

Automated and Continuous-Flow Platform to Analyze Semiconductor–Metal Complex Hybrid Systems for Photocatalytic CO₂ Reduction

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ABSTRACT: Su considered as a carbon-neutral fu	nlight-driven CO ₂ reductio promising approach to con el cycle, but most photoca	n is increasingly ntribute toward a talyst systems are C_{0_2}	

carbon-neutral fuel cycle, but most photocatalyst systems are currently studied individually under batch conditions with manual, labor-intensive analytical procedures. Here, we present the advantages of a continuous-flow setup to study photocatalytic CO_2 to CO reduction systems, which also benefits from aspects of automation (using programmed in-line gas quantification of multiple samples in parallel). The capabilities of the methodology are demonstrated using a state-of-the-art light absorber platform based on ZnSe quantum dots (QDs) in combination with a series of molecular co-catalysts based on Ni and Co for visible-lightdriven CO_2 reduction in aqueous ascorbate solution. A newly



synthesized Co-tetraphenylporphyrin featuring three sulfonate groups and one amine group (Co(tppS3N1)) is identified to exhibit a benchmark photocatalytic activity (18.6 μ mol of CO, 79.7 mmol of CO g_{ZnSe}^{-1} , TON_{Co} (CO) of 619, external quantum efficiency (EQE) >5%). The utility of our methodology is further shown by applying the setup to study the photocatalyst systems under lower light intensities, low CO₂ concentration, and aerobic conditions, which impact the photocatalytic activity and selectivity. Overall, this work reports an improved methodology for studying photocatalytic CO₂ reduction alongside advancing the understanding of QD molecular co-catalyst hybrids using ZnSe QDs as a versatile light absorber based on earth-abundant components that operate under fully aqueous conditions.

KEYWORDS: artificial photosynthesis, CO₂ reduction, photocatalysis, quantum dots, automation

INTRODUCTION

Photocatalytic solar fuel systems are most commonly studied in batch reactors with gaseous reaction products (H_2, CO, CH_4) accumulating in the reactor headspace.¹⁻⁵ While such batch systems are easy to set up and offer a high product sensitivity, they possess a number of drawbacks such as buildup of gaseous reaction products, which can lead to overpressure and subsequently aid product leakage, accumulating products reducing photocatalytic efficiency by undergoing back-reactions or catalyst poisoning as well as the requirement of laborintensive manual sampling and gas analysis. Some of the most successful photocatalytic systems for CO₂ reduction comprise two distinct functional materials, a solid-state light absorber combined with an additional catalyst based on transition-metal complexes.^{4,6,7} Such hybrid photocatalysts are promising because they combine the favorable photophysics and stability of solid semiconductors with the selectivity of (molecular) catalysts, herein referred to as co-catalyst. Within the search for new hybrid photocatalysts, it is necessary to study large libraries of light absorbers and co-catalysts as well as optimize experimental conditions, which results in high numbers of permutations and therefore individual experiments.

Hence, high-throughput techniques utilizing continuous-flow methodologies and an increasing degree of automation with reliable product analysis are desirable for the development of next-generation photocatalysts and optimization of conditions. While continuous-flow photocatalysis is used in the synthesis of organic pharmaceuticals,⁸ photodegradation of organic compounds,⁹ and photoredox catalysis,¹⁰ there has been relatively little activity in the production of solar fuels.¹¹ Some continuous-flow photocatalytic CO₂ reduction systems have been reported previously, but they were generally limited to gas-phase reactions employing low-yield titania photocatalysts without

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Figure 1. Continuous-flow photocatalytic CO_2 reduction with automated in-line gas chromatography. (A) Schematic diagram of the automated continuous-flow setup. (B) Schematic representation of the photocatalyst system consisting of ligand-free ZnSe-BF₄ QDs (yellow sphere; BF₄⁻ anions are omitted for clarity) in combination with molecular co-catalysts for visible-light-driven CO_2 to CO reduction in water using ascorbic acid (AA) as the sacrificial electron donor. (C) Overview of the molecular co-catalysts studied in depth during this work.

consideration to match light absorbers and co-catalysts in the assembly of photocatalytic hybrid architectures.^{12–14} Progress has also been made in high-throughput screening of molecular dyes with H₂ evolution co-catalysts, but the detection methodology was limited to colorimetric methods,¹⁵ whereas a different study utilized an automatic H₂ monitoring system consisting of mass flow controller (MFC) and photoreactor directly coupled to a gas chromatograph (GC).¹⁶ An automated robotic station for the screening of organic polymer photocatalysts for photocatalytic H₂ evolution was presented recently, but this system was also based on a batch operation with the products accumulating in the headspace.¹⁷

