in toluene solvent respectively (1 mmol in 1 mL). (C) Schematic adsorption mechanism and relation to the product selectivity based on data in panel A.

The alkyne adsorption on Au_2Co alloy NPs in the dark is much larger than that on Au NPs, the irradiation destabilizes the strong alkyne adsorption on Au_2Co/ZrO_2 catalyst. The UV-VIS absorption spectra of aniline and phenylacetylene adsorbed Au/ZrO_2 and Au_2Co/ZrO_2 catalysts are shown Figure S8. A damping of the surface plasmon absorption band (at ~ 530 nm) is observed only for phenylacetylene adsorbed onto the Au_2Co/ZrO_2 catalyst, indicating strong interaction between phenylacetylene and the alloy particles. This damping induced by strong adsorption is not observed on other Au alloys. The strong interaction is consistent with the high alkyne adsorption of Au_2Co/ZrO_2 catalyst in the dark and should facilitate activation of the alkyne molecules at the Au_2Co NP surface. However this strong interaction was not reflected in FTIR spectra (Figure S9), which indicated that the phenylacetylene adsorption proceeds by a multilayer physical adsorption on the AuCo surface (although not as strong as chemisorption, this amount is sufficient to induce LSPR damping). A strong interaction between aniline and Co sites at alloy NP surface was observed in the FTIR spectra. When light irradiation increased aniline adsorption on the alloy catalyst this effect may benefit to activation of aniline for reaction. The unique role of Co in the alloy is the increased adsorption to alkyne molecules. The enhanced adsorption subsequently increased the catalytic activity of Au and induced the photo-switchable reaction pathway of alkyne and aniline.

We applied alkyne as the sole reactant to conduct the homo-coupling reaction on Au_2Co/ZrO_2 (Table S5). When irradiated with light (photo-reaction), the alkyne conversion rate (30%) on Au_2Co catalyst was lower than that of the reaction in the dark (45%). The reason for this reduction of catalytic performance can be explained by a decreased alkyne adsorption on Au_2Co NPs during irradiation. This result is consistent with the irradiation induced release of alkyne from Au_2Co catalyst discussed above. The aforementioned results suggest that light irradiation altered the product selectivity by significantly changing the ratio of adsorbed aniline to adsorbed alkyne on Au_2Co NPs.

The changes in reactant adsorption on Au_2Co/ZrO_2 should affect reaction kinetics. In Figure 4A the reaction rates are expressed in turnover frequency (TOF, $mmol \cdot g^{-1} \cdot h^{-1}$) and plotted against the initial concentration of aniline. In the dark, the rate increased as aniline concentration was increased. Under irradiation of 1.0 W/cm^2 intensity light, at a very low initial aniline concentration of 5×10^{-3} M a TOF of 200 $mmol \cdot g^{-1} \cdot h^{-1}$ was achieved. It is also noted that the product selectivity towards imine (the cross-coupling product) increased significantly with the increasing aniline concentration when aniline concentration was above 0.5 M (Figure 4B) even in the dark.

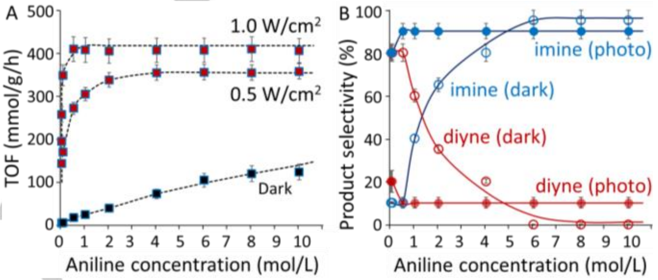

Figure 4. Influence of reactant concentration on reaction rate on Au_2Co/ZrO_2 catalyst. (A) Phenylacetylene concentration was kept constant at 0.5 M while aniline concentration was continually increased from 0.5 mM to 10 M. The reactions were conducted at the same temperature with and without irradiation. (B) Product selectivity analysis of panel A.

The unusually high TOF at very low concentration (Figure 4A) and the selectivity difference in Figure 4B support the conclusion that the aniline surface concentration at the illuminated catalyst solid-solution interface was considerably higher than in the bulk of the solution. This would accelerate the reaction as we have observed, when higher aniline concentrations resulted in faster reaction rates in the dark (Figure 4A). The increased aniline concentration at the catalyst surface and the photodesorption of alkyne from the catalyst work together, to switch the product selectivity.

The selective attraction of aniline molecules to the catalyst surface is generated under illumination of Au_2Co NPs. We tried to understand the nature of this force. It is known that when irradiated with light, plasmonic metal NPs generate an intense electromagnetic (EM) field in close proximity to the NPs and hot spots (plasmon field enhancement),[5,7,8] which is accompanied by generating a force [8] similar to the optical force generated by laser.[9] It has been predicted that laser irradiation of closely spaced silver NPs can result in steep field gradients that may trap small particles and large biomolecules.[8] We measured Surface Enhanced Raman Scattering (SERS) spectra of aniline adsorbed on catalysts (Figure S10). The enhanced SERS signals can be attributed to two factors: EM enhancement and chemical enhancement (interaction between adsorbed molecules and the surface).[10] Vibration bands of aniline adsorbed onto the Au_2Co/ZrO_2 catalyst are observed with considerably higher intensity compared to the weak SERS peaks of aniline adsorbed on Au/ZrO$_2$ or ZrO$_2$. This demonstrated that Au$_2$Co alloy NPs of the catalyst system can generate a stronger EM field, compared to Au/ZrO$_2$, under the same conditions. More aniline molecules adsorbed on Au$_2$Co/ZrO$_2$ catalyst can also lead to the higher SERS signal intensity. However the photo-responsive reversible adsorption and desorption of aniline on Au$_2$Co indicated that the higher aniline adsorption is due to the enhanced EM field of Au$_2$Co.

