Semiconductor-based nanocomposites for selective organic synthesis

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Funding information
National Natural Science Foundation of China, Grant/Award Numbers: 21931005, 21720102002, 22071146; Shanghai Science and Technology Committee, Grant/Award Numbers: 19JC1412600, 20520711600; SJTU-MPI partner group

Abstract
Organic synthesis, as a kind of important chemical process closely related to the industry production, environment and energy of human society, is in urgent need of safe, clean, and environmentally benign reagents and routes to realize sustainable chemistry. In last decade, heterogeneous semiconductor nanomaterials catalyzed organic system has long been a promising technology for advanced chemicals manufacturing due to their advantages of durability, low-pollution, and high-scalability. To overcome the limitation posed by unsatisfied reactivity, compositing active components with semiconductor-host that can endow highly interacted nanohybrids with enhancement of surface chemical properties has proved to be an indispensable technique for achieving high-efficiency performance. This review summarizes recent progress on typical semiconductor-based composites including traditional metal oxide, polymeric carbon nitride, N-doped carbon and metal-organic framework (MOFs) applied in organic synthesis. We focus on the compositing promotion mechanism based on semiconductor-host composites and structure-performance relationship in catalytic process. This review is anticipated to provide sparking inspiration for designing next-generation heterogeneous nanocatalysts towards practical application.

KEYWORDS
composites, green catalysis, mutual interaction, organic synthesis, semiconductor

1 | INTRODUCTION

Organic synthesis has been closely related to existence and development of the human society, which involves various aspects of the industrial production, energy-related utilization, and living needs.\[1\] The pursuit of chemical synthesis using easily available reactants in an environmentally benign manner has been a long-standing challenge in replacement of energy-intensive multiple-step reactions with undesired side-products.\[2\] To address this challenge, numerous efforts have been devoted to the exploration of powerful catalytic systems in terms of methodology inventing, ligand designing, feedstock expanding, and renewable energy converting etc.\[3\] In comparison with well-defined transition-metal or organo catalysts that are suffering from easy deactivation and difficulty in removing metal contamination, nanostructured materials featuring peculiar properties of easy separation, good recyclability, scalable preparation and low cost are feasible to overcome these drawbacks of homogeneous counterparts,\[4\] starting...
a popular trend in the interdisciplinary field of organic catalysis and nanomaterials.

Design of real-life catalysts needs to meet the requirements of production process as follows:\[5\] firstly maximize reactant conversion; secondly minimize by-products; thirdly resist on deactivation; As regarding this direction, the qualities of high reactivity, selectivity, and durability are expected to concentrate on an elaborate solid-state ensemble towards significant chemical process, however, which is difficult to be satisfied by one-component catalyst.\[6\] Thus, many kinds of promising composites on the basis of carbon, metal nanocluster, metal oxide, polymer, MFOs (MOFs), and others enabled by good yield and production specificity in the application of photo/thermal/photo-thermal catalysis start to be exploited.\[7\] Over the past decade, semiconductor-based nanocomposites serve as an attractive candidate used to catalyze organic feedstocks into value-added chemicals because of versatile preparation, programmable composition, diverse structure and exclusive properties.\[8\]

A large number of nanostructured semiconductors, simplified by metal oxide, polymeric carbon nitride, N-doped carbon, and MOFs here, as a host material can be used to combine with another one or more components referring to non-metal species (oxide graphene, h-boron nitride) or metal species (coordinate complex, nanoparticle and alloy etc.) via designated methods, generating highly integrated semiconductor-guest combinations (supported structures and core-shell structures).\[9\] Here single metal atom containing composites is not covered in this review because several excellent reviews have highlighted the recent achievements in this realm. From the point of catalysis view, typical host semiconductors play a powerful role on boosting catalytic performance of nanocomposite collective owing to their intrinsic features in active redox interface, unique adsorption capability, and good resistance against complex reaction environment. In this end, feasible tactics exemplified by heteroatom dopant, chemical modification, porosity tailoring have been dedicated to optimize these physicochemical properties of semiconductor surface in terms of enabling overall catalytic system with high solar/thermal-chemical energy conversion, enhanced substrate adsorption, and durable substrate resistance.\[10\] Furthermore the introduction of another active counterpart can not only increases reactive centers but also modify host semiconductors of redox intrinsic capability. In contrast, the catalytic role derived from guest counterpart can be enhanced through support effect of semiconductor. To the best knowledge of us, large number of compelling results have been witnessed with an emphasis on synergistic role of different components.\[11\]

Even though dense of semiconductor-based nanocomposites have presented an emerging application in area of organic synthesis, and the reviews of synthesis methods, characterization and catalytic performance of related combinations were reported.\[12\] Nonetheless fundamental principle of the real function of mutual promotion between multiple components on catalytic property needs to be unlocked with the guidance of future design of advanced nanocomposite catalysts towards important but challenge organic chemicals production. Given this regard, we aim to assess the recent progress of representative semiconductor-based nanocomposites including metal oxide, polymeric carbon nitride, N-doped carbon, and MOFs catalysing organic reactions under mild reaction conditions with the utilization of light/thermal energy. The promotion mechanism of catalytic property induced by guest-semiconductor nano-hybrids will be particularly discussed in detail coupling with the insight into intrinsic property of nanocomposites.

