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Modulation of Silver–Titania Nanoparticles on Polymethylhydrosiloxane-based Semi-Interpenetrating Networks for Catalytic Alkynylation of Trifluoromethyl Ketones and Aromatic Aldehydes in Water

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Dedicated to Professor Han-Qing Wang on the occasion of his 80th birthday

In this work, we have developed a new approach to monodispersed hybrid Ag@TiO$_2$ nanocomposites using a titanium-promoted cross-linking reduction in the Si–H functional material, polymethylhydrosiloxane (PMHS)-based semi-interpenetrating networks (PMHSIPN). The titania was designed to be highly dispersed on the functional material and then the Ag@TiO$_2$ nanoparticles were formed in uniform size and shape under mild conditions. The experimental results reveal that the nanosilver catalysts (the fabricated Ag@TiO$_2$ located on the PMHSIPNs, namely, nanoAg@TiO$_2$@PMHSIPN) have enhanced catalytic activities in the alkynylation of trifluoromethyl ketones or α,β-unsaturated trifluoromethyl ketones with terminal alkynes. In this reaction, the hybrid Ag@TiO$_2$ nanoparticles exhibited a high level of catalytic activity for the selective 1,2-alkynylation of various trifluoromethyl ketones and α,β-unsaturated trifluoromethyl ketones into a wide range of fluorinated alcohols in water. Finally, on the basis of the nanoAg@TiO$_2$@PMHSIPN-catalyzed alkynylation of trifluoromethyl ketones, we developed a new concept whereby highly reactive substrates act as a "reactive tractor" or "reactive springboard" to drive the transformation of poorly reactive substrates as springboard chemistry. Consequently, we found that trifluoromethyl ketone can be used as an efficient additive in the nanosilver-catalyzed alkynylation of aldehydes.

Introduction

Silver is an extremely attractive noble metal and has some outstanding characteristics such as antimicrobial activity, environmental friendliness, and silver is particularly suitable for industrial catalysis and heterogeneous catalysis because of its relatively low prices, for example, less than 1/50 of that of gold or platinum, and approximately 1/25 of that of palladium, and the ease of accessibility of the nanosilvers if compared to other metals.[1] Besides the catalytic application, nanosilver has also found application in medicinal and pharmaceutical chemistry, purification and wastewater industry, washing machines, food chemistry, air conditions, and so on.[2] Especially in the field of nanosilver catalysis and green chemistry, nanosilver supported on titania (Ag@TiO$_2$) has attracted much attention as it combines the advantages of a nontoxic, catalytically active silver metal and a chemically stable, low-cost supported material with enhanced catalytic activity and optoelectronic properties.[3] TiO$_2$ is the most famous photocatalysts for environmental cleanup applications, owing to its unique ability in photocatalytic degradation of a variety of organic contaminants in wastewater, and silver is usually used as a suitable substance to improve the photocatalytic features of TiO$_2$.[4] Furthermore, the physicochemical characteristics of nanosilver supported on titania (Ag@TiO$_2$ nanocomposites), such as particle size, dispersion, size distribution, stability, and shape, are important factors to concern to achieve excellent catalytic activity.[5] To maintain and enhance the catalytic activity of both silver and TiO$_2$, there is need to find a synthetic approach of novel Ag@TiO$_2$ nanocomposites for high efficiency in catalytic organic transformations. Thus the controllable construction of Ag@TiO$_2$ nanocomposites is extremely attractive because they represent efficient bifunctional catalysts.[3–5]

In the past years, the high-yield deposition of silver nanoparticles on TiO$_2$ has proven challenging, although it is expected to achieve well-tailored chemical–physical characteristics for

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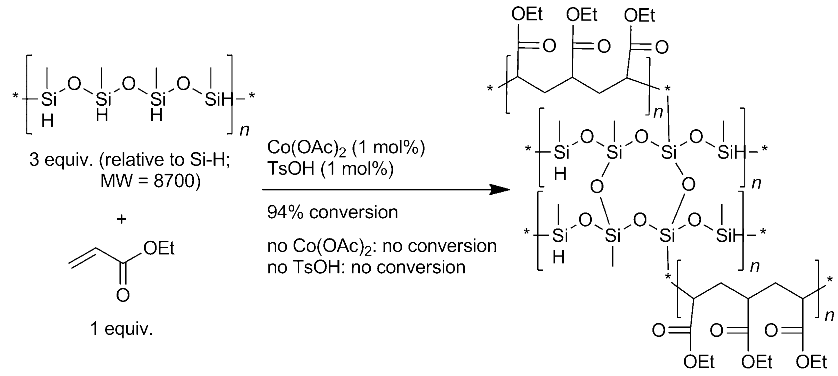


Scheme 1. Synthesis of SIPN made of PMHS and poly(ethyl acrylate) catalyzed by cobalt and TsOH.

advanced applications. In addition, the development of new synthetic procedures to nanosilver or Ag@TiO_2 nanocomposites should offer opportunities for the establishment of new characteristics of nanosilver and related functional materials. In the past decade, several approaches have been developed for the synthesis of hybrid Ag@TiO_2 including conventional impregnation, low-temperature solvothermal techniques, chemical reduction, deposition–precipitation techniques, photodeposition, and so on.[6] The TiO_2 used in these approaches was usually in the form of an extended network or nanocrystals. However, the use of a large amount of surfactant leads to the covering of the TiO_2 surface, which can decrease the sites for the growing of silver clusters.[7] Meanwhile, polymeric materials have been developed that possess certain functional groups, such as polyvinylpyrrolidone, polyvinyl alcohol, polyethylene glycol, and gelatin, which have also been used as stabilizers to prevent nanosilver particles from aggregation and control their particle size and shape.[8] Accordingly, the development of new synthetic procedures to nanosilver or Ag@TiO_2 nanocomposites should offer opportunities for the establishment of new chemical reactions or synthetic methods utilized with good catalytic activity of silver nanoparticles. In this context, environmentally benign nanosilver-catalyzed organic transformations of functional molecules with nanosilver-based nanoparticles are becoming a pressing concern to organic and catalyst chemists.[9] However, most of these examples have, so far, been limited to previously known transformations such as oxidation of alcohols or reduction. In particular, there are few examples reported on the application of nanosilver or Ag@TiO_2 nanocomposites in the synthesis of complex molecules. Herein, we describe the preparation of Ag@TiO_2 nanocomposites for environmentally benign and catalytic 1,2-alkynylation of trifluoromethyl ketones in water: 1) We developed a new route to the synthesis of hybrid Ag@TiO_2 nanocomposite located on a novel polysiloxane-based material; 2) The fabricated nanosilver catalysts exhibited high catalytic activity for the selective alkynylation of various trifluoromethyl ketones into fluorinated alcohols in water.

Results and Discussion

A new synthesis route toward nanoAg@TiO_2@PMHSIPN with a titanium-promoted reduction of organosilicon material

Very recently, we have developed a novel method for the preparation of polymethylhydrosiloxane (PMHS) and poly(ethyl acrylate) (PEA) based semi-interpenetrating networks (SIPN), and the structure and properties of the resulting SIPNs of PMHS/PEA (PMHSIPN) features good miscibility between PMHS and PEA (Scheme 1).[10] Especially, we found that the weight loss of PMHS/PEA SIPNs was 56.9 % at 700 °C (see the Supporting Information, p. 2–6, Figure S1 a–e), which may be attributed to the incorporation of the partially cross-linked polysiloxane with polyacrylate through the formation of the stable SIPN structure. Thus, on the basis of past findings and inspired by previous reports on the polysiloxane-based Ag-based nanocomposites,[11] we hypothesized that the highly thermally stable PMHS/PEA SIPNs could be used as a polymeric support in the construction of nanocomposites.