The low flux visible-light irradiation employed in this study (0.5-1.0 W/cm^2) is usually considered insufficient to produce a plasmon-generated optical plasmon force.[8a] However, any alloy surface-molecule interaction is also strongly dependent on the molecular polarizability.[8c-e] When a molecule can be promoted to an excited electronic state by absorption of incident light, the molecule's polarizability increases and so its response to the optical plasmon field-gradient will increase significantly.[8c,8d] The absorption spectra of reactants aniline and alkyne in toluene solvent are shown in Figure 3B, aniline absorbs light at wavelengths 400-440 nm. Electronically excited aniline, having greater polarizability, may experience a stronger optical plasmon-based force of attraction. The alkyne which does not absorb in the visible-light range is not affected. Thus, this compound-selective force generated by irradiation can superpose with the ubiquitous van der Waals force to overcome the Brownian motion of the excited molecules. The excited aniline molecules should, by this tentative mechanism, be attracted from the bulk of the solution to the metal NP surface, while the light is on. In the absence of the metal NPs, the excitation of aniline due to the light absorption cannot induce chemical transformation under the conditions applied for the photocatalytic hydroamination.

According to the proposed mechanism, the higher light intensity should result in stronger force and faster cross-coupling reaction. Indeed, the cross-coupling proceeds faster under 1.0 w/cm^2 irradiation than under 0.5 W/cm^2 irradiation (Figure 4A). It is also noted that the fastest reaction was observed faster at 400 nm wavelength (Figure S11), this should be attributed to the more intense light absorption of aniline in the range of 400-440 nm (Figure 3B), which induces higher activation of aniline.

We also conducted the reaction using catalysts with different Au$_2$Co alloy contents. As shown in Table S6 the cross-coupling product selectivity of the reaction over the catalyst with 1 wt% of Au$_2$Co alloy NPs is significantly lower than occurs with the catalysts with 3 wt% and 5 wt% of alloy content, and the homo-coupling product selectivity is higher, compared with those of the other two catalysts. The number of hot spots in the catalyst with 1 wt% of alloy NPs is lower than those in the catalysts with 3 wt% and 5 wt% of alloy content. The optical plasmon force attracting aniline to the catalyst with 1 wt% of Au$_2$Co alloy NPs is the weakest among the catalyst. Hence, under light irradiation aniline adsorption on this catalyst is less than that on the catalyst with higher alloy NP contents, resulting in less cross-coupling product but more homo-coupling product. The results support that optical plasmon effects play a key role in switching the product selectivity.

The recyclability of Au$_2$Co/ZrO$_2$ catalyst was investigated for up to 6 cycles (Figure S12). The efficiency of conversion started to decline after the fourth cycle, however, the product selectivity switching-effect remained. The Co is slightly oxidised after each cycle. A reduction treatment can reduce the oxidized Co. There was no change in NP size or morphology after recycle tests (Figure S13).

We have demonstrated that low intensity visible-light irradiation of Au$_2$Co alloy NPs can significantly change the adsorption of both reactants of alkyne hydroamination on Au$_2$Co/ZrO$_2$ catalyst and switch the product-selectivity of the reaction, in addition to the generation of hot electrons in metal NPs to induce the reaction. This function allows us to achieve high turnover frequency at very low concentration in catalytic reactions and to tune the product selectivity readily by visible-light irradiation. A number of evidences suggest that the light irradiation of Au$_2$Co NPs generates an optical plasmon force that can add to van der Waals force and selectively attract aniline molecules to the catalyst. The light irradiation also weakens adsorption of alkyne. The simultaneously selective trapping and releasing of reactants by light may provide a new technology to engineer product selectivity for chemical syntheses as illustrated with the substrate scope.

Experimental Section

The catalysts were prepared by reducing the metal salts in the presence of ZrO$_2$ powder with NaBH$_4$. The photocatalytic reaction were conducted in Pyrex glass tube irradiated with light source at controlled temperatures. The light irradiation induced reactant adsorption and desorption on catalyst in the light-on and light-off cycle process was conducted using a Nelson halogen lamp with a light intensity of 0.5 W/cm^2. The concentration changes of each reactant in the bulk liquid phase were measured by a gas chromatography (GC). Details of the methods and catalyst characterisation are provided in SI.

Acknowledgements

We gratefully acknowledge financial support from Australian Research Council (ARC DP150102110).

Keywords: visible light photocatalysis • plasmonic metal nanoparticles • reaction pathway • product selectivity • selective adsorption

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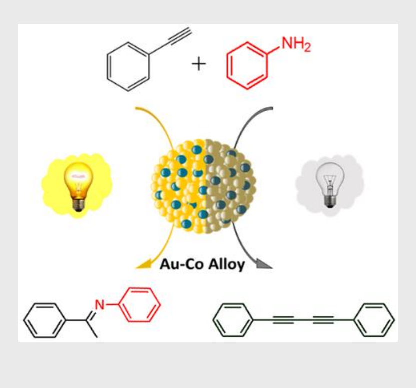

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