2 | METAL OXIDE-BASED NANOCOMPOSITES FOR ORGANIC SYNTHESIS

Since Fujishima and Honda discovered that the water splitting took place on a TiO\(_2\) electrode under ultraviolet (UV) light irradiation in 1972.\[13\] The most widely used semiconductor of metal oxides based (such as Nb\(_2\)O\(_5\), ZnO, Cu\(_2\)O) began to arouse ubiquitous attention to develop advanced photo, thermal, photo-thermal catalysts for producing valuable chemical fuels and degrading organic pollutants.\[14\] However, the facts that large band gap and limited amount of active sites of metal oxides make single-component host afford unsatisfied energy converting ability and poor catalytic reactivity in related organic process. Because semiconductor oxide hosts encounter the intrinsic restriction as follows: (1) hard to adsorb visible-light; (2) weak adsorption and following activation capability to reactants and/or intermediate. To enable high conversion and selectivity of specific chemical synthesis, aligning guest components of electron mediate (dye molecular), and active centers (complex or metal nanoparticles) with host semiconductor oxides undoubtedly offers a solution, in which semiconductor oxides serve as light-sensitizer and/or active component of promoter.\[15\] The activity of various photo/thermal catalytic reactions of oxidation, dehydrogenation and hydrogenation was thus remarkably boosted under mild condition over well-designed semiconductor-oxides-based composites.

Solar-driven organic synthesis is a powerful technology to improve current status of energy-consuming-type chemical industry. Because the usage of clean and sustainable solar energy to trigger organic synthesis can diminish the detrimental environmental impact and the apparent
thermodynamic equilibrium of redox reactions would be shift in favor of mild reaction condition, thus avoiding thermally induced side reactions and waste pollution. Nonetheless, because of the energy-intensive light source and the generation of non-selective free radical, metal-oxides photocatalysts are mostly used for non-selective organic photodegradation under UV irradiation. Since nanocomposites composed of certain metal and semiconductor can improve the light absorption of semiconductor by surface plasmon resonance (SPR) effect. Currently, numerous progresses have been made for selective organic transformation under visible-light irradiation over plasmonic metal/semiconductor-oxides composites. For example, through a facile calcination method, Kominami and co-workers successfully prepared a series of partially spherical gold particles supported on TiO₂ as plasmonic photocatalysts (Au/TiO₂) for efficiently selective oxidation of benzyl alcohol to benzaldehyde under visible light irradiation with the apparent quantum efficiency of 7.2% and 4.2% at the light wavelength of 625 and 700 nm, respectively.

In another work, Tsukamoto et al. synthesized an active plasmonic photocatalyst for aerobic oxidation of alcohols through loading Au nanoparticles on the mixture of anatase/rutile TiO₂ particles. The Au nanoparticles with diameter of < 5 nm at the interface of the two crystal phase of TiO₂ act as catalytic active sites, and the reaction mechanism is proposed as following: the photogenerated hot electrons in Au transfer to the tightly bound rutile (Figure 1A), and then transfer to well-conjugated anatase (Figure 1B). The injected electrons in rutile from Au would result in a negative shift of conduction band potential (ECB), which is favorable for the electron transfer from rutile to anatase. Surface-bound $\cdot$O₂⁻ active radical is formed through the reduction of absorbed O₂ by electrons in anatase TiO₂’s ECB (Figure 1C). The H atom of alcohol is attracted by $\cdot$O₂⁻ while the maintained hole in Au would adsorb alcohol and produce Au-alcoholate species (Figure 1D). Finally, carbonyl product is formed after the removal of H atom (Figure 1E).

The introduction of oxygen vacancies in plasmonic catalyst can lead to a synergistic action with plasmonic hot electrons and holes and thus influence the photocatalytic performance. Li et al. developed a plasmonic catalyst through depositing Au nanoparticles on BiOCl with oxygen vacancies (Au-BiOCl-OV) that are effective for the enhancing the O₂ adsorption and activation (Figure 2A). The synergistic action of oxygen vacancies and plasmonic effect contributes to a new reaction pathway of selective alcohol oxidation, in which oxygen atom in product comes from O₂ instead of alcohol reactant (Figure 2B). Based on the experimental and characterization results, a photocatalytic mechanism of benzyl alcohol oxidation to benzaldehyde with high selectivity is proposed as following (Figure 2C): After the absorption of benzyl alcohol on Au-BiOCl-OV through deprotonation pathway (i in Figure 2C), the photogenerated hot electrons in Au transfer and are trapped at oxygen vacancies in BiOCl, while hot holes remain on Au (ii in Figure 2C). A carbon-centered radical is formed through the hot holes on Au abstracting α-H of BiOCl, and surface-bound $\cdot$O₂⁻ is formed through the absorption of O₂ and then trapped by hot electrons (iii in Figure 2C). The above-formed radicals are prone to recombine to form an oxygen-bridged structure (iv in Figure 2C). Benzaldehyde and BiOCl-bound peroxide-bridge structure are formed that is favored by the simultaneous cleavage of the C-O bond in alcohol and the O-O bond in O₂ (v in Figure 2C). O₂ is used to label the source of oxygen atom in the product, where 66% oxygen percentage is from O₂.

Apart from utilizing plasmonic metal component to enhance light harvesting ability of semiconductor-oxides, another effective strategy to warrant catalytic selectivity and visible-light absorb of single-component semiconductor was observed in the photocatalytic system of dye/TiO₂/TEMPO. Zhao, Ma and co-workers reported a highly selective oxidation of alcohol catalyzed by dye/TiO₂/TEMPO composites under the irradiation of visible-light. The perfect match of redox potential of commercial anthraquinone dye Alizarin Red, TiO₂, and TEMPO leads to controllable photocatalytic oxidation with high TON value and product selectivity, in which dye and TEMPO serve as light-sensitive agent and cocatalyst.
respective with the avoidance of over oxidation of photo-generated hole in TiO$_2$. As the Figure 3 depicted, electron migration from dye molecule to TiO$_2$ conduction band and the dye-triggered TEMPO oxidation as two key cycles are included for catalytic pathway.