As shown in Scheme 1, the PMHSIPNs have hydrosilane (Si–H) and ester moieties. Initially, we wanted to utilize the functional groups on PMHS/PEA SIPNs to attach titanium and silver nanoparticles, thus we suggested that the titanium-catalyzed reduction of ester[12] could be a facile procedure to introduce titanium on this cross-linked polysiloxane with polyacrylate, which may also provide dispersed titanium on organosilicon-based material (Figure 1). Additionally, according to hypothesis, the classic sol–gel process then led to the formation of TiO_2.[13] Subsequently, in the last step, nanosilver was prepared according to a previous reduction method,[14] which deposited on TiO_2@PMHSIPN composite support (Figure 1). As a key innovation step in this approach, the introduction and adherence of titanium to organosilicon material was based on the titanium-catalyzed reduction of esters to primary alcohols with hydrosilane that has been reported by Buchwald and coworkers.[12] To the best of our knowledge, there is no report on the application of the present reduction reaction in the dispersion and synthesis of the interesting organic material/TiO_2 composite.

To accomplish the hypothesis that the titanium salt could be absorbed in this silicone-based material by the titanium {Ti(O*i*Pr)$_4$}-directed intermolecular reduction reaction in the PMHSIPNs, we performed the experiment under previously described reaction conditions[12] adding a treatment with a small amount of HNO_3, in which the yellow powder was obtained by a sol–gel approach in high yield.[15] As shown in the TEM images (see the Supporting Information), the TiO_2 membrane formed on the surface of the PMHSIPN. In Figure 2, the Ti(2p) X-ray photoelectron spectroscopy (XPS) analysis of TiO_2–PMHSIPN polymeric composite films reveal that TiO_2 was

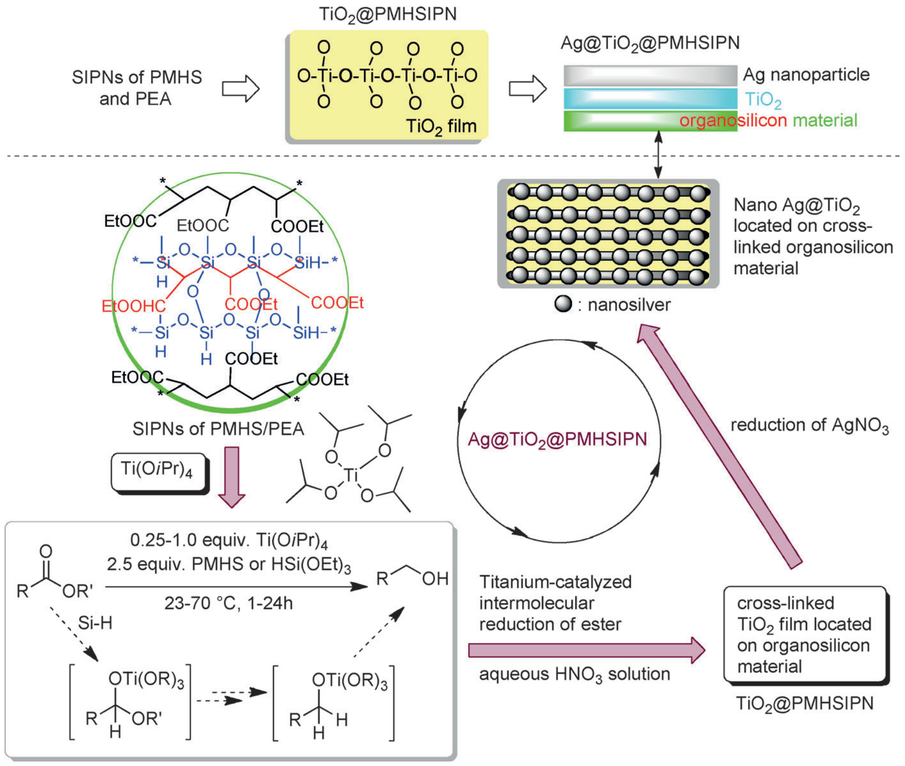


Figure 1. Synthesis of $Ag@TiO_2$ nanocomposite by the concept of TPR of ester with hydrosilane: Well-distributed dispersion of titanium and nanosilver on cross-linked PMHSIPN support ($Ag@TiO_2$@ PMHSIPN).

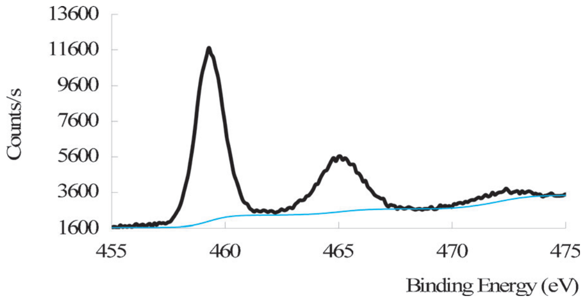


Figure 2. X-ray photoelectron spectra of TiO_2@PMHSIPN.

formed but did not exist as nanoparticles (see also Figures S7–S9).

In the last reaction step, the desired $Ag@TiO_2$ nanoparticles were obtained successfully (Figure 2). Thus, the supported and dispersed TiO_2 on the reactive organosilicon material facilitated the uniformly formation of $Ag@TiO_2$ nanoparticles. Their XRD patterns, energy-dispersive spectroscopy (EDS) results, SEM and TEM images, and Raman spectra of hybrid $Ag@TiO_2$ located on PMHSIPNs are shown in Figure S4–S6 and Figure 3, which support the formation of hybrid $Ag@TiO_2$ located on organic PMHS-based semi-interpenetrating networks. More importantly, the XPS spectrum of hybrid $Ag@TiO_2$ located on organic PMHSIPNs confirmed the formation of Ag^0 nanoparticles (Figure 4), and the shape, size, and distribution of $Ag@TiO_2$ nanoparticles (average 100 nm) can be clearly observed in the TEM images. As shown in Figure 3, TEM images of the hybrid $Ag@TiO_2$ nanocomposites reveal a large number of $Ag@TiO_2$ nanoparticles with uniform size (80–120 nm), which were highly dispersed on the surface of cross-linked organosilicon-based materials. Notably, with a similar procedure, we also successfully prepared a nano-$Ag@TiO_2$@PMHSIPN with smaller sizes (10–30 nm), in which the size of nano$Ag@TiO_2$@PMHSIPN could be controlled by the synthetic procedure and affected by the reaction time (see the Supporting Information).

Alkynylation of trifluoromethyl ketones catalyzed by nano-$Ag@TiO_2$@PMHSIPN

In the light of the successful construction of monodispersed $Ag@TiO_2$ nanoparticles (i.e., nano$Ag@TiO_2$@PMHSIPN) with unique size and shape, we then turned our attention to the most important aim of this work, which was the development of an efficient and environmentally benign alkynylation of trifluoromethyl ketones on the basis of the unique catalytic activity of

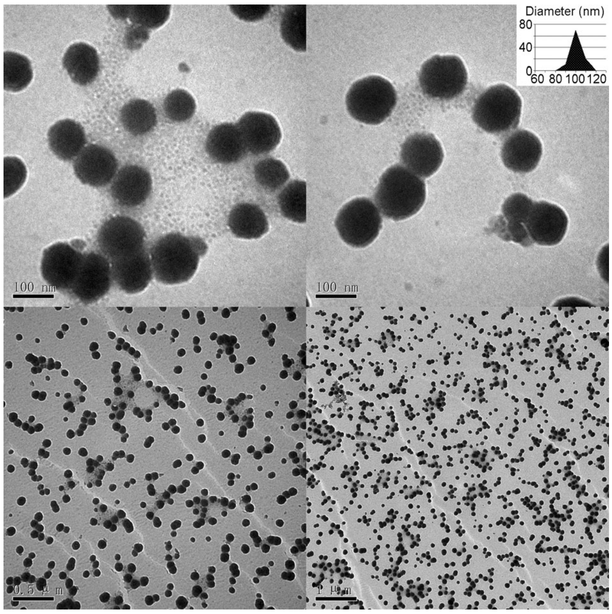


Figure 3. TEM images of hybrid $Ag@TiO_2$ located on PMHS-based semi-interpenetrating networks (nano$Ag@TiO_2$@PMHSIPN). Inset: Size distribution of $Ag@TiO_2$ nanoparticles.