Here, we present a continuous-flow methodology to study photocatalytic CO_2 to CO reduction alongside H_2 evolution in aqueous solution. The developed setup uses automated in-line gas chromatography of multiple samples in parallel (Figure 1), and features a high measurement frequency (up to 0.25 min⁻¹) with a remarkable sensitivity (10^{-12} mol of CO s⁻¹). The capabilities of the continuous-flow system are investigated for semiconductor-metal complex hybrid photocatalysts, using ZnSe quantum dots (QDs) as a versatile light-absorbing platform (Figure 1B). We show that ZnSe QDs can drive a range of molecular CO₂ reduction co-catalysts based on metal porphyrins, cyclams, and quaterpyridines (Figure 1C) in aqueous ascorbate solution. Finally, we illustrate the versatility of the system by studying the influence of the light intensity, the effect of exposure to O_2 on the hybrid photocatalysts, and the consequence of varying the composition of feed gas from pure CO_2 to dilute CO_2 , which paves the way to study simulated real-life conditions.

RESULTS AND DISCUSSION

Method Development. The continuous-flow setup was assembled as depicted in Figures 1 and 2, and the technical details can be found in the Experimental Section. Gas cylinders containing balance gas (e.g., CO_2 , N_2 , air) were connected to a set of three-way valves, which were attached to a set of MFCs that provide a defined gas stream to each photoreactor. The MFCs allow for precise control of the flow rates, whereas the valve enables convenient switching between the desired balance gas. The outlets of the MFCs were connected to gas saturators filled with water to humidify the gas stream and then to the photoreactor with Teflon tubing. The photoreactors (volume 7.9 mL) consist of glass vials containing stirrer bars, sealed with septa, and filled with photocatalyst solution (3 mL). The gas



Figure 2. (A) Technical diagram of the continuous-flow setup. Photographs of (B) the photoreactors illuminated by the solar light simulator (three out of six photoreactors in operation), (C) the mass flow controller (MFC) setup, and (D) the gas chromatograph (GC) equipped with a flow-selection valve.

stream is routed through the entire vial by bubbling through the photocatalyst solution. Each sample outlet was connected with Teflon tubing through a particulate filter and shutoff valve to a flow-selection valve controlled by the GC. The flow-selection valve can be programmed to select one sample stream at a time, purge it through the sample loop, and inject it into the GC, after which the next sample stream can be selected.

This setup enables the analysis of multiple samples in parallel with a single experimental setup by sampling through every photoreactor one after the other. The measurement frequency is thereby determined by the number of samples and the run time of a GC analysis, which is approximately 4.25 min. In a typical experiment, six samples (each sample injected every 25.5 min) were measured in parallel, which was found to be a good balance between sample throughput and time resolution from GC analysis. The outlet of the sample loop was connected to a mass flow meter to verify the set flow rate prior to an experiment and detect potential leakage. The system is very sensitive to leakage, and verifying the flow rate prior to starting an experiment is required to ensure that the setup was correctly assembled. The automated nature of the system eliminates the human error of manual syringe injection and leaves a deviation from the set flow rate due to leaks in the setup as the key origin of error. An internal standard would not provide an added benefit because its concentration in the sample loop is unchanged, independent of a

deviating flow rate. The GC consists of two separate columns, a precolumn and a main column, connected to a high-sensitivity barrier discharge ionization detector. The precolumn made of a polymeric material (HayeSep D) separates the (target) gases (H₂, CO, CH₄, N₂, O₂) from CO₂ and moisture and blocks the latter two components from accessing the main column, which is made from Molsieve. The raw data acquired by the GC provide the momentary product evolution rate \dot{n}_{gas} (in mol s⁻¹) for each injection, which is calculated using the formula given in the Experimental Section.

The flow rate is a key variable that requires careful consideration because of its interplay with the sample loop size and the GC's sensitivity. A high flow rate results in increased dilution of product and a low flow rate is therefore favorable for higher product accumulation within the sample loop to ensure sufficient sensitivity for the GC analysis. On the other hand, very low flow rates result in unstable gas flows, a delay in product detection, and difficulty to avoