Photocatalytic dehydrogenative C-C coupling of acetonitrile to succinonitrile

Succinonitrile (SN), an important C₄ intermediate, is mainly used to synthesize 1,4-diaminobutane (DAB) for the production of high-performance polyamides, such as nylon-4,6 (Stanyl®) and nylon-4,10 (EcopaXX®). Due to the wide applications in automobile, electronics and other industries, the annual demand of succinonitrile is growing rapidly. Additionally, succinonitrile is used to synthesize paints and electrolyte additives for lithium batteries.

Succinonitrile is commercially produced by the addition of hydrogen cyanide to acrylonitrile. Although high yield is achieved in this atom economic pathway, the highly toxic hydrogen cyanide is used as both reactant and catalyst. Thus, strict safety regulation and hazardous substance control are required during the operation and post-treatment procedures (Fig. 1a). The dehydration reaction between succinic acid and ammonia produces SN in the presence of solid acid. But the relatively low yield and harsh condition significantly limit its applicability. To overcome these shortcomings, researchers have turned to the SN synthesis based on acetonitrile, a byproduct of acrylonitrile production (Sohio process) and mainly burned out as fuel (releasing large amount of NOx pollutant). Both anionic coupling assisted with an organometallic complex and radical coupling initiated with radicals from peroxides (Fig. 1b, c) have been proposed to synthesize SN. Despite of high chemoselectivity, these synthetic routes require the use of stoichiometric amount of expensive butyllithium and peroxide as the hydrogen acceptors of the

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sp³ bond of CH₃CN, which is not desirable for large-scale production. If CH₃CN molecules could be coupled via a catalytic dehydrogenation route, the whole process can be cleaner with even improved atom economy. The generated hydrogen can be used as clean energy. However, due to the thermodynamic limit (Fig. S1), it is impossible to achieve this reaction via traditional thermal catalysis.

The development of photocatalyst provides opportunities to synthesize chemicals in a cleaner manner using renewable solar energy, by overcoming the thermodynamic limit under ambient conditions. Using semiconductor-based heterogeneous photocatalysts, facile product separation and catalyst regeneration could be fulfilled. As illustrated in Scheme 1d, we aim to synthesize succinonitrile by a light-driven direct dehydrogenation of CH₃CN together with the evolution of high purity hydrogen using semiconductor photocatalysts. In this process, the precise activation of sp³ C-H bonds and keeping -CN intact are the prerequisites.

Here, we report a one-step synthesis of succinonitrile from CH₃CN via light driven C-H bond cleavage and subsequent C-C dehydrogenation. By the Pt/TiO₂ (anatase) photocatalyst, the formation rate of succinonitrile reached 6.55 mmol/(gcat*h) with >97.5% selectivity. As illustrated in Scheme 1d, we aim to synthesize succinonitrile by a light-driven direct dehydrogenation of CH₃CN together with the evolution of high purity hydrogen using semiconductor photocatalysts. In this process, the precise activation of sp³ C-H bonds and keeping -CN intact are the prerequisites.

Results and discussions

Synthesis and characterization of photocatalysts

All the Pt or other metal based photocatalysts were prepared using the photo-deposition of metal precursors on commercial anatase, rutile or P25 titanium oxides. The resulting catalysts were denoted as M/TiO₂-A, -R or -P. The XRD patterns of as-prepared Pt/TiO₂ catalysts indicate that the loaded metal species were fully reduced. The fitting results of EXAFS spectra (Table S1) showed that the Pt-Pt first shell coordination numbers of each of the catalysts were in the range of 8.9~9.9, indicating the average particle sizes of around 3 nm. The high angle abbreviation dark field scanning transmission electron microscope (HAADF-STEM) images showed that the photo-deposited Pt NPs were in irregular shape (Fig. 2d-f), with an average Pt size of 3 nm. The UV-Vis spectroscopy (Fig. S2) showed that the bandgaps of photocatalysts were 3.20 eV for Pt/TiO₂-A, 2.95 eV for Pt/TiO₂-P, and 2.98 eV for Pt/TiO₂-R. The photocurrent density (Fig. S3) decreased in the following...
order: Pt/TiO₂-A > Pt/TiO₂-P > Pt/TiO₂-R, suggesting that the light harvesting ability of catalysts increased with the percentage of anatase phase in the support.