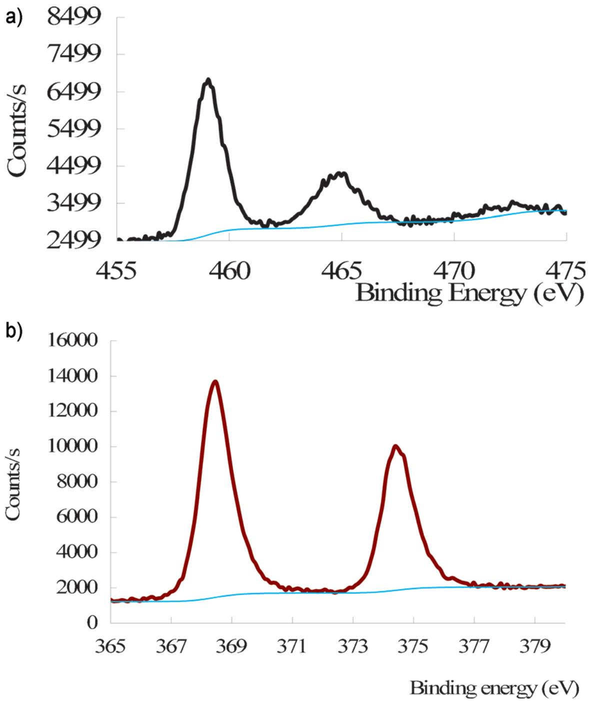
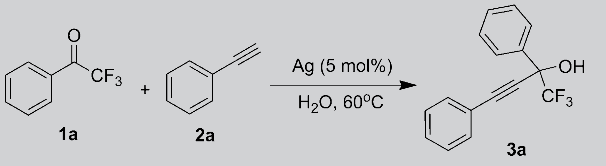


Figure 4. X-ray photoelectron spectra of nanoAg@TiO_2@PMHSIPN. a) Ti(2p) spectrum; b) Ag(3d) spectrum.

silver@TiO_2 nanoparticles. Catalytic alkynylation of trifluoromethyl ketones into fluorinated propargylic alcohols is an important reaction in both organic synthesis and pharmaceutical science as well as organofluorine chemistry.[16] Not surprisingly, many methods have been developed for the efficient synthesis of such fluorinated alcohols.[17] However, a common approach to this transformation involves the use of at least an equivalent of strong metallic base (BuLi or organozinc reagent) to guarantee its smooth addition. To the best of our knowledge, there is almost no report on the catalytic alkynylation of trifluoromethyl ketones in water.[18,19] Thus in spite of recent progress in the exploring of catalytic method for this practical transformation, development of simple, efficient, and environmentally benign methodologies for alkynylation of trifluoromethyl ketones is important for the advancement of practical synthetic organic chemistry.

In an initial investigation, we examined the alkynylation of 2,2,2-trifluoro-1-phenylethanone (**1a**) with 1-ethynylbenzene (**2a**) by optimization of the reaction conditions. After screening organic bases, phosphine ligands, solvents, and reaction temperatures, we found that the alkynylation of **1a** with **2a** proceeded smoothly in the presence of Et_3N and triphenylphosphine at room temperature, giving the desired product **3a** in excellent yield if water was used as a solvent and the reaction time was 2 h (see the Supporting Information, Table S1). Next, a large number of silver salts and nanosilver without PMHSIPN supporter were investigated in the controlled experiments for the alkynylation.

Table 1. Optimization and comparison of reaction conditions for the silver-catalyzed alkynylation of 2,2,2-trifluoro-1-phenylethanone (**1a**) with 1-ethynylbenzene (**2a**).[a]

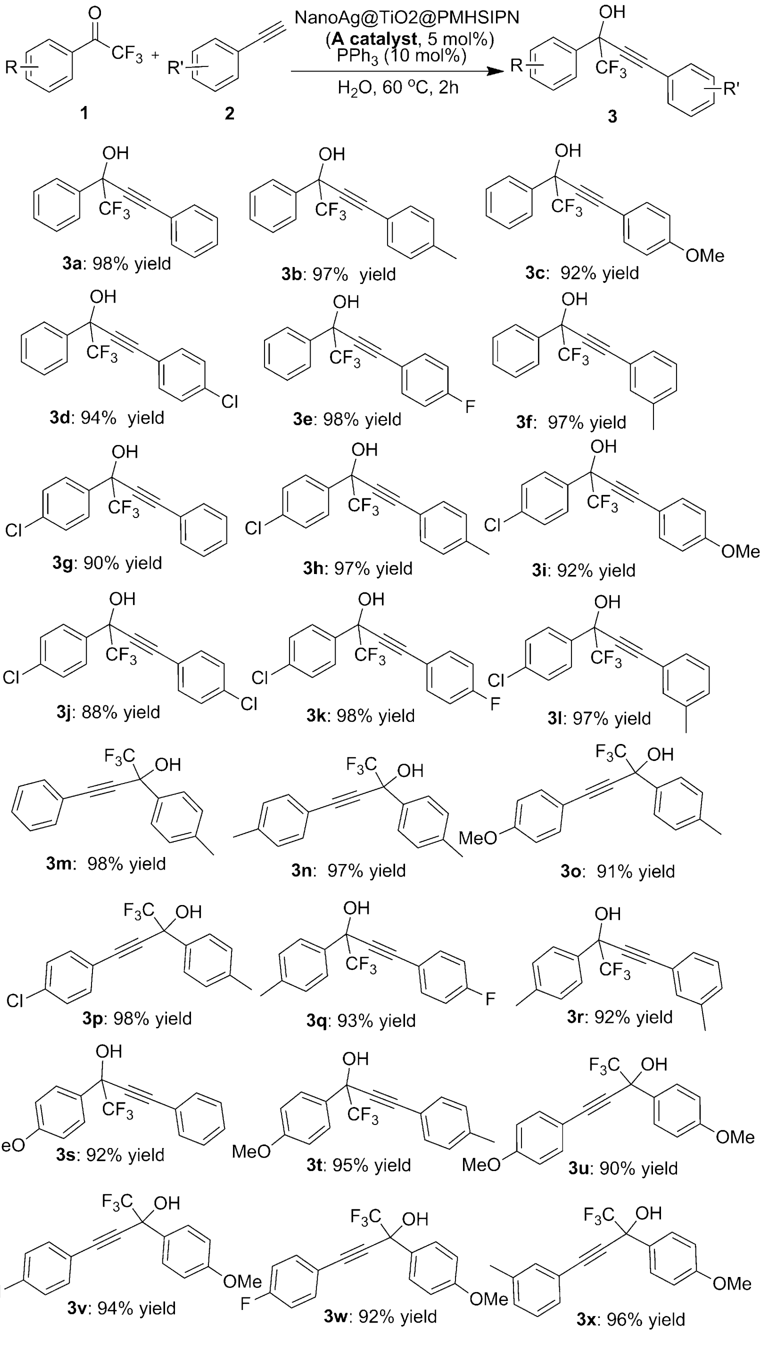


Entry	Catalyst	*t* [h]	Yield [%][b]
1	$AgNO_3$	2	<10
2	AgOAc	2	<10
3	AgOTf	2	<10
4	AgO	2	<10
5	AgF	2	<5
6	$AgClO_4$	2	<10
7	nanoAg@TiO_2@PMHSIPN (**A**)	2	98[c,d]
8	nanoAg@TiO_2@PMHSIPN (**A**)	2	95[e]
9	Ag@TiO_2	15	88
10	Ag@TiO_2	2	<20
11	Ag nanoparticle	2	<10
12	Ag nanoparticle	15	75
13	TiO_2	15	0
14	nanoAg@TiO_2@PMHSIPN (**B**)	2	98[c,f]

