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A supported-catalyst of grafting [Co(TPA)Cl]Cl molecular catalyst onto SiO₂ nanoparticles to achieve robust syngas production in a photochemical system



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ABSTRACT

A novel supported-catalyst **SiO₂-TPACo** of covalently anchoring a [Co(TPA)Cl]Cl moiety onto SiO₂ nanoparticles (NP) was prepared and characterized. The **SiO₂-TPACo** exhibits robust dual activity of mediating CO₂ and protons reduction to CO and H₂, respectively, in a noble-metal-free photochemical system; the CO/H₂ ratio satisfies requirement of syngas.

1. Introduction

Carbon dioxide (CO₂) is a cheap and widely available feedstock for fuels or value-added chemicals production [1-4]. However, the direct reduction of CO_2 is high energy consuming [5,6]. The conversion of CO₂ to solar fuels via photochemical system represents a sustainable way of CO₂ utilization. Much effort had been devoted to pursuit high selectivity of CO2 reduction, because the generation of H2 as a byproduct is inevitable in most cases. Actually, simultaneous reduction of CO₂ and protons to syngas, a mixture of carbon monoxide (CO) and hydrogen (H_2) with reasonable ratio, is an alternative strategy of CO_2 utilization. The CO/H₂ ratio of syngas in the range of 1:1 to 1:3 satisfies different chemicals production in petrochemical industry. For example, syngas with a CO/H₂ ratio of 1:1, 1:2, and 1:3 is used for gasoline, methanol, and methane production, respectively, in Fischer-Tropsch (F-T) synthesis [7]. However, the fabrication of catalyst/photocatalyst of dual CO2 and proton reduction activity to produce CO and H2 with reasonable ratio is challenging [8-12]. In this endeavour, representative works contributed by Beller and Kang recently (Table S1).

The former realized photocatalytic syngas production with a CO/H_2 ratio of 1:1 by employing a Fe-carbonyl complex as catalyst and an Ircomplex as a photosensitizer (PS) [13]. Kang et al. fulfilled controllable syngas production by smartly designing a hybrid photocatalyst of anchoring two molecular catalysts, a Re(CO)₃(bpy)Cl complex as a CO₂ catalyst and a cobaloxime complex as a proton reduction catalyst, onto the surface of dye-sensitized TiO₂ particles [14].

Molecular cobalt complexes had long been used as catalysts for either proton reduction or CO_2 reduction in homogeneous photocatalytic systems [15–26]. However, these catalysts suffer from low stability in homogeneous system and excessive CO/H₂ or H₂/CO production ratio, which cannot meet the requirements of industrial syngas. Immobilizing molecular catalysts onto solid support to fabricate supported-catalyst would enhance stability of the catalyst. [27–30]

Herein, we covalently grafted the active [Co(TPA)Cl]Cl moiety onto the surface of SiO₂ NP to obtain a supported-catalyst SiO₂-TPACo (Scheme 1) [31–33]. Interestingly, the SiO₂-TPACo showed dual- activity of CO₂-to-CO and 2H⁺-to-H₂ conversions in particular photochemical conditions. The system containing SiO₂-TPACo as a catalyst,

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Scheme 1. The preparation of SiO₂-TPACo and the photocatalytic syngas (CO + H₂) production system based on SiO₂-TPACo.

graphitic carbon nitride (g-C₃N₄) as a PS, and triethylamine (TEA) as an electron donor produced syngas with high activity and stability. At the optimal conditions, this noble-metal-free system maintains activity for over 120 h. A total amount of syngas (CO + H₂) of 10.18 µmol with a CO/H₂ ratio of *ca.* 1:1 was produced; the catalyst-based efficiency is up to 10.18 µmol mg_{cat}⁻¹.