Photocatalytic dehydrogenative coupling of acetonitrile

The photocatalytic reactions were performed in 20 mL parallel batch reactors (Fig. S4) using aqueous solution of CH₃CN as both reaction medium and reactant. In a typical test, 20 mg fine powder of catalyst was placed into the system, working at 60 °C for two hours. The 365 nm 10 W LED light was used as the light source. In Fig. 3a, no reaction occurred in the absence of light radiation, suggesting that acetonitrile was stable in aqueous solution at 60 °C. Only a small amount of CO₂ (0.31 mmol/(gcat·h)) was produced over TiO₂-P, which can be attributed to the overoxidation of CH₃CN as the bare support (Table S2). No coupling products appeared under the catalysis of pure TiO₂ semiconductors. The loading of transition metal cocatalysts had significant influence on the catalytic activity and product distribution (Table S2). When Pt was introduced onto the catalyst, 1% Pt/TiO₂-R exhibited weak H₂ evolution together with the formation of CO₂ as the only carbon-containing product. In contrast, a high activity of SN at 6.55 mmol/(gcat·h) was achieved by the 1% Pt/TiO₂-A with a selectivity of 97.5% and quantum yield of 4.4%. Only a trace amount of CO₂ (1.4%) and acetamide (1.1%) were detected, which were the by-products from overoxidation and acetonitrile hydrolysis. Simultaneously, about 9.76 mmol/(gcat·h) H₂ was produced, suggesting that the SN was overoxidation and acetonitrile hydrolysis. Furthermore, the function of different transition metal cocatalysts was investigated (Fig. 3b). Among all the M/TiO₂-A catalysts, Pt/TiO₂-A showed the highest SN activity, which was 5 times higher than that of Au or Rh/TiO₂-A and more than one order higher than that of Pd, Ag or Fe/TiO₂-A. Moreover, Pt/TiO₂ had the highest selectivity towards SN. The SN selectivity over Au and Rh/TiO₂-A catalysts were about 94%. In contrast, the 13% and 26% of consumed CH₃CN was transformed into the overoxidized product CO₂ by Pd and Fe/TiO₂, respectively. Pd and Ag/TiO₂ exhibited 12.2% and 97.7% selectivity towards acetamide (AM), respectively. For Ag/TiO₂-A, the AM formation rate reached as high as 32.0 mmol/g·h, indicating that it is highly active for the hydrolysis side reaction.

The ratio of water and acetonitrile is an important factor for SN synthesis (Fig. 3c). Without water, SN was merely observed. Only when H₂O and CH₃CN were both presented, considerable amount of SN was generated with a maximum rate at CH₃CN/H₂O = 7:3, suggesting that water was probably involved in the dehydrogenative coupling reaction. The change of substrate/catalyst ratio (Fig. 3d) showed that the mass specific activity of Pt/TiO₂-A reduced sharply with the increasing substrate/catalyst (S/C) ratio. When S/C = 1100:1, the coupling rate was 2.65 mmol/(gcat·h), only 40% of that under the optimal condition. Thus, the dilution of catalyst with excessive amount of reactant had negative effect on the reaction. The coupling reaction may not occur fully on the surface of photocatalyst. Otherwise, the coupling rate should not have changed with a reduced amount of catalyst. The time-dependent reaction rate from 0 to 6 h is presented in Fig. 3e. The accumulated
Mechanism investigation of the dehydrogenative coupling of acetonitrile

Detailed reaction mechanism of the acetonitrile dehydrogenative coupling was studied. The coupling reaction was a photocatalytic process which occurred in the presence of water. To identify the role of photo-excited holes, electrons and radical intermediates, mechanism studies employing scavengers were performed (Fig. 4a). When Na2S was introduced into the system as the hole scavenger, the formation of SN was completely ceased. When AgNO3 was added as electron scavenger, only small amount of SN formed in 2 h (0.17 mmol/(gcat*h)). Simultaneously, significant amounts of overoxidation product CO2 and hydrolysis byproduct acetic acid formed with rates of 15.56 and 9.75 mmol/(gcat*h), respectively. This result suggested that the product in 6 h was estimated to 26 mmol/gcat, equivalent to a turnover number (TTN) of 570 per Pt atom in 6 hrs.

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accumulation of holes on the catalysts tended to promote the oxidation of CH$_3$CN to CO$_2$. Meanwhile, the proton formed in the water oxidation reaction by the hole could protonate the terminal N of cyanide, which facilitated the acetonitrile hydrolysis side reaction. The AM byproduct in the normal catalytic reaction was generated via proton-assisted hydrolysis. Therefore, the prevention of accumulation of holes and protons from the water oxidation reaction are highly important to reduce or eliminate the side reactions. Furthermore, dimethyl pyridine N-oxide (DMPO) was added as radical scavenger. A strong deactivation of catalysts was observed (SN formation rate was only 1/550 of the reference test), indicating that the radicals were probably the key intermediates in the CH$_3$CN coupling reaction.