[a] Reaction conditions: 2,2,2-trifluoro-1-phenylethanone (**1a**, 0.5 mmol), 1-ethynylbenzene (**2a**, 1.5 mmol), silver catalyst (5 mol%), PPh_3 (10 mol%), Et_3N (40 mol%), and distilled water (3 mL), at 60 °C, for 2–15 h. [b] The isolated yield was obtained after purification with flash column chromatography. [c] No addition of Et_3N. [d] The size of nanoAg@TiO_2@PMHSIPN was 80–120 nm (**A** catalyst). [e] The Ag@TiO_2 nanocomposite (**A** catalyst) was recycled and reused for the second time, the isolated yield was 95%. [f] The size of nanoAg@TiO_2@PMHSIPN was 10–30 nm (**B** catalyst), the synthetic procedure of **B** catalyst is shown in the Supporting Information.

As shown in Table 1, under the same reaction conditions except for the reaction time, various silver salts, including $AgNO_3$, the precursor of nanosilver, resulted in poor levels of catalytic performance (<10% yield, entries 1–6). Notably, these commercial available silver salts, such as $AgNO_3$, AgOTf, AgOAc, AgO, AgF, and $AgClO_4$, also exhibited relatively poor catalytic activity at longer reaction times, and low yields of products were determined in these cases. In contrast, our nanoAg@TiO_2@PMHSIPN catalyst gave complete conversion (>99%) in 2 h and in the absence of Et_3N (for **A** catalyst, 98% isolated yield, entry 7). Additionally, the possibility of recycling of the nanoAg@TiO_2@PMHSIPN catalyst was also investigated. As shown in the same entry 7, the recovered nanocatalyst gave good catalytic performance in this reaction (98% yield), however, the addition of catalytic amounts of PPh_3 was necessary. Comparably, although the general nanosilver and Ag@TiO_2 nanocomposite prepared without PMHSIPN could reach good yields (75% and 88%, respectively, entries 9–12), the catalytic performances of these classic nanocatalysts and general silver salts in this reaction were far lower than that of nanoAg@TiO_2@PMHSIPN in shorter time (after 2 h, <20% isolated yields were achieved with Ag@TiO_2 and nanosilver without silicone support). It should be mentioned, that silver-free TiO_2 was not effective in this reaction (entry 13). It should also be noted that the nanoAg@TiO_2@PMHSIPN with smaller size (10–30 nm, catalyst **B**) exhibited the same excellent catalytic activity as catalyst **A** (entry 14). These results clearly indicate the nanostructure of the Ag@TiO_2 catalyst located on PMHS-based semi-interpenetrating networks plays a crucial role for the current transformations. Notably, the unique catalytic activity of present organosilicon-supported Ag@TiO_2 nanoparticles in water provides an alternative and environmentally benign example to the synthesis of fluorinated propargylic alcohols through catalytic nucleophilic additions of terminal alkynes.

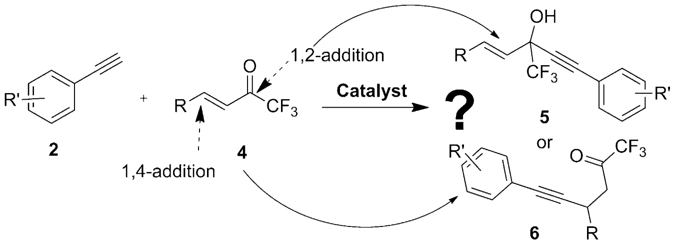
The reaction scope for the nanoAg@TiO_2@PMHSIPN in the catalytic alkynylation of trifluoromethyl ketones was then carefully investigated. As shown in Scheme 2, this nanoAg@TiO_2@PMHSIPN could promote 1,2-addition of aromatic terminal alkynes to various trifluoromethyl ketones, affording the corresponding fluorinated propargylic alcohols in excellent isolated yields (24 examples, 88–98% yield). For example, both aromatic terminal alkynes and trifluoromethyl ketones with chloride, bromide, fluoride, methyl, and methoxyl groups on aromatic rings were successfully employed, and almost all transformations were completed in quantitative yields (≤98% isolated yields, Scheme 1). Notably, nanoAg@TiO_2@PMHSIPN catalyst **B** (smaller sizes of 10–30 nm) also exhibited excellent catalytic activity in this reaction, and the isolated yields of these products were achieved at the same level. We also tried to expand the scope of aromatic trifluoromethyl ketones to alkyl trifluoromethyl ketones, however, the reactivity of alkyl trifluoromethyl ketones was very low under the optimized reaction conditions. Likewise, the alkynylation of trifluoromethyl ketones with alkyl alkynes, such as ethynyltrimethylsilane, led to poor conversion. All these results demonstrate that the efficiency of the nanoAg@TiO_2@PMHSIPN-catalyzed alkynylation reaction is sensitive to the electronic demand of trifluoromethyl ketones and alkynes.



Scheme 2. NanoAg@TiO_2@PMHSIPN (**A** catalyst)-catalyzed alkynylation of various trifluoromethyl ketones and terminal alkynes in water.

Alkynylation of α,β-unsaturated trifluoromethyl ketones catalyzed by nanoAg@TiO_2@PMHSIPN

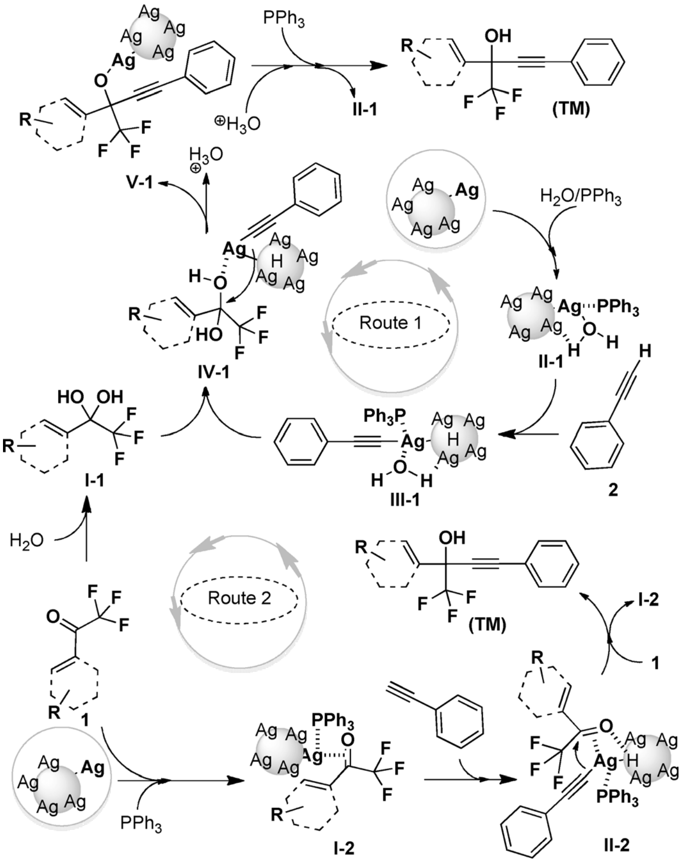
To the best of our knowledge, there are no reports on the alkynylation of α,β-unsaturated trifluoromethyl ketones to date. In general, the α,β-unsaturated trifluoromethyl ketones might result in two possible products because of two different reaction paths of 1,2-addition or 1,4-addition of alkynes to α,β-unsaturated trifluoromethyl ketones (Scheme 3). Interestingly, in this study, α,β-unsaturated trifluoromethyl ketones were also good substrates in the nanoAg@TiO_2@PMHSIPN-catalyzed 1,2-alkynylation reaction. As illustrated in Table 2, the selective 1,2-addition occurred smoothly instead of the 1,4-addition. No byproducts were detected in this reaction, and the desired tertiary alcohol products containing trifluoromethyl, alkynyl, and alkenyl groups were obtained in good



Scheme 3. Possible alkynylation of α,β-unsaturated trifluoromethyl ketones in the presence of catalyst.

to excellent isolated yields (58–95 % yields for two different nanoAg@TiO$_2$@PMHSIPN catalysts). Interestingly, the size dependence of the catalytic alkynylation of α,β-trifluoromethyl ketones was obvious. As shown in Table 2, smaller sizes of nanoAg@TiO$_2$@PMHSIPN catalyst **B** (10–30 nm) led to higher catalytic activity (entries 1–8), which differed from the nanoAg@TiO$_2$@PMHSIPN catalyzed 1,2-alkynylation reaction of aromatic trifluoromethyl ketones **1**.

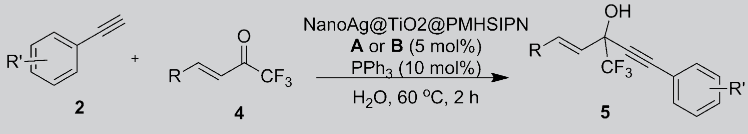
From the data in Scheme 2 and Table 2, it is obvious that our method has following advantages over existing methods: 1) high catalytic activity and selectivity to a wide range of terminal aromatic alkynes and substituted trifluoromethyl ketones; 2) clean reaction without byproduct, for example, dimer of terminal alkyne that was usually encountered in the cross-coupling reaction of alkynes with other reagents, was not detected in this aqueous reaction; 3) the use of nontoxic, safe, and easy-to-handle water as the solvent and a simple purification procedure owing to easy separation of the solid catalysts from the reaction mixtures, and the recyclable nanocatalyst could be used in the next catalytic cycles.



Scheme 4. Possible reaction pathways for the silver-catalyzed addition of terminal alkynes to trifluoromethyl ketones.

Although the detailed reaction mechanism remains unclear, two proposed mechanistic pathways (route 1 or route 2) are illustrated in Scheme 4. On the basis of experimental results, the transformation of trifluoromethyl ketones is probably initiated by the formation of key hydrate intermediate (**I-1**) in a stable form.[20] Both the kinetic isotope effect (k_H/k_D ratio), which was determined to be 1, and the inverse solvent isotope effects (SIE = 2.11)[21] gave useful experimental evidences (Figure 5) to verify the presence of **I-1**, which indicates the oxidative addition of silver to alkyne is not the rate-determining step, and the solvent effect is largely owing to the nucleophilic addition of water to trifluoromethyl ketone. Simultaneously, oxidative addition of alkyne with the active silver–phosphine complex **II-1**, which is generated in situ and fast by the release of silver from nanosilver particles and phosphine ligand, results in the generation of intermediate **III-1**.[22] Then, the interchange of hydrate intermediate of trifluoromethyl ketone (**I-1**) with water on the intermediate **III-1** occurs quickly to form the key species **IV-1**. Finally, the intramolecular addition of alkyne and subsequent releasing of silver complex from **V-1** with the aid of water and phosphine can occur smoothly to generate the desired product and regenerate silver–phosphine complex **II-1**, which can continue the catalytic cycle (route 1 in Scheme 4). Notably, route 2 is also reasonably. However, there is no direct evidence to

Table 2. NanoAg@TiO$_2$@PMHSIPN-catalyzed alkynylation of various α,β-unsaturated trifluoromethyl ketones and terminal alkynes in water.



Entry	Nanosilver catalyst	R	R′	Yield [%][b]
1	nanoAg@TiO$_2$@PMHSIPN (**A**: 80–120 nm)	Ph	*p*-Me	**5 a**: 62
2	nanoAg@TiO$_2$@PMHSIPN (**B**: 10–30 nm)	Ph	*p*-Me	**5 a**: 82
3	nanoAg@TiO$_2$@PMHSIPN (**A**: 80–120 nm)	Ph	*p*-Cl	**5 b**: 61
4	nanoAg@TiO$_2$@PMHSIPN (**B**: 10–30 nm)	Ph	*p*-Cl	**5 b**: 95
5	nanoAg@TiO$_2$@PMHSIPN (**A**: 80–120 nm)	Ph	*p*-F	**5 c**: 58
6	nanoAg@TiO$_2$@PMHSIPN (**B**: 10–30 nm)	Ph	*p*-F	**5 c**: 84
7	nanoAg@TiO$_2$@PMHSIPN (**A**: 80–120 nm)	Ph	*m*-Me	**5 d**: 58
8	nanoAg@TiO$_2$@PMHSIPN (**B**: 10–30 nm)	Ph	*m*-Me	**5 d**: 83
9	nanoAg@TiO$_2$@PMHSIPN (**B**: 10–30 nm)	*p*-Cl–Ph	*p*-Me	**5 e**: 85
10	nanoAg@TiO$_2$@PMHSIPN (**B**: 10–30 nm)	*p*-Cl–Ph	*p*-OMe	**5 f**: 89
11	nanoAg@TiO$_2$@PMHSIPN (**B**: 10–30 nm)	*p*-Cl–Ph	*p*-Cl	**5 g**: 92
12	nanoAg@TiO$_2$@PMHSIPN (**B**: 10–30 nm)	*p*-Cl–Ph	*p*-F	**5 h**: 87

[a] Reaction conditions: α,β-unsaturated trifluoromethyl ketones (**4**, 0.5 mmol), alkynes (**2**, 1.5 mmol), nanosilver **A** or **B** catalyst (5 mol %), PPh$_3$ (10 mol %), and distilled water (3 mL), at 60 °C, for 2 h. [b] Isolated yields.