2. Materials and methods

2.1. Reagents and instruments

All chemicals, including Tetraethyl orthosilicate (TEOS), γ -aminopropyltrimethoxysilane (APTMS), triethylamine, ammonium hydroxide (NH₃·H₂O, 25 %–28 %), triethylamine (TEA), 2, 6-bis(chloromethyl) pyridine, 2, 2-dipicolylamine (DPA), potassium carbonate, and cobalt chloride hexahydrate (CoCl₂·6H₂O) were purchased from commercial suppliers (Sinopharm chemical reagent co., LTD, Adamas and Sigma-Aldrich) and used without further purification. CO₂ (99.999 %), CO (99.999 %), CH₄ (99.99 %) were purchased from commercial supplier (Huaerwen). ¹³CO₂ (99 % ¹³C atom) were purchased from Aldrich. All solvents of analytical grade were purchased from commercial suppliers and used without further purification. **g**-C₃N₄: **g**-C₃N₄ were synthesized

observed by using a Nova Nano SEM 450 high resolution scanning electron microscope operated at 20 kV. High-resolved TEM images were recorded by Titan G2 60-300 with image corrector high resolution transmission electron microscopy (HTEM) operated at 300 kV. The Xray photoelectron spectroscopies (XPS) were measured on an ESCALAB 200i-XL spectrophotometer with Al-Ka radiation. The emission spectra were measured by a Shimadzu RF-5301PC. Cyclic voltammetry and Mott-Schottky measurements were performed by an electrochemical analyzer (CHI660E, Chenhua Instruments Co. Shanghai, China) with a working electrode (glassy carbon electrode), a Pt counter electrode and an Ag/AgNO₃ (0.01 M, AgNO₃) reference electrode. Photoelectrochemical measurements were performed by an electrochemical analyzer (CHI660E, Chenhua Instruments Co, Shanghai, China) with a working electrode with a bias of -0.3 V (vs SCE), a Pt counter electrode and an SCE reference electrode in Na₂SO₄ aqueous solution (0.1 M). A 300 W Xe lamp with an AM1.5 simulated sunlight was used as the light source.



2.2.1. TPA-CH₂Cl ligand



according to previously reported procedures by heating approximately 5 g of melamine at a rate of 5 K min^{-1} to 823 K and then maintaining this temperature for another 2 h.

The diffuse reflectance spectra (DRS) were recorded on UV–vis spectro-photometers (Shimadzu UV-3600PC). FT-IR spectrum on KBr was performed with Nicolet-20DXB Fourier Transform Infrared Spectrometers. The amount of cobalt in **SiO₂-TPACo** was determined by ICP-AES analysis (Optima 5300, PerkinElmer). The SEM images was

The TPA-CH₂Cl was synthesized according to literature method [34]. To a solution of 2,6-bis(chloromethyl)pyridine (1 g, 5.68 mmol) and potassium carbonate (300 mg, 2.17 mmol) in 10 mL acetonitrile with continuous stirring, 2,2-dipicolylamine (300 μ L, 1.67 mmol) was added. The reaction mixture was then refluxed for 10 h. Reaction process was tracked by thin layer chromatography. Then the reaction mixture was evaporated by vacuum-rotary and purified through column chromatography over silica gel (DCM/MeOH = 20/1) to give gray

solid, yield: 50 % [34]. ¹H NMR (400 MHz, CDCl3) & 8.53 (d, J = 4.7 Hz, 2 H), 7.74 – 7.62 (m, 3 H), 7.58 (d, J = 7.8 Hz, 2 H), 7.54 (d, J = 7.8 Hz, 1 H), 7.33 (d, J = 7.6 Hz, 1 H), 7.18 – 7.09 (m, 2 H), 4.65 (s, 2 H), 3.90 (s, 6 H).