Kinetic isotope effect experiments suggested that both the O-H and C-H dissociation steps had significant influence on the reaction rate (Fig. 4b), suggesting that the water actually participated in the dehydrogenation coupling reaction. The hydrogen atom in the H$_2$ originated from water rather than CH$_3$CN. Therefore, water acted as a cocatalyst during the dehydrogenative coupling reaction.

To investigate reaction pathways and identify major radical intermediates, electron spin resonance spectroscopy (EPR) assisted by radical trap reactions were performed using DMPO as trapping reagent (Fig. 4c). In the presence of UV radiation and catalysts, both the signals of trapped -OH and -CH$_2$CN radicals (marked as red and green respectively) were observed. In comparison, no radical was trapped without light. When radiation was removed after the system reached steady state, an instant consumption of hydroxyl radical occurred. The trapped -CH$_2$CN was stable, and the -OH radical was a more active radical that could extract H from the sp$^3$ hybridized CH$_3$ of acetonitrile. Meanwhile, the intensity of hydroxyl radical signals was relatively weaker in the presence of CH$_3$CN than in pure water (Fig. S5), indicating that the -OH was probably the primary radical species generated from the single electron water oxidation process. The -CH$_2$CN radical was generated from CH$_3$CN via a selective α-C-H bond cleavage process initiated by -OH. The SN was a product of the coupling reaction between two -CH$_2$CN. Combining with the KIE results ($k_{H}/k_{D} = 4.3$ for CH$_3$CN/CD$_3$CN), we deduced that the radical propagation from -OH to -CH$_2$CN was the rate-limiting step.

Based on the results of mechanism studies, the preferential dehydrogenative coupling reaction of acetonitrile to succinonitrile is a light-driven catalytic process with free radicals as key intermediates.
The synergy between the anatase TiO₂ semiconductor with selectivity and 4.4% of quantum yield. Mechanism studies suggested biting a high SN formation rate of 6.55 mmol/(g*h) with over 97.5% of metal cocatalyst is crucial for H⁺ removal. Those noble metal centers control of radical diffusion is highly important (Fig. 4e). As the bond fusion layer can be very thin38. The radical transfer from hydroxyl to (con probe method, Fig. S9)32. In comparison, the rutile phase TiO₂ have concentration of been widely studied as a material that is inefficient for the -OH radical formation in water. The surface O tended to form >Ti-O-Ti- bridge rather than release as radicals33. The difference in hydroxyl radical formation rates accounts for the support effect in the CH₃CN coupling reaction. In the subsequent step, the -OH radical selectively activated the α C-H bond, generating the CH₂CN radicals as the coupling intermediate. The competitive reactions of -C-H cleavage and -CN protonation by H⁺ generated in the water oxidation step was the important factor determining the reaction selectivity. If the N terminal of cyamide group was protonated, the carbon atom of -CN could be more vulnerable to the attack of water34. Acetamide and acetic acid byproduct could be formed subsequently. To prevent the hydrolysis process, efficient hydrogen evolution reaction over the transition metal cocatalyst is crucial for H⁺ removal. Those noble metal centers with good H₂ evolution abilities (e.g., Pt and Rh) were able to consume the excessive H⁺ and suppressed the hydrolysis selectivity36. Fe and Ag were less efficient for H₂ evolution exhibiting high side reaction selectivity43. Hence, the synergy between Pt and TiO₂ is important to achieve a high yield of SN. Except for the photocatalyst design, the control of radical diffusion is highly important (Fig. 4e). As the bond dissociation energy (BDE) of water is large (497 kJ/mol), the -OH diffusion layer can be very thin45. The radical transfer from hydroxyl to -CH₂CN can only occur in the diffusion layer, and the coupling possibility of two -CH₂CN radicals (second order kinetics) can be much smaller in the outer region of the layer than in the vicinity of catalyst surface (where radical concentration is much higher)9. Therefore, the majority of products should be generated from the catalyst surface. We anticipate that methods that can significantly enhance the steady state concentration of -OH and -CH₂CN can significantly benefit the reaction rate and yield.

In summary, we demonstrated that succinonitrile could be prepared with high selectivity and considerable rate via a UV light driven dehydrogenative coupling reaction of acetonitrile. Anatase TiO₂ supported Pt NPs were identified as the efficient catalytic system, exhibiting a high SN formation rate of 6.55 mmol/(g·h) with over 97.5% of selectivity and 4.4% of quantum yield. Mechanism studies suggested that the reaction proceeded via a hydroxyl radical initiated radical pathway. The synergy between the anatase TiO₂ semiconductor with the loaded Pt cocatalyst enhanced the rate of -OH radical formation, radical propagation, coupling and hydrogen evolution, leading to the good performance of catalysts. This work paves a new way towards transforming low-value organic molecules to value-added terminal biofunctionalized compounds in a green, nontoxic and atomic efficient manner.

**Methods**

**Materials**

All chemicals were used directly without further purification. Anatase TiO₂ (TiO₂-A) and rutile TiO₂(TiO₂-R) were purchased from Aladdin. TiO₂(P25) (TiO₂-P), which contained 25% rutile and 75% anatase, was purchased from Degussa. H₃PtCl₆-6H₂O, HAuCl₄-4H₂O, PdCl₂, RhCl₃-3H₂O, AgNO₃, and Fe(NO₃)₃.9H₂O were purchased from Macklin.

Catalyst preparation

The M/TiO₂ catalysts were prepared by photodeposition method. In the photodeposition (PD) of metal over TiO₂ support, 200 mg TiO₂ powder and metal precursor (H₃PtCl₆-6H₂O / HAuCl₄-4H₂O / PdCl₂ / RhCl₃-3H₂O / AgNO₃) were dispersed in 15 mL 20% methanol aqueous solution (v/v) in a quartz flask. Subsequently, the flask was placed in the 365 nm photo-radiation generated by a 1 W LED lamp under argon protection with vigorous stirring for 3 h. After the PD procedure, the M/TiO₂ was separated from the suspension by centrifugation, washed 3 times using DI water and dried at 333 K for 12 h before use.

The other Pt modified semiconductor catalysts were prepared using similar procedure as the M/TiO₂ photocatalysts.

Sample characterizations

The photocatalysts were characterized by X-ray diffraction, X-ray absorption spectrometry, transmission electron microscopy, EXAFS spectroscopy, ESR spectroscopy, UV-Vis spectroscopic, photoluminescence spectroscopy, and photoelectrochemical measurements were used to study the structure and photocatalytic properties of the catalysts. The experimental details are described in Supplementary Information.

Photocatalytic reaction test

Photocatalytic experiments (acetonitrile dehydrogenative coupling to succinonitrile) were performed in a top-irradiation Pyrex flask. A 10 W LED light (wavelength 365 nm) (PLS-SXE300, Beijing Trusttech Co., Ltd.) was used as the light source. Typically, 20 mg photocatalysts were dispersed in 10 mL 70% volume acetonitrile aqueous solution under magnetic stirring. Prior to the irradiation, the reaction mixture was deoxygenated repeatedly with Ar gas for 5 times to thoroughly remove air and dissolved oxygen. During the reaction, the photocatalytic reaction system was kept at 60 °C. To evaluate the photocatalytic hydrogen production and analyze other gas products, the gas-phase composition of the photocatalytic reactor was analyzed by an Agilent 8860 gas chromatograph equipped with 5 Å molecular sieves and HP-Plot columns and thermal conductivity cell (TCD) detector. Liquid products were analyzed by Agilent 8860 gas chromatograph equipped with a column of SH-1 with flame ionization detector (FID).

Data availability

The data that support the plots within this paper and other finding of this study are available from the corresponding author upon reasonable request.

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Author contributions
S.Yao and D.M. and L.L. proposed the project and designed the experiment. X.Z. performed most of the experiments, analyzed the data and prepared the manuscript. X.G., H.F., W.Z. and J.L. carried out the part of the project. Z.G. carried out the TEM characterization. X.Q. performed the in-situ XAFS characterization. Z.G. carried out the TEM characterization. S.F., W.X. and S.Y. prepared the catalysts and evaluated the performance. S.Yao and D.M. and L.L. proposed the project and designed the experiment and the measurement and analysis of transient photocurrent. X.Q. performed the in-situ XAFS characterization. Z.G. carried out the TEM characterization. S.F., W.X. and S.Y. prepared the catalysts and evaluated the performance. S.Y. helped to improve the photocatalytic reactor. S.Yao and D.M. and L.L. revised the manuscript. J.F. and D.X. modified the style of manuscript.

Competing interests
The authors declare no competing interests.
Additional information

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