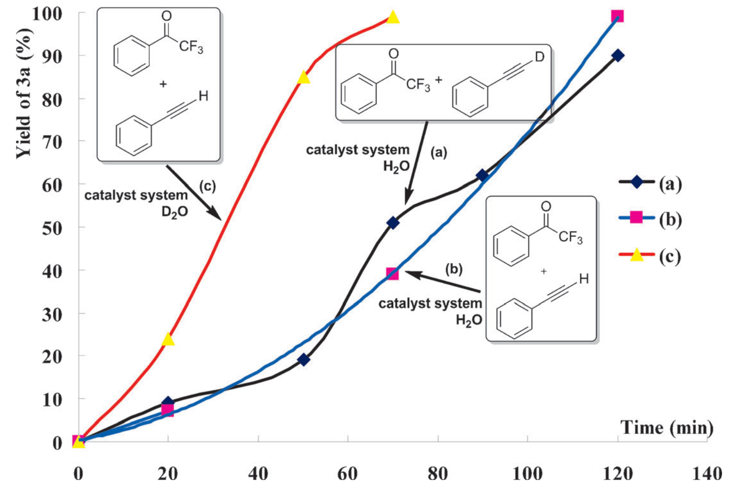


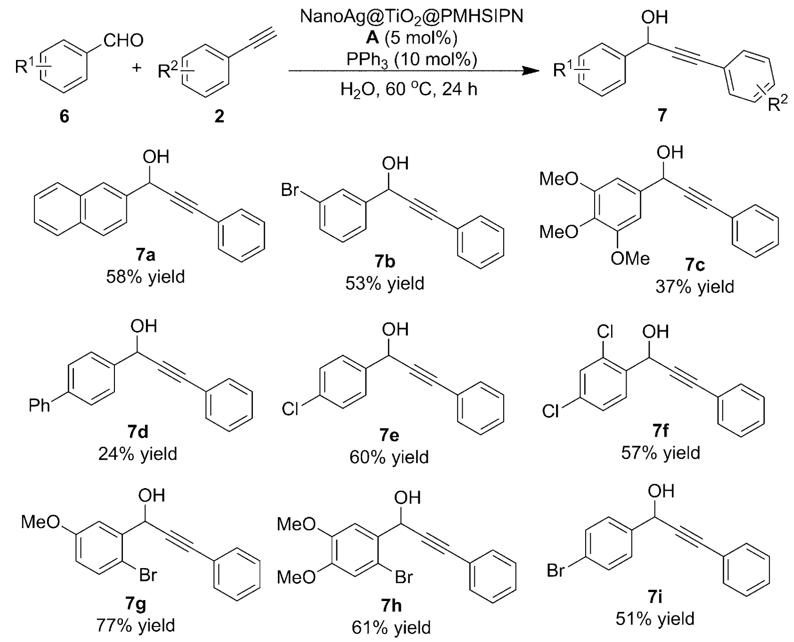
Figure 5. Plot of yield of **3 a** over time showing the different reaction rates in the alkynylation reactions of 2,2,2-trifluoro-1-phenylethanone (**1 a**) with a) deuterium-modified 1-ethynylbenzene in water, b) 1-ethynylbenzene in water, and c) 1-ethynylbenzene in heavy water.

support the formation of molecular interaction between trifluoromethyl ketones and nanosilver–phosphine complex. Fortunately, the released and trace silver–phosphine complex **II-1** from supported nanosilver was confirmed by ESI(+)–MS analysis (see Figure S14–15), which supports the possible formation of activated silver complex in aqueous reaction media.

Alkynylation of aromatic aldehydes catalyzed by nanoAg@-TiO2@PMHSIPN: Enhanced activity by using trifluoromethyl ketones

Although the catalytic alkynylation of trifluoromethyl ketones catalyzed by nanoAg@-TiO_2@PMHSIPN performed smoothly in excellent yields, the nanoAg@TiO_2@PMHSIPN-catalyzed alkynylation of aromatic aldehydes was not satisfying regarding the isolated yields. As shown in Scheme 5, the nanocatalytic process revealed that the alkynylation reaction led to only low to moderate yields (25–77%) for most aromatic aldehydes and aliphatic aldehydes. For example, with 2-naphthaldehyde (**6 a**) as the substrate, only moderate conversion and isolated yield were observed, which indicated the reactivity of aromatic aldehyde was lower than that of trifluoromethyl ketones. From the results shown in Scheme 5, it an important observation that only those aromatic aldehydes bearing an *ortho*-substituted bromide resulted in promising yields (**7 g** and **7 h**, 77% and 61% isolated yields, respectively). This result might suggest that the presence of the neighboring bromide group on the aromatic ring increased the interaction between silver nanoparticles and substrates.[9m] The limited substrate scope for aromatic aldehydes in this alkynylation promoted us to improve the catalytic activity of our nanoAg@-TiO_2@PMHSIPN catalyst by modification of reaction conditions. Thus subsequent studies on the effect of additives in the improvement of nanocatalytic alkynylation of aromatic aldehydes is highly desired.

In catalytic organic reactions, it is unusual for analogous substrates with various substituted groups to afford different product yields or selectivities varying from almost no reaction to perfect conversion.[23] To overcome low catalyst activity associated with substrate-dependent reactions, the use of a suitable additive for the optimization of corresponding organic reactions is effective and practical. In particular, additives have been recognized as indispensable and tunable tools in chirality enhancement of asymmetric catalysis and in the effort “towards perfect asymmetric catalysis”.[24] Moreover, in the past decades, significant advances have been made in exploiting the use of additives to improve catalytic performances for many organic transformations and many groups reported the irreplaceable role of additives on various transition-metal-catalyzed transformations.[25] However, it is not an easy task to enhance the activity of unreactive or poorly reactive substrates/catalysts by the optimization of reaction conditions or modulation of chemical environment with the aid of additives. Very recently, a good example was reported by Pfaltz and co-workers,[26] in which they disclosed an iridacycle catalyst



Scheme 5. NanoAg@TiO_2@PMHSIPN (**A** catalyst)-catalyzed alkynylation of various trifluoromethyl ketones and terminal alkynes in water.

in situ activated by a highly reactive substrate with improved reactivity and enantioselectivity in the hydrogenation of dialkyl ketimines. However, in their early study,[27] the Ir–phosphinooxazoline (PHOX) complex generally suffered from low yields for dialkyl ketimines but gave excellent enantioselectivities and high turnover numbers for the hydrogenation of analogous aryl alkyl *N*-arylketimines. On the basis of the mechanistic study, the authors found that the addition of an equimolar equivalent of acetophenone imine to Ir–phosphinooxazoline (PHOX) complex resulted in the formation of an active catalyst that displayed higher reactivities and better enantioselectivities in the hydrogenation of both aryl alkyl *N*-arylketimines and analogous dialkyl ketimines. The present study[26] provides an excellent example on the substrate-type additive-activated asymmetric catalysis as well as the catalyst–substrate interaction-based reactivity enhancement.

Inspired by previous results on additive-enhanced chemical reactions,[25,26] we hypothesized that highly reactive substrates could react with transition metal complexes to improve their catalytic performance because of the formation of a new activated intermediate, thus the corresponding substrate could be used as an additive to initiate the transformation of nonreactive or poorly reactive analogous substrates. In other words, the mechanistic procedure could be changed possibly by the addition of highly reactive substrates through noncovalent interactions between additive and catalyst. Thus the concept of springboard chemistry that highly reactive substrate act as a "reactive tractor" or "reactive springboard" to drive the transformation of poorly reactive substrates would be a practical principle to enhance or improve the activity of transition-metal catalysts in many reactions (Figure 6).

Very recently, we have reported that substituted amide-derived olefins could be used as a reactive springboard/ligand to promote the palladium-catalyzed hydrogenation of olefins and reductive decarbonylation of acyl chlorides with hydrosilane, in which the *Z*-to-*E* isomerization of substituted amide-derived olefins initiated and enhanced the palladium catalyst to reach a good level of catalytic performance in these reactions.[28] Although the mechanism of isomerization-initiated transformation was not clear, the reaction results revealed that the in situ generated hydride palladium complex was a key catalyst in the presence of amide-derived olefin. Encouraged by this work, we herein report our recent findings on the concept of springboard chemistry that highly reactive substrate act as a "reactive tractor" to drive the transformation of poorly reactive substrates. Thus we found that trifluoromethyl ketone could be used as a very efficient additive in the nanosilver-catalyzed alkynylation of aldehydes. The new example of reactive additive-enhanced transformations revealed that the springboard chemistry would be an effective strategy and concept in the enhancement of catalytic organic transformation.