2.2.2. SiO2-TPACo

The synthesis of raw SiO₂ and SiO₂-NH₂ NP was performed according to methods in literatures [35–37]. The SiO₂-TPA was synthesized by refluxing the mixture of SiO₂-NH₂ (600 mg), TPA-CH₂Cl (90 mg), and TEA (300 μ L) in ethanol (30 mL) at 79 °C for 24 h. The SiO₂-TPA was obtained as yellow powder by centrifugation and washed several times with ethanol and methanol. The **SiO₂-TPACo** was synthesized by stirring a mixture of SiO₂-TPA (230 mg) and CoCl₂·6H₂O in acetonitrile at room temperature; after washing with methanol for several times and drying under vacuum overnight, the **SiO₂-TPACo** as pale blue powder was obtained.

2.3. Photocatalysis

Photocatalytic reactions were performed at room temperature in a glass tube. A typical procedure for photocatalytic reaction is as follows: certain amount of g-C₃N₄ and **SiO₂-TPACo** were put into the tube; certain volume of CH₃CN and TEA were taken to mix in the tube. The sample was sealed and purged with CO₂ for 25 min and then a certain amount of (500 μ L) CH₄ as internal standard for quantitative GC analysis was injected into the sample. The sample was irradiated under LED-photoreactor ($\lambda_{max} = 450$ nm). The gaseous products were extracted and analyzed by Techcomp GC7900 gas chromatography equipped with a thermal conductivity detector (TCD) for H₂ and CH₄ analysis and flame ionization detector (FID) for CO analysis. The Ar was used as carrier gas. The response factors of H₂/CH₄ and CO/CH₄ were 0.23 and 0.14, respectively, which were established by calibration with known amounts of H₂, CO, and CH₄ before and after a series of measurements.

3. Results and discussion

The supported-catalyst SiO₂-TPACo was prepared by covalently linking TPA (TPA = tri(2-pyridylmethyl)amine) ligand onto SiO_2 surface. To this end, a TPA ligand derivative TPA-CH₂Cl (Scheme 1), bearing a -CH₂Cl group at one of pyridine, and amino groups modified SiO₂-NH₂ (SiO₂-NH₂ is modified by -CH₂CH₂CH₂NH₂ ligands, Scheme 1) NP were synthesized according to literature methods [11,38]. The covalently linking of TPA-CH₂Cl ligand onto the NP was achieved by refluxing of TPA-CH₂Cl and SiO₂-NH₂ in a TEA/EtOH mixture for 12 h. The successful grafting of TPA ligand onto the surface of SiO₂ was characterized by UV-vis diffuse reflectance spectra (DRS) and solid state ¹H NMR (SS-¹H NMR). As shown in Fig. 1a, in comparison to the DRS spectrum of SiO₂-NH₂, SiO₂-TPA shows a characteristic absorption at 265 nm, which are in consistent with those of the precursor TPA-CH₂Cl ligand. SS-¹H NMR spectra of SiO₂-NH₂ and SiO₂-TPA in Fig. 1b show obvious difference. In the spectrum of SiO_2 -NH₂, two signals at δ = 2.67 ppm and δ = 1.29 ppm are attributed to protons of methylene groups nearby and far away -NH2 groups. However, in the spectrum of SiO₂-TPA, except two signals of -CH₂CH₂CH₂NH₂ moiety at ca. 2.72 ppm and 1.24 ppm, two characteristic signals at $\delta = 3.61$ ppm and δ =7.31 ppm assigning to methylene groups and pyridines, respectively, in TPA moiety were also observed. These evidences indicate the successful grafting TPA ligand onto SiO₂ NP.

Further coordination of cobalt ion (Co^{2+}) to SiO₂-TPA was conducted by simply stirring of SiO₂-TPA and CoCl₂**=**6H₂O in methanol at room temperature for 1 h. After washing with ethanol and drying under vacuum, the solid **SiO₂-TPACo** as pale blue powder was obtained. In comparison to XPS spectrum of SiO₂-TPA in Fig. 1c, the newly emerged signals of Co and Cl in XPS spectrum of **SiO₂-TPACo** demonstrate that the coordination between Co²⁺ and N-donor ligands on SiO₂ surface operates. Different from the DRS spectrum of SiO₂-TPA, an obvious broad absorption at *ca.* 457 – 750 nm emerged in spectrum of **SiO₂-TPACo**. The absorption at 457 – 750 nm is attributed to *d*-*d* absorption



Fig. 1. (a) UV-vis diffuse reflectance spectra of SiO₂-TPACo and its precursors. (b) Solid-state ¹H NMR spectrum of SiO₂-NH₂ and SiO₂-TPA. (c) Full XPS spectra of SiO₂-TPACo and its precursors. (d) HTEM image of SiO₂-TPACo and the elements mapping images of SiO₂-TPACo.