Among metal-semiconductor-oxides hybrids, supported non-plasmonic metal nanoparticles especially Pt group is capable of being activated by semiconductor-oxides via strong metal-support interaction.\textsuperscript{[18]} For example, Li et al.\textsuperscript{[18a]} developed a high-capacity of reversible hydrogen addition/release cycle catalyzed by Pt@TiO$_2$ hybrids with high quantum efficiency of visible-light irradiation. The high electron density of Pt nanoparticles was achieved because of strong electron transfer of TiO$_2$ support (Figure 4A), as well reflected by a high cyclohexane dehydrogenation performance at ambient condition (Figure 4B). The Pt nanoparticle as visible light sensitizer promotes activation of absorbed reactant and homolytical C-H cleavage that will enable dehydrogenation reaction with excellent yield under visible light (Figure 4C-D). In the other Pt-containing composites case,\textsuperscript{[18b]} TiO$_2$-WO$_3$ along with matched band alignment was chosen as visible-light-sensitized support to inhibit electron-hole recombination aiming at enhancement of the light utilization efficiency for effective photo-thermal oxidation of propane. On the other hand, photo-generated charge accumulated on supported Pt nanoparticle is responsible for the rapid desorption of excessive O$_2$ in favor of avoiding poison of active metal sites.

The promotion of oxides support to metal component on catalytic reactivity has even been expanded to more challenging application for thermal organic catalysis. In typical catalysis scheme, adsorption/desorption capability to reactants/products on surface active sites acts a key factor that can affect reaction activity. To this end, the widely used
approaches of modifying support, controlling metal size and varying bimetal compositions have been exploited to optimize absorption/desorption property of nanocomposites surface, which is highly linked with catalytic property referring to conversion, selectivity, and stability.\[19\]

Firstly, the modification of pore structure of support-oxides can not only confine metal particle with homogeneous distribution but also be used for exposure of more active sites with reactants finally being working to prompt catalytic activity. For instance, Pt nanoparticles/porous TiO₂ support nanohybrids was prepared via salt-hard-template and following NaBH₄ reduction method for reductive animation of levulinic acid.\[15b\] They reasoned that maximized exposure of positive-charged Pt supported on porous TiO₂ nanosheets is indeed conducive to its stronger interaction with the carbonyl groups and mass transfer therefore this nanocomposite acquired high reductive conversion and functional group tolerance in a complicated reaction system.

Secondly, metal-semiconductor-oxides nanocomposites have a great advantage that metal/support interface is flexible for tuning selectivity to specific product, which occupies a crucial position in assessment criteria of catalyst. In this case, Du and co-authors successfully applied size-dependent metal-oxides composites to realize selective hydrogenation of 3-nitrostyrene with H₂.\[19a\] Different size Au nanoparticles were coupled with TiO₂ support using colloidal-deposition preparation, of which larger-size Au composites shown more distinct and strong metal-support interaction phenomenon owing to the presence of surface tension in size-dependent Au nanoparticles. Based on this principle, size-dependent selectivity enhancement in 3-nitrostyrene hydrogenation reaction was efficiently catalyzed via a selective pathway on Au/TiO₂ assemblies surface where negatively charged Au surface possesses strong interaction with NO₂-containing substrates.

Compared with monometallic semiconductor-oxides catalysts, bimetallic alloy supported on semiconductor-oxides, which affords favorable surface atomic configuration and electron structure, is exploited for engineering nanocatalyst with high catalytic property.\[19b-c\] Mori et al investigated the positive correlation of electronic effect on the reactivity for CO₂ hydrogenation to formic acid by the mean of rationally fabricating exposed Pd/Ag atom ratio on alloy particle surface loaded on TiO₂ support (Figure 6).\[19b\] In the scope of semiconductor-supports, TiO₂ that was screened to be optimal promoter of PdAg alloy particles can considerably contribute to catalyze

\[\text{FIGURE 4}\] A, XPS spectra of Pt 4f for different Pt@semiconductor composites and (B) corresponding the cyclohexane dehydrogenation activity. C, Schematic representation of the photoinduced electron transfer between Pt and adsorbed cyclohexane. D, Proposed dehydrogenation mechanism over Pt@TiO₂. Reproduced with the permission.\[18a\] Copyright 2015, American Chemical Society
Figure 5  A, Typical HRTEM image of Au-3 nm/TiO$_2$. (B-C) In situ DRIFT spectra of CO adsorption over Au-3 nm/TiO$_2$ and Au-9 nm/TiO$_2$. D, Selective 3-nitrostyrene hydrogenation over size-dependent Au/TiO$_2$ composites. Reproduced with the permission [ref19a]. Copyright 2020, Springer Nature

Figure 6  Catalytic performance of CO$_2$ hydrogenation over Pd/TiO$_2$ and PdAg supported on TiO$_2$ nanocomposites with controlled bimetallic compositions. Reproduced with the permission [ref19b]. Copyright 2018, American Chemical Society

Hydrogenation of CO$_2$. Furthermore, electron-rich Pd sites resulted from ligand effect of adjacent Ag atom in alloy lead to the superior activity of CO$_2$ hydrogenation over Pd@Ag/TiO$_2$ where the determining step is that adsorbed HCO$_3^-$ reacts with H on active Pd atom.

Based on the basic insight into metal-oxides composites in various chemical processes, multifunctional tandem catalysts consisting of different metal/semiconductor-oxides interfaces were well designed and prepared for the utilization of multiple steps organic transformation. A classical case is from Yang’s research group.[20] They constructed a bilayer structure of nanocubic CeO$_2$-Pt-SiO$_2$ through sequential Langmuir-Blodgett deposition method. The highly integrated interaction between nanocubic Pt and CeO$_2$ and SiO$_2$ nanocrystal is formed after removing capping agent. The CeO$_2$-Pt-SiO$_2$ composites can complete conversion of ethylene hydroformylation with methanol in a tandem manner. Firstly decomposition of methanol on Pt-CeO$_2$ boundary leads to in situ generation of CO and H$_2$ that reacts with ethylene following on adjacent Pt-SiO$_2$ boundary to produce propanal selectively.