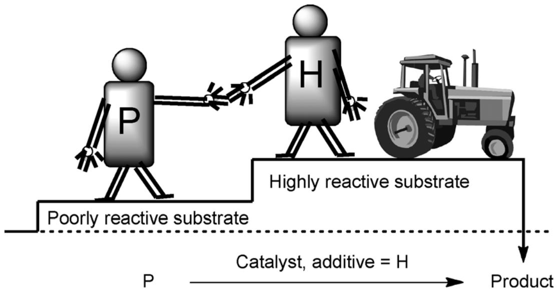
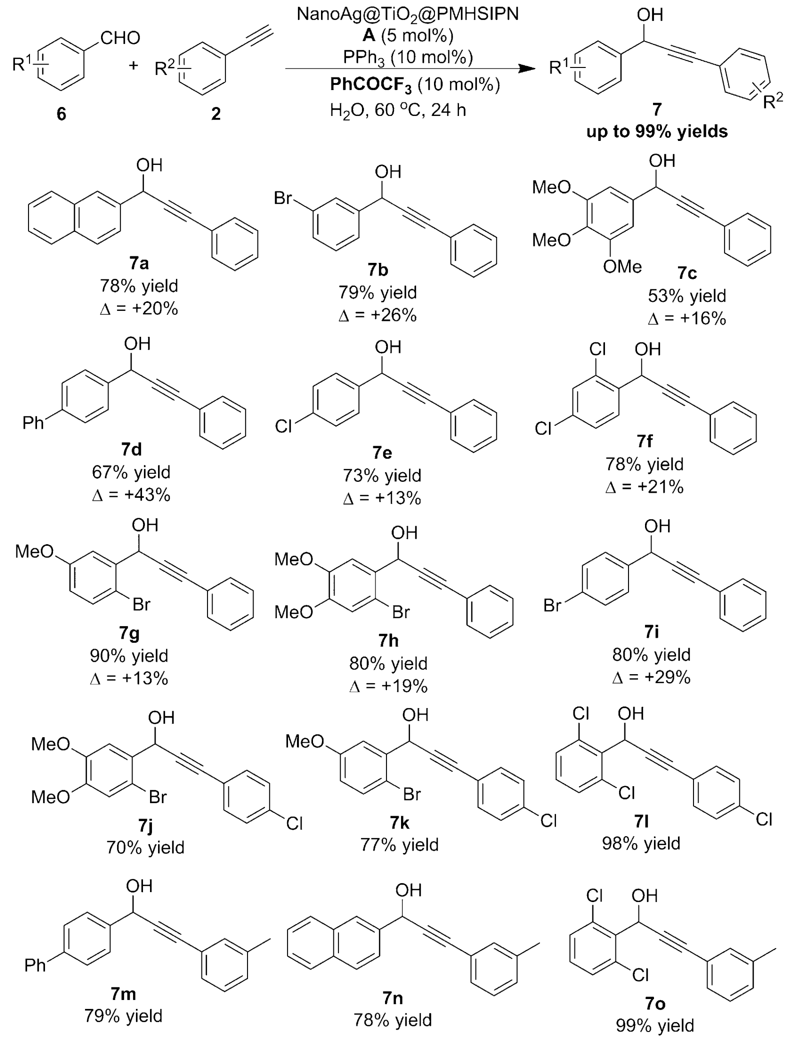


Figure 6. The hypothesis of springboard chemistry that highly reactive substrates can act as a "reactive tractor" or "reactive springboard" to drive the transformation of poorly reactive substrates.

On the basis of previous work on the highly efficient nanoAg@TiO$_2$@PMHSIPN-catalyzed alkynylation of trifluoromethyl ketones ($\leq$98% isolated yields), we felt that the use of an appropriate trifluoromethyl ketone would allow us to enhance the catalytic alkynylation of aromatic aldehydes. Fortunately, using catalytic amounts of 2,2,2-trifluoro-1-phenylethanone (**1a**, 10 mol%) as an additive when the coupling reaction of 2-naphthaldehyde (**6a**) and 1-ethynylbenzene (**2a**) was performed with 5 mol% of nanoAg@TiO$_2$@PMHSIPN, good yield of the desired product **7a** were achieved. In comparison to that of the additive-free alkynylation, the yield was increased from 58% to 78% (Scheme 5 and Scheme 6, difference = +20%). Therefore, this is a good example of highly reactive substrates acting as a "reactive tractor" to initiate and drive the transformation of poorly reactive substrates. With this finding, we continued to examine the catalytic alkynylation of general aromatic aldehydes in the presence of **1a** (10 mol%) as well as the nanosilver catalyst in water. As shown in Scheme 6, it was found that all aromatic aldehydes we chose resulted in good to excellent yields on these conditions. The isolated yields of the aromatic aldehydes were increased by at least 13%. Especially for substrate 4-phenylbenzaldehyde (**6d**), the yield of **7d** could be increased from 24% to 67%. We reasoned that this enhancement might result from the interchange between the nanosilver–trifluoromethyl ketone intermediate (for example, intermediate **V-1** or **IV-1** of Scheme 4) and the aromatic aldehyde. Similarly, the enhanced interaction between nanocatalyst and substrate initiated by 2,2,2-trifluoro-1-phenylethanone led to the decreasing of the activation energy for the 1,2-addition reaction of the terminal alkyne to the aldehyde.

To clarify the dramatic increase in yield promoted by trifluoromethyl ketone, we performed a kinetic study of trifluoromethyl ketone promoted alkynylation of aromatic aldehydes under different conditions. As shown in Figure 7, the time dependence of the conversion of 4-bromobenzaldehyde **6i** reveals that **1a** has a pronounced promoting effect on the conversion of **6i**, especially in the initial stage. Thus, we demonstrated the positive activation of aromatic aldehydes by trifluoromethyl ketone for the proposed mechanism. As shown in Scheme 7, we propose a "reactive tractor" like mechanism for this trifluoromethyl ketone promoted silver-catalyzed addition of terminal alkynes to aromatic aldehydes. This proposed mechanism is consistent with the observation in Figure 7 and Figure 5 that both water and trifluoromethyl ketone are important for the catalytic cycle owing to the existence of activated intermediates (from **I-1** to **IV-1**). Although the true mechanism is not clear at present, this simple reaction path will provide



Scheme 6. NanoAg@TiO$_2$@PMHSIPN (**A** catalyst)-catalyzed alkynylation of various trifluoromethyl ketones and terminal alkynes in the presence of trifluoroacetophenone. Δ values represent the difference in yield compared to the reactions without trifluoroacetophenone.

access to the structurally important propargylic alcohols and increased scopes relative to previous methods, the operational simplicity and environmental friendliness of this process should render this protocol as well as the concept of springboard chemistry attractive to synthetic chemists.

Conclusions

We have developed a new approach to monodispersed hybrid Ag@TiO$_2$ nanocomposites using a titanium-promoted cross-linking reduction in the Si–H functional material, polymethylhydrosiloxane(PMHS)-based semi-interpenetrating networks (PMHSIPN). The titania was designed to be highly dispersed on the functional material and then the Ag@TiO$_2$ nanoparticles were formed in uniform size and shape under mild conditions. The experimental results reveal that the nanosilver catalyst (the fabricated Ag@TiO$_2$ located on PMHSIPNs, namely, nanoAg@TiO$_2$@PMHSIPN) has enhanced catalytic activities in the alkynylation of trifluoromethyl ketones or α,β-unsaturated trifluoromethyl ketones with terminal alkynes. In this reaction, the hybrid Ag@TiO$_2$ nanoparticles exhibit a high level of catalytic activity for the selective 1,2-alkynylation of various trifluoromethyl ketones and α,β-unsaturated trifluoromethyl ketones into a wide range of fluorinated alcohols in water (≤98% yield). This protocol offers considerable benefits including environmentally benign aqueous transformation. Finally, on the basis of the nanoAg@TiO$_2$@PMHSIPN-catalyzed alkynylation of trifluoromethyl ketones, we developed a new concept whereby highly reactive substrates act as a "reactive tractor" to drive the transformation of poorly reactive substrates as springboard chemistry. Consequently, we found trifluoromethyl ketones can be used as efficient additives in the nanosilver-catalyzed alkynylation of aldehydes. The nanosilver-catalyzed alkynylation of aromatic aldehydes proceed in good to high yields under optimized reaction conditions (≤99% yield). Further studies to elucidate the catalytic activity of PMHSIPN-supported/dispersed Ag@TiO$_2$ in organic reaction as well as the biological utility of nanocomposites are in progress.

Experimental Section

All the chemicals were of analytic reagent grade and were used as received without further purification. AP-grade ethyl acrylate, Co(OAc)$_2$, TsOH, and chloroform were used as received. The molecular weight of PMHS was $\approx 8684\ \mathrm{g\,mol^{-1}}$. Attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy was performed on a VERTEX 70 IR (Bruker). The data were collected over 32 scans with a resolution of $4\ \mathrm{cm^{-1}}$ at RT. The morphology of the polymer fracture surface was characterized by scanning electron micrographs (SEM, Hitachi S3000N). The samples were frozen in liquid nitrogen and snapped immediately. TEM studies were performed by the phosphotungstic acid staining method on a Hitachi H-7650 transmission electron microscope. Flash column chromatography was performed over silica (200–300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 or 500 (for ^{1}H NMR) and 100 or 125 MHz (for ^{13}C NMR), respectively, on an Advance (Bruker) 400 or 500 MHz Nuclear Magnetic Resonance Spectrometer, and were referenced to the internal solvent signals. ^{19}F NMR spectra were recorded at 470 MHz on an Advance (Bruker) 500 MHz NMR spectrometer. Thin-layer chromatography was performed by using silica

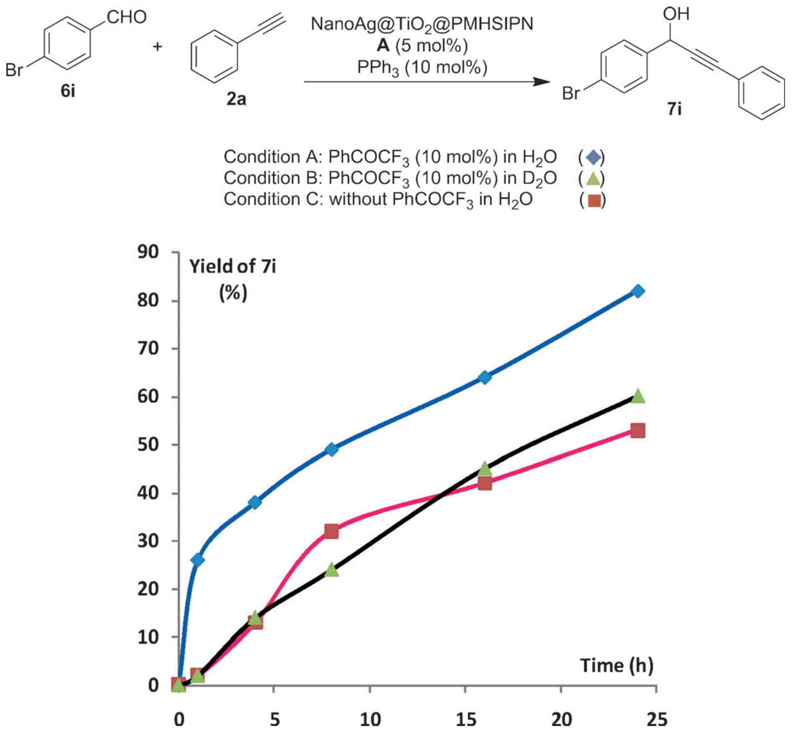
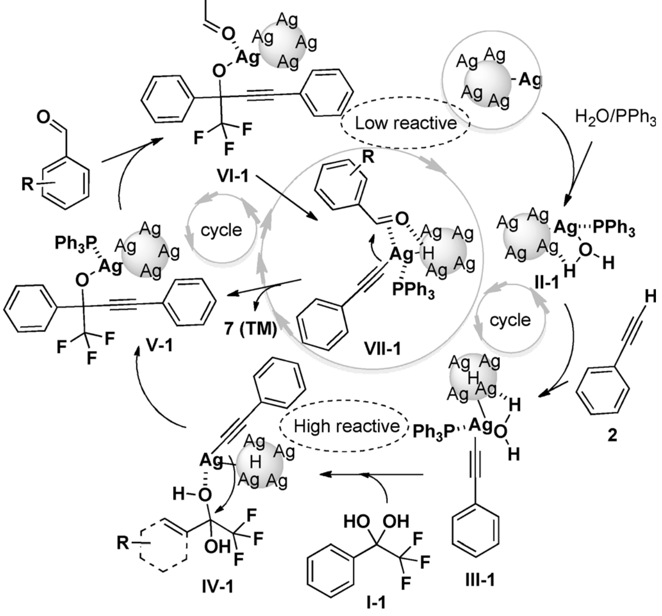


Figure 7. Plot of yield of **7 i** versus time showing the different reaction rates in the alkynylation reactions of aromatic aldehyde in the presence or absence of 2,2,2-trifluoro-1-phenylethanone promoter (**1 a**) in water or heavy water.



Scheme 7. Proposed mechanism for the trifluoromethyl ketone promoted silver-catalyzed addition of terminal alkynes to aromatic aldehydes.

gel; GF254 TLC plates and visualized with UV light. The products were confirmed by GC–MS, and usual spectral methods (NMR methods). In the nanosilver-catalyzed alkynylation of trifluoromethyl ketones or α,β-unsaturated trifluoromethyl ketones, both method A and method B with different catalysts, respectively, led to the same products (see the Supporting Information), in which their differences only rely on the yields. The reaction results are collected in the product characterization part.

NanoAg@TiO$_2$@PMHSIPN-catalyzed 1,2-addition reaction of terminal alkynes and trifluoromethyl ketones

General procedure: Trifluoroacetophenone (**1 a**, 71 μL, 0.5 mmol), phenylacetylene (**2 a**, 165 μL, 1.5 mmol), nanoAg@TiO$_2$@PMHSIPN (4.25 mg, 0.025 mmol, 5 mol% of Ag), PPh$_3$ (13.1 mg, 0.05 mmol, 10 mol%), and distilled water (2 mL) were added into a 15 mL Schlenk tube under nitrogen, and then the reaction mixture was stirred at 60 °C for 2 h. The mixture was extracted by ethyl acetate (3×3 mL). The extraction was dried with anhydrous sodium sulfate and concentrated by rotary evaporation. The residue was purified by flash column chromatography (10:1 hexane and ethyl acetate) to give **3 a** with 98% yield. Most products **3** were known compounds and products **5** were new compounds. All these molecules were confirmed by NMR and IR spectroscopy and GC–MS or HRMS . The detailed experimental procedures and characteristics of the corresponding products are provided in the Supporting Information.

Trifluoroacetophenone-promoted nanoAg@TiO$_2$@PMHSIPN-catalyzed alkynylation of aromatic aldehydes

General procedure: 2-Naphthaldehyde (**6 a**, 0.078 g, 0.5 mmol), phenylacetylene (**2 a**, 165 μL, 1.5 mmol), nanoAg@TiO$_2$@PMHSIPN (4.25 mg, 0.025 mmol, 5 mol%), PPh$_3$ (13.1 mg, 0.05 mmol, 10 mol%), trifluoroacetophenone (7.1 μL, 0.025 mmol, 5 mol%), and distilled water (2 mL) were added into a 15 mL Schlenk tube under nitrogen, and then stirred at 60 °C for 24 h. The mixture was extracted by ethyl acetate (3×3 mL). The extraction was dried with anhydrous sodium sulfate and concentrated by rotary evaporation. The residue was purified by flash column chromatography (10:1 hexanes and ethyl acetate) to give **7 a** with 78% yield. All products **7** are known compounds and all these molecules were confirmed by NMR and IR spectroscopy and GC–MS or HRMS. The detailed experimental procedures and characteristics of corresponding products are provided in the Supporting Information.

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Keywords: alkynes · green chemistry · nanoparticles · silver · water

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