Fig. 2. (a) Photocatalytic syngas (CO + H₂) production under visible light irradiation (Blue LED, $\lambda_{max} = 450$ nm); the standard sample composition: SiO₂-TPACo (5.0 mg), g-C₃N₄ (10.0 mg), TEA (1 mL); irradiation time: 20 h. (b) Long-time photocatalysis of the sample containing SiO₂-TPACo (1.0 mg), g-C₃N₄ (10.0 mg), TEA (1 mL) in a CO₂-saturated CH₃CN solution. (c) Luminescence spectra of g-C₃N₄ in CH₃CN in the absence and presence of [Co (TPA)CI]Cl ($\lambda_{ex} = 380$ nm). (d) Transient photocurrent response to on-off illumination of g-C₃N₄ modified electrode in the presence and absence of [Co(TPA)CI]Cl; light source: Xe lamp ($\lambda_{>} + 420$ nm).

of cobalt complexes formed on the SiO₂ [39]. The amount of cobalt in as-prepared **SiO₂-TPACo** is 0.524 %, which was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

The **SiO₂-TPACo** NP and its precursors were further characterized by SEM and TEM. The SEM images (Fig. S1) show that SiO₂, SiO₂-NH₂, SiO₂-TPA, and **SiO₂-TPACo** exist as spheres with a unified size of *ca*. 100 nm. Especially, the **SiO₂-TPACo** NP are monodispersed and no aggregation were observed, indicating the Co²⁺ ions are mainly coordinated by TPA ligands but residual amino groups on SiO₂ surface. Because the cross-linking between SiO₂-NH₂ and Co²⁺ will lead aggregation of SiO₂ NP, which was observed from our previous studies [11]. The TEM image of **SiO₂-TPACo** (Fig. 1d) further shows the monodispersity of the NP. The element mapping images of **SiO₂-TPACo** (Fig. 1d) show that cobalt, chlorine, and nitrogen elements are distributed uniformly on the surface of SiO₂ n anoparticle. All of these results indicate the successful formation of **SiO₂-TPACo** supportedcatalyst.

The activity of SiO₂-TPACo catalyst (5.00 mg) was firstly evaluated in a photochemical system containing polymeric graphitic carbon nitride (g-C₃N₄, 10.00 mg) as a PS [40–43], and trimethylamine (TEA) as an electron donor (v(TEA)/v(CH₃CN) = 1/4, total volume = 5.00 mL) in a CO2-saturated CH3CN solution. After irradiated under blue LED light (λ_{max} = 450 nm) for 20 h, the standard sample (sample A in Fig. 2a) produced 1.33 μ mol CO and 4.20 μ mol H₂ (CO/H₂ ratio = 1:3); the oxidized TEA releases protons during photocatalysis, which is the proton source of H₂ production in the system [44]. The sample B without SiO₂-TPACo catalyst produced, however, only 0.13 µmol CO and 0.63 µmol H₂, which are far less than that of the standard sample. It is interesting that the sample C without TEA produced only a small amount of CO (0.20 µmol); presumably, the residual amino groups on SiO₂-TPACo function as electron donor. The standard sample (sample D) under N_2 atmosphere produced only H_2 (1.20 µmol). Control experiment in dark demonstrated that neither CO nor H₂ was obtained from this three-component system. By using molecular catalyst [Co (TPA)Cl]Cl (0.05 mM) to replace SiO₂-TPACo, the system (sample E) produced only 0.73 μ mol CO and 3.80 μ mol H₂ (CO/H₂ ratio = 1:5); the amount of CO production in this system is only a half in comparison to the standard sample, indicating that the CO₂ reduction activity is

improved by anchoring [Co(TPA)Cl]Cl onto SiO₂ NP. These findings revealed that all of the components: **SiO₂-TPACo**, *g*-C₃N₄, TEA, CO₂, and light irradiation are essential for efficient syngas production.