3  POLYMERIC CARBON NITRIDE BASED NANOCOMPOSITES FOR ORGANIC SYNTHESIS

Compared to large-bandgap metal oxides semiconductors, polymeric carbon nitride material as a polymer semiconductor featuring suitable bandgap (2.7 eV) and chemically stable structure earns considerable attention in field of promising photocatalytical water splitting to make O$_2$ and...
H₂ by sunlight driven. Wang and co-worker reported crucial first example of carbon nitride in the application of solar-to-hydrogen. Sequently a train of modifying strategies that porosity introducing and heteroatom doping are complimented to a big family of carbon nitride materials because of the rapid development of nanocasting technology. Note that the as-prepared pure carbon nitride as well as their modified derivates (such as mesoporous or heteroatom-doped carbon nitride) make a significant stride for catalysis applications, in particular, organic synthesis in which involves a broad range of functional reactions for example selective oxidation, hydrogenation, C-H activation, activation of CO₂, or elemental sulfur and cross-coupling. It is well-known that catalytic activity of carbon nitride in catalytic process mainly originates from redox property on semiconductor surface. The construction of multiple-components nanocomposites are believed to be an advisable approach that can break dynamic limitation to bring out better reactivity. Consequently, various carbon nitride semiconductor-based composites comprising of monometal/carbon nitride, bimetal/carbon nitride and nonmetal/carbon nitride, have been well explored to accomplish desired organic transformation.

Monometal/carbon nitride that refers to incorporate monometallic nanoparticles (Pd, Au, Pt, Co etc.) or monometallic derivates (AgI, NiS₂, V₂O₅, CuO etc) with carbon nitride can be used as an high-performance catalysts for specific organic transformation such as suzuki/stille/ullmann coupling, formic acid/ammonia borane dehydrogenation, olefins oxidation and nitroarenes/phenol hydrogenation. In order to avoid metal species aggregation in preparation process, mesoporous carbon nitride was designed as active substrate to load homogeneously dispersed metal component (Figure 7A). The strong electron interaction between monometal nanoparticle and carbon nitride support analogue as ligand-metal charge transfer in organometallic catalysis is founded to ensure activity derived from metal nanoparticle towards predominant organic transformation. Typically, taking Pd nanoparticle-mesoporous carbon nitride composites (Pd@mCN) for example, host semiconductor-support acting as stabilizer and electron mediate of active metal-component enables electron-rich Pd nanoparticle with higher amount of H₂ produced by formic acid dehydrogenation than other common used non-semiconductor support of carbon...
black or layer carbon (Figure 7B). Not only in that case, SiO$_2$@carbon nitride semiconductor-substrate with porous structure also was empowered as mesoporous carbon nitride surrogate to further facilitate dehydrogenation efficiency of formic acid under ambient condition.\(^{[25c]}\) Upon Pd@mCN nanocomposites catalyzed formic acid dehydrogenation, sustainable synthesis of value-added biofuels and amines in good yield was accomplished over Pd@mCN composites via hydrogen-transfer protocol where formic acid as safe liquid hydrogen resource can in situ generates active hydrogen species on Pd nanoparticle surface sequently hydrogenating starting materials (nitrobenzene, furfural, olefin etc)\(^{[26]}\) into final desired products (Figure 7C).

Inspired by above results, efficient Pd@mCN composites with tunable metal electron-density promoted highly selective multistep hydrogenations by more challenging H$_2$, widely used hydrogen resource in industrial fine-chemicals production, are documented.\(^{[27]}\) Specifically, active Pd component with enhanced electronstastic potential induced by semiconductive support was proved to be effective for selective production of tetrahydrofurfuryl alcohol via hydrogenation of furfural (Figure 7D). The preferred adsorption property toward C = O bond of furfural in favor of reaction routine for target product (Figure 7E) can be further stimulated by photoinduced in-built electric-field on the metal-support interface thus overcoming dilemma of poor selectivity posed by single-component Pd nanomaterial catalyzed hydrogenation. In recent research, immobilizing homogeneous metal macrocyclic complex (cobalt thioporphyrazine) on carbon nitride promoter was applied for selective 5-hydroxymethylfurfural photo-oxidation. The structural characterization evidently revealed important influence of strong semiconductor-to-guest molecule electron communication on the high photoconversion efficiency.\(^{[23c]}\)

The other successful examples of monometal/carbon nitride composites applied in organic synthesis involve typical Pd (Au) catalyzed C-C bond formation reactions including suzuki and stille cross coupling.\(^{[25a]}\) Under irradiation of solar-light, separated electron-hole pairs located on monometal-carbon nitride terminals can simultaneously activate electrophilic-nucleophilic partners to complete final organocatalytic cross coupling conversion (Figure 7F). Such similar catalytic protocol even can be observed in low reactive Au nanoparticle-containing monometal/semiconductive support composites system.\(^{[24a]}\)

In parallel with monometal/carbon nitride combinations, bimetallic counterparts aligned with carbon nitride into joint nanocomposites is as well as active for catalytic hydrogen storage system due to synergetic functionalization impact of multiple active components in combinations.\(^{[28]}\) For instance, using a modified wet impregnation method, Guo and co-workers successfully obtained magnetically recyclable carbon nitride supported Au and Co nanoparticles (Au-Co@CN) for photocatalytic aqueous ammonia borane dehydrogenation.\(^{[28b]}\) The mutual interaction between bimetal nanoparticle and semiconductor support is well reflected as Figure 8A shown, speaking for prerequisite role of semiconductive carbon nitride for ensuring high-performance dehydrogenative catalysts. The synergetic work of Au-Co bimetallic-component further improves ammonia borane activation and hydrogen desorption that determines the increase in H$_2$ production efficiency than single metal samples (Figure 8B). The resulting TOF value of Au-Co@CN driven by visible light is high up to 2897 mol H$_2$ mol$^{-1}$ metal h$^{-1}$ far outperforming those of non-semiconductor-based nanocomposites.

The issues related to cost of metal-based nanocatalysts and environmental concerns caused by metal-leaching severely impair industrial progress in the large-scale production. The usage of metal-free carbon nitride-based nanocomposites instead of aforementioned metal-based one was examined as an emerging candidate for important organic processes.\(^{[29]}\) Incorporating monolayer graphene sheet (GS) into carbon nitride (CN) host with intensive distribution was successfully realized after in situ condensation of cyanamide in presence of well-dispersed reduced graphene oxide (Figure 9A-C).\(^{[23c]}\) The highly integrated nanocombination in which two counterparts of guest-host components feature evident charge-transfer interaction is used to modify valence and conductor band position for CN semiconductor-host. Resulting “two-in-one” dyads with redox areas on GSCN composite surface have dual functions in terms of reducing O$_2$ molecule to superoxide radical anion as well as activating hydrocarbon reactant for selective transformation of nonactive hydrocarbons to ketones without metal-catalyzed system (Figure 9D). The recent effort on organic catalysis of metal-free composites associated with carbon nitride host focuses on amorphous metallic B nanoparticles as functionality embedded in carbon nitride framework for gas-phase photo-oxidation of 2-propanol under continue-flow reaction condition.

## 4 N-DOPED CARBON BASED NANOCOMPOSITES FOR ORGANIC SYNTHESIS

For pursuit of sustainability in heterogeneous catalysis, a variety of carbonaceous hybrid nanocomposites composed of carbon hosts including active carbon, carbon black, carbon nanotube, graphene, and mesoporous carbon with active inorganic/organic compounds share
**FIGURE 8** A, Catalytic dehydrogenation activity over bimetallic Au-Co coupled with or without semiconductor support. B, Catalytic dehydrogenation activity over monometallic Co@CN and Au@CN and bimetallic Au-Co@CN composites. Reproduced with the permission ref.[28b] Copyright 2014, American Chemical Society

**FIGURE 9** A, UV-vis absorbance spectra and (B) XRD results of GSCN and reference samples. C, Typical SEM image of GSCN composite. D, Schematic illustration of the oxidation process based on GSCN composite. Reproduced with the permission ref. [23c] Copyright 2011, American Chemical Society
acknowledged features of rich surface properties and
flexible functionalization.\cite{30} That makes advanced
carbon-based nanohybrids assembles an epidemic
approach expand their application in organic synthesis
field. Taking into consideration of pure-carbon nano-
composites with poor catalytic activity, it is available to
introduce nitrogen heteroactom in nanostructured carbon
framework denoted as N-doped carbon for high-quality
nanocatalysts. In this context, Beller and co-workers have
made a series of seminal progresses of which N-doped
carbon supported hybrids with nanostructured precious
metal/metal-oxides found a wide application in important
organic transformations.\cite{31} The involved chemical pro-
cesses mainly cover hydrogenation of nitroarenes, ketone,
and N-heteroarenes, oxidation of N-heterocycles and
alcohol, transfer hydrogenation, reductive animation and
epoxidation of alkene et al. Subsequently, well-established
preparation strategy's simplified by impregnation,
deposition-precipitation, small molecule polyconden-
sation and MFOs confinement offer a powerful tool
box for controllable synthesis of N-doped carbon based
composites with “functional particles” (such as noble
metal/transition metal and their related derivative,
metal-free compound).\cite{12} With the assistance of such
advanced synthesis, rational macroscopic, and electronic
structure designing enabled by morphology regulation,
porosity integration, dopants enrichment, and interface
optimization can be used to modulate nanocatalysts
surface properties in terms of key reactants/products or
intermediates adsorption/desorption, redox potential and
acid-base behavior. It is imperative for high-performance
nanocatalysts toward practical chemicals production.
In this section, we will discuss representative examples
associated with area of concrete organic catalysis on the
basis of N-doped carbon semiconductor host supported
efficient nanocomposites with catalytic counterparts,
categorized as metal-free compounds, noble metal and
transition metal/derivatives.

As we all known, a huge family of heteroatom (gen-
erally N, B, O and S) doped carbon of which dopants act
as function of electron-acceptor or donor for modifying
HOMO-LUMO energy gap is a promising and sustain-
able metal-free promoter at initial stage used in typical
liquid-phase organic reactions including oxidation of
amines, benzene, alcohols even C-H bond and alcohols
animation.\cite{33} Nevertheless, this class of catalysts still
suffer from relatively low activity that is difficult to stand
up nonactive starting reactants available for conversions.
To circumvent this problem in a sustainable way, there is
no doubt that engineering 2D layer-nanostructured dyadic
hybrids comprised of N-doped carbon and another func-
tional semiconductor without metal is a vital strategy to
prompt reactivity for development of advanced metal-free
nanocatalysts in organic reactions. Zhang et al reported\cite{34}
a direct solid synthetic routine of small molecules confine-
ment pyrolysis to give dyadic nanocomposite of N-doped
graphene and hexagonal boron nitride (h-BN-C/G) (Fig-
ure 10A) for efficient photooxidation coupling of amines.
It is noted that ultrathin bilayer structure between N-
doped graphene and carbon-doped h-BN on one hand can
ensure sufficient exposure of active surface to reactants,
on the other hand retard photogenerated electron-hole
recombination because of short charge transport route
(Figure 10B). In combination with carbon-doped h-BN
responsible for visible-light harvesting (Figure 10C),
photocatalytic oxidation in good yield and a high turnover
frequency value (4.0 mmol benzylamine (simplified
with BA) g\(^{-1}\) h\(^{-1}\)) is achieved as expected for h-BN-C/G
composite metal-free catalytic system (Figure 10D).

As so far, heterogeneous carbon-based metal-free
nanocomposites catalyzed organic synthesis mostly
either involves simple model reaction of highly reactive
substrates or encounters harsh reaction condition
due to limited reactivity resulted from their intrinsic
nature of non-metal elements. Active metal nanoparticles
especially noble metal (Pd, Pt, Au, Rh, Ru) anchored
on N-doped carbon supports with porous morphology
and/or basic sites have a intriguing focus in various
green organic catalysis.\cite{35–39} In early stage, representa-
tive progresses in N-doped carbon based nanocatalysts
catalyzed transformations include Pd-nanoparticle
catalyzed (de) hydrogenation, suzuki coupling, and four-
component domino carbonylation to form pyrazoles,\cite{35}
Au-nanoparticle catalyzed liquid oxidation and acetylene
hydrochlorination,\cite{36} Pt-nanoparticles catalyzed oxida-
tion of 5-hydroxymethylfurfural or glycerol,\cite{37} Ru-clusters
catalyzed formic acid decomposition to H\(_2\) production,\cite{38}
Rh catalyzed benzoic acid hydrogenation.\cite{39} Even though
a number of endeavor made, the exploration of activation
approach aiming at metal centers enhancement toward
demanding catalysis still lies at the heart concerned by
high-yield N-doped carbon based composites designing
since their ultimate catalytic performance depends on
physiochemical factors of metal phase to great extent.
Together with advanced characterization technologies
for nanohybrid, it is founded that N-doped carbon fea-
tured with semiconductive properties can affect catalytic
efficiency for active metal components.

Tunable chemical state of metal surface enabled by
electronic interaction between metal and N-doped carbon
can facilitate organic transformation to proceed in a green
manner. For instance, in Su et al reported results,\cite{37b}
electron enrichment Pt nanoparticle loaded on N-doped
carbon tube furnished higher performance for selective
halonitrobenzenes hydrogenation than that of Pt nanopar-
ticle/active carbon sample. More importantly, increasing
N dopants content in carbon framework can further boost electron transfer from carbon semiconductor to metal nanoparticles whose located charge state is strongly modified accordingly. The utilization of controllable pyrolysis method based on bio-chitosan-based raws successfully produced high N concentration doped carbon support which endows Pd nanoparticle with excellent formic acid dehydrogenation activity at room temptation even under base-free condition.\[35b\] The similar phenomenon as described by abovementioned case was confirmed again in aromatic ring hydrogenation reaction.\[35g\] From what has been discussed above, strong metal-support interaction on the basis of N-doped carbon host indeed exhibits its effectiveness on enhancement of reactivity in organic synthesis, which provide a new opportunity for practical application in crucial industrial process.

In addition, seeking for concurrent improvement of selectivity and activity in chemicals manufacturing has been a long-standing pursuit for heterogeneous catalysts engineering. Because adsorption property of active reaction intermediates generally follow the scaling relation that thus could bring about “seesaw” type of imbalance between catalysts conversion and selectivity to product. With the regard to such restriction, explosive popular of N-doped carbon supported metal-based composites offers a powerful platform to realize completed conversion as well as in a high selective way towards chemical processes particularly hydrogenation. Taking Pd-catalyzed alkyne semihydrogenation as example,\[35h\] well-defined Pd nanocube was integrated with N-doped carbon substrate in homogeneous distribution through two-step synthesis strategy. The work function discrimination of Pd nanocube and carbon support (Figure 11A) which triggers to electron redistribution at metal-support interface makes Pd surface possess increased positive charge (Figure 11B). It should be noted that strong phenylacetylene adsorption (Figure 11C) as well as decreased hydrogen coverage (Figure 11D) bound on electron-deficiency Pd (100) facet was clearly demonstrated from theoretical calculation results, that is conducive to suppress phenylacetylene overhydrogenation path (Figure 11E). As a result, positive charged Pd nanocubes induced by N-doped carbon host finally obtain specific selectivity in alkyne hydrogenation (Figure 11F).
From the viewpoint of economic and friendly environmental catalysis, there is a urgent task that exploiting earth-abundant nonprecious metal as preferable counterpart instead of noble metal ones in nanocomposites is used for value-added chemicals production. With the continuous improvement of synthesis methods of N-doped carbon-based materials, well-defined non-precious metal/metal oxide/metal carbide/alloy nanoparticle embedded into N-doped carbon support has an explosive leap.[40–42] These core-shell structured nanohybrids, that feature good stability and controllable electronic property, contribute to enormous chemicals manufacturing even catalyzed by homogeneous noble metal complex such as esters, quinolines, 2-methoxy-4-methylphenol, anilines, 2,5-dimethylfuran et al.

Among commonly used transition-metal-based nanohybrids, combining highly activated cobalt particles as mainly catalyzed center with N-doped carbon promoter upon nitrogen dopants enrichment enables challenging synthesis with novel chemical reactivity. As a typical example, cobalt nanoparticles enveloped with nitrogen-rich carbon (Co@NC) as effective catalyst system have been successfully documented through direct calcinating metal-organic-complex-coated graphitic carbon nitride for oxidation of alcohol to ester based on base-free reaction system under mild conditions.[11a] A series of resultant Co@NC samples with controllable nitrogen content maintain their similar morphology and metal content but exhibit N-dopant-dependent electronic state for supported metal nanoparticles. As a result, the optimized sample gives a TOF value as high as 8.12 mol methyl benzoate mol\(^{-1}\) Co h\(^{-1}\) which represents a record in nanostructured transition-metal catalyzed aerobic esterification (Figure 12A-B).

The resulting nanostructure with metal core and N-doped carbon shell is beneficial to mutual enhancement of catalytic activity for exposed metal sites and semiconductor-carbon at highly integrated interface (Figure 12C).[40b] The reversible dehydrogenation-hydrogenation transformations have proved to be effectively catalyzed by distinct core-shell-like Co-based composite (Figure 12D). Because (de)hydrogenative substrates affinity of active terminals with pronounced electron-rich and electron-deficiency by optimizing interfacial Co-carbon composition can be simultaneously reinforced. Inspired by high-efficiency enzymes catalysis,[40c] artificial biomimetic nanocomposite coupling spatial three-dimension morphology with robust Co-carbon boundary can further facilitates highly active Co accessible with reactants whereby affording concurrently improved conversion and selectivity to 2-methoxy-4-methylphenol for vanillin hydrogenation.
By applying MOF-derived Co-nanoparticle-containing N-doped carbon combinations, carbonyl compounds as starting material can react with NH_3 and H_2 to produce a plethora of amines up to 140 examples even complicated drug targets, which is a significant step towards vision of non-precious metal catalyzed chemicals synthesis.\[^{40d}\]

Except for above-mentioned cobalt-based catalysts, other cheaper non-precious metal comprised nanocomposites with fine-tuning redox ability has been even expanded to conversion of inert small molecules (e.g., methanol, CO\textsubscript{2}) of high activation barrier into useful chemicals.\[^{41}\] There are several noticeable progress reported by group of Li. In detail, N-doped carbon encased Ni (Ni/NC) derived from a solvent-free conventional process exhibits superior dehydrogenative performance for converting gas-phase methanol into high-energy-density H\textsubscript{2} molecule under high raw gas flow rate. Increasing nitrogen doping concentration of carbon support induced cooperative adsorption of methanol contributes to O-H and C-H bond activation on metal-support interface thus resulting in best-performance dehydrogenation of methanol with a record-breaking TOF value (Figure 13A). In another research, combinations composed of Lewis acid Cu and Lewis base N-doped carbon (Cu/NC) that simultaneously favor strong CO\textsubscript{2} affinity and epoxides activation thereby displays outstanding catalytic efficiency of CO\textsubscript{2} fixation for the production of cyclic carbonates (Figure 13B). For selective hydrogenation of CO\textsubscript{2}, molybdenum carbide core with N-doped carbon shell (MoC/NC) drawing parallels to noble-metal-based catalysts has been designed and applied to rationally tailor preferential adsorption model of reactants at metal-support surface for achieving an extraordinary selectivity towards formic acid as well as high CO\textsubscript{2} conversion (Figure 13C).

Parallels to non-precious monometal nanohybrids with similar core-shell structure, employing non-precious bimetal alloy loaded carbon framework for improvement of catalytic conversion and chemselectivity is also of sufficient importance. Recently, alloyed Fe-Co nanoparticles used for selective cinnamaldehyde hydrogenation towards thermodynamically unflavored cinnamyl alcohol in water was reported by Lv and co-workers.\[^{42}\] Through successive pyrolysis-adsorption-pyrolysis strategy using MFOs, as-obtained Fe-Co alloy nanohybrids with controllable Fe/Co ratio not only regulate selectivity for cinnamyl alcohol up to 91.7 % but also remain high conversion of cinnamaldehyde ultimately rendering optimized product yield. Both experimental and calculated results confirms that beneficial absorption of C = O bond on Fe-Co alloy surface is a key factor to ensure overall catalytic
5 MOFS-BASED NANOCOMPOSITE FOR ORGANIC SYNTHESIS

MOFs that a porous crystalline material, with unique structural merits of large surface area, tunable organic linker and metal nodes, and periodic network have gained of great interests in the application of photocatalytic H₂ production. Benefiting from semiconductor-like MOFs with light harvesting tunability, functionalized MOFs by Brønsted acid group or metal ion has a strong effect on their intrinsic electronic structure of MOFs surface which directly refers to acidity/redox ability, thereby holding great potential for expansion of sunlight-driven conversions. To enable high-efficiency conversion of desired organic process, incorporating guest components in terms of heterogeneous (metal particles) and homogeneous (soluble complex) species into MOFs host gives rise to the formation of combination wherein synergistic promotion of each component makes composites furnish higher performance than single counterparts. In this context, recent representative works on MOFs-semiconductor-based nanocomposites for organic synthesis will be presented.

The mesoporous and highly stable MOFs have abundant accessible confinement sites used to immobilize and modify high-activity metal nanoparticles for boosting catalysis. A class of MOFs namely MIL-101, by virtue of proper cavitied diameters and high tolerance to water/alcohol was screened to be a common host support for rational envelopment of metal. Double solvent synthesis strategy reported by group of Jiang overcomed the problem of metal out-pore deposition that ensures monometallic or bimetallic particles with uniform size distribution well encapsulated into MIL-101 crystal. Furthermore, advanced characterization tools of HAADF-STEM tomography with the slice technology, hyperpolarized ¹²⁹Xe NMR spectroscopy, and positron annihilation spectroscopy was employed to determine real configuration between ultrafine metal nanoparticles and MOFs host. The well-defined structure of metal encased inside MOFs pore enables maximized combination with respective advantage of host-guest components, which endows metal@MOFs nanohybrids superior catalysis and stability for various liquid reactions including selective aerobic oxidation and nitroarene hydrogenation with ammonia borane et al. Apart from confinement of active metal nanoparticles,
steric hindrance role derived from MOFs pore structure is also able to elevate regioselectivity which is well validated in the example of CuPd@ZIF-8 composites catalyzing alkyne hydrogenation reaction.\cite{45c}

More importantly, the pore microenvironment of MOFs architecture that can be influenced significantly by organic/inorganic building units pre-designing acts critical role in catalytic fine-chemicals generation. In 2016, Yaghi et al. founded that there is electronic interaction between guest Cu and inorganic Zr oxide node of the MOF host that can expedite selective conversion of CO$_2$ and H$_2$ to methanol.\cite{45d} In recent results, Chen and co-workers also selected 3D UiO-66 as parent MOFs,\cite{45e} then by varying linker substituent group in solvothermal process of metal ion and organic building precursors modulates coordination environment of pore wall of MOFs host resulting in generation of high-activity guest metal species (Figure 14A). Resultant Pd@UiO-66-X composites (X represents H, OMe, NH$_2$, 2OH, 2OH) afford discriminated catalysis rate in consistence with corresponding Pd electron density and binding energy of substrate on composites surface as following sequence (Figure 14B-D): Pd@UiO-66-OH > Pd@UiO-66-2OH(HF) > Pd@UiO-66-NH$_2$ > Pd@UiO-66-OMe > Pd@UiO-66-H. This experimental phenomenon suggests that the boosted hydrogenation efficiency of controlled MOFs-based nanocomposites benefits from Pd surface electronic-environment-dependent adsorption property that can be prompted via tuning composition of MOFs.

Except for the advantage of microstructure of MOFs as host support, there is a common sense that metal node and organic linker long-range orderliness constructed MOFs possess semiconducting behavior which endows MOFs based nanohybrids with light-enhanced performance for photocatalytic processes. For this regard,\cite{45f} the typical porphyrin-ligand linked MOFs after light excitation becomes a stronger redox promoter in comparison with original ligand that can facilitate generation of reactive oxygen species in oxidative coupling reaction. Given limited oxidative ability of MOFs semiconductor, compositing Pt particles with porphyrinic MOFs was proposed to further complete oxidation of alcohols under visible-light irradiation where photothermal activation of O$_2$ located on MOFs host and the electronic state of Pd surface are improved concurrently.

Apart from compositing metal particles guest with MOFs host, exploiting homogeneous molecular complex heterogenized MOFs composites has a great significance. Cai et al. develops a template-directed preparation to construct a yolk-shell-type hollow nanohybrids of MOFs
(ZIF-8, ZIF-67 or MOF-74), functional porphyrin molecular, and layered double hydroxides (LDHs) in which molecular complex-yolk is well encaiced by MOFs-shell grown on LDHs.\textsuperscript{[46]} Such hybrids nanostructure can perfectly combine high-reactivity of homogeneous molecular catalyst with shape-selective and reusability inherited from heterogeneous MOFs into a catalytic integration that is successfully applied in CO\textsubscript{2} cycloaddition even organic cascade reactions.

\section{CONCLUSION AND PERSPECTIVE}

Through facile and sustainable fabrications rationally constructing nanostructured composites of semiconductor behavior hosts for green organic synthesis as an emerging cutting-edge field has been rapidly developed. In this review, we give a presentation on typical cases of organic transformation with high performance on the basis of representative semiconductor-based composites in which the functional guests range from metal and non-metal components. As extensively depicted by these concrete examples of various semiconductor-host nanocomposites, definite phenomenon has been demonstrated that the mutual interaction between guest-host multi-counterparts allow concurrent enhancement of physicochemical properties of respective components including electronic states, adsorptive capability, energy harvesting, redox potential and resistance for integrating high conversion, selectivity and tolerance into overall catalytic nanocomposites. Obviously, deeply understanding on the property-performance promoted mechanism of semiconductor-based nanocomposites by sounded experimental and theoretical evidences will provide an informative design principle to break the bottleneck of heterogeneous synthetic systems.

In foregoing context, recently updated versions of semiconductor inorganic/organic supports, including carbon nitride, N-doped carbon, and MFOs, have been discussed here. Exploring cheap and robust polymeric semiconductors host with catalytic activity is also in progress as a promising research direction at the moment. The recent examples of semiconducting polyimide and its composites as electrocatalysts for oxygen evolution and nitrogen reduction reactions again speak for the potential of various novel polymeric semiconductors for selective organic synthesis driven by alternative types of energies.\textsuperscript{[47]}

Based on above-discussed mutual promotional principle of multi-components of nanocomposites, it can be envisaged that well-elaborated polymer-based nanocomposites which possesses enhanced chemical and electronic property, would make it rather possible for achieving extraordinary performance toward organic catalysis and even practical chemicals synthesis. Apart from strong interaction between guest and host components, the existence of electronic connection of separated guest-to-guest domains in semiconductor supported multiple-equivalents composites is also discovered to account for high electron-to-chemical conversion efficiency. In the work reported by Xue et al.,\textsuperscript{[48]} selectively electrocatalytic ammonia synthesis from N\textsubscript{2} with high-Faradaic-efficiency was achieved by separated Au-Ni guests in N-doped carbon host. Au nanoparticles with high electron-density are highly active for activating N\textsubscript{2} and sequently coupling with proton which can be further reinforced by distinct electron-transfer effect of Ni-to-Au domains in nanocomposites. It implies that nanostructure engineering of functional guest components in the form of spatial distribution will offer an interesting platform model for investigating the catalytic mechanisms. A number of “black boxes” on unknown relationships of structure-property-performance based on semiconductor-based nanocomposites yet need to be further unlocked, which will help to produce diversive high-reactivity nanomaterials for catalysis.

\section{ACKNOWLEDGMENTS}

This work was supported by the National Natural Science Foundation of China (21931005, 21720102002, and 22071146), Shanghai Science and Technology Committee (19JC1412600 and 20520711600) and the SJTU-MPI partner group.

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the controllable preparation of porous transition metal oxides catalysts for renewable energy applications.

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**How to cite this article:** Su J, Su H, Chen J-S, Li X-H. Semiconductor-based nanocomposites for selective organic synthesis. *Nano Select.* 2021;1–19. https://doi.org/10.1002/nano.202100065