The bifunctional activity of **SiO₂-TPACo** for either CO₂ or protons reduction in photochemical condition was also confirmed by a system of using Ir(ppy)₃ as a PS. As shown in Fig. 2a, sample F containing Ir (ppy)₃ as a PS and **SiO₂-TPACo** as a catalyst in CO₂-saturated CH₃CN solution produced 0.60 µmol CO and 0.68 µmol H₂, the CO/H₂ ratio achieves 1:1. Control experiments revealed that Ir(ppy)₃ only functions as PS and doesn't catalyze CO₂ or protons reduction in our conditions employed. Although the syngas production efficiency is less than that of using g-C₃N₄, this result further proves that **SiO₂-TPACo** has bifunctional activity for mediating CO₂ and proton reduction in particular photochemical system.

The efficiency and CO/H₂ ratio of this three-component system can be tuned by adjusting the amount of SiO₂-TPACo or g-C₃N₄ (Fig. S3). For example, by increasing the amount of the g-C₃N₄ from 5.00 mg to 25.00 mg, the total amount of syngas (CO + H_2) produced from these three-component systems increased from 4.03 µmol to 7.32 µmol, the CO/H_2 ratio increased from 1.0 : 3.5 to 1.0 : 2.8. In contrast, decreasing the amount of SiO₂-TPACo from 5.00 mg to 1.00 mg, the total amount of syngas decreased from 5.53 μ mol (CO/H₂ = 1.0 : 3.2) to 3.42 μ mol $(CO/H_2 = 1.0 : 1.6)$, however, the catalyst-based efficiency increased from 1.11 μ mol mg_{cat}⁻¹ to 3.42 μ mol mg_{cat}⁻¹. Based on above results, a long-time irradiation experiment was performed at optimal condition by using 1.00 mg SiO₂-TPACo and 10.00 mg g-C₃N₄ in CO₂-saturated CH₃CN/TEA mixed solution. As shown in Fig. 2b, the system continuously produced CO and H₂ in the first 120 h, indicating high stability for syngas production. After 160 h of irradiation, the system produced 10.18 µmol syngas, the catalyst-based efficiency is up to 10.18 μ mol mg_{cat}⁻¹ and 0.064 μ mol mg_{cat}⁻¹ h⁻¹. The turnover numbers (TON) based on cobalt are 56 and 59 for CO and H₂ production (TON_{total} = 115), respectively. Notably, the CO/H_2 ratio during this long time photocatalysis kept in the range of 1.0: 1.6 - 1.0: 1.0, which are very suitable for syngas requirements used in F-T synthesis.

To gain an insight into the system, the interaction between $g-C_3N_4$ and active [Co(TPA)Cl]Cl moiety in **SiO₂-TPACo** was investigated by using molecular [Co(TPA)Cl]Cl complex as a model. The $g-C_3N_4$ as a



Scheme 2. The proposed mechanism of the system.

polymeric semiconductor can be excited to generate electron-hole pair [40–45]. The photo-generated electrons at conduction band (CB) of *g*-C₃N₄ are expected to deliver to the cobalt center of [Co(TPA)Cl]Cl moiety in **SiO₂-TPACo**. This process is able to repress the electron-hole recombination occurring in *g*-C₃N₄ and thus improves the quantum yield of the photocatalysis. According to Mott-Schottky curve of *g*-C₃N₄ measured in CH₃CN solution (Fig. S4), the flat band potential, which can be considered as CB potential, is -1.54 V *vs*. NHE [40]. According to cyclic voltammetry measurement (Fig. S5), the first reduction event of [Co(TPA)Cl]Cl operates at a potential of $E_{pc} = -1.25$ V in CH₃CN. The photoinduced electron transfer (PET) from CB of *g*-C₃N₄ to [Co (TPA)Cl]Cl moiety of **SiO₂-TPACo** is therefore thermodynamically feasible.

The PET process was further evidenced by the quenching experiment and photoelectrochemical (PEC) measurements. As shown in Fig. 2c, the g-C₃N₄ dispersed in a CH₃CN solution exhibited a maximal luminescence at 450 nm after excitation ($\lambda_{ex} = 400 \text{ nm}$)[48] [11,40]. This luminescence can be quenched obviously by addition of [Co (TPA)Cl]Cl complex [45,46]. The FTO electrode modified by g-C₃N₄ in a PEC cell exhibited a transient photocurrent of -0.50 μ A cm⁻² under Xe lamp ($\lambda = 420$ nm) irradiation [47]. However, the g-C₃N₄ photocathode loading with [Co(TPA)Cl]Cl complex showed enhanced photocurrent of -1.33 µA cm⁻² under the same condition, indicating the consumption of excited electrons in g-C₃N₄ by molecular catalyst. Although the photocurrent enhancement of loading SiO₂-TPACo onto g-C₃N₄ photocathode was not observed due to shading effect and insulation of bulk SiO₂ NP (Fig. 2d). Above results prove that the interfacial PET process from excited g-C₃N₄ to [Co(TPA)Cl]Cl moiety on SiO₂ NP operates in photocatalysis.

On the basis of the above analysis, a plausible mechanism of the system can be depicted as shown in Scheme 2. Upon irradiation under visible light, *g*-C₃N₄ adsorbs photon to generate electron and hole at CB and VB band, respectively. Part of electrons on CB band transfer to the [Co(TPA)Cl]Cl moiety in **SiO₂-TPACo** to form Co^I species. The photogenerated Co^I species, as an active species for CO₂ and proton reduction [11,15–18], binds CO₂ or protons to afford CO and H₂ production. As single *g*-C₃N₄ also produce a small amount of CO and H₂, which indicates a part of excited electrons in *g*-C₃N₄ participate CO₂ and proton reduction cocurring at its own surface [40–43]. The photogenerated holes in *g*-C₃N₄ can be consumed by TEA [11,44]; the hole-oxidized TEA releases proton as the source of H₂ production in the system [45].

4. Conclusions

In summary, a novel supported-catalyst of anchoring [Co(TPA)Cl]Cl moiety onto SiO₂ NP was prepared and characterized. The **SiO₂-TPACo** exhibited dual activity of CO₂-to-CO and 2H⁺-to-H₂ conversions to produce syngas in particular photochemical systems. At the optimal condition, the noble-metal free system of containing **SiO₂-TPACo** as a catalyst and g-C₃N₄ as a PS maintains activity of syngas production over 120 h and a total 10.18 umol syngas (CO/H₂ = 1.0 : 1.6 – 1.0 : 1.0) was obtained, exhibiting high stability and efficiency (10.18 µmol mg_{cat}⁻¹). The photoinduced electron transfer from g-C₃N₄ to [Co(TPA)Cl]Cl moiety onto SiO₂ NP operates during photocatalysis.

Author statement

Meng-Xi Gui is responsible for synthesis and photocatalytic experiments.

Jin Wu is responsible for mechanism studies, electrochemical and photoelectrochemical measurements.

Jun-Chao Hu and Wu Xia is responsible for characterization.

Hongfang Liu and Weijun Li are responsible for data analysis.

Ningdong Feng is responsible for solid-state ¹H NMR measurements.

Feng Wang is responsible for project design, guidance and analysis on experiments, manuscript writing.

Declaration of Competing Interest

The authors declared that they have no conflicts of interest to this work.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2020. 112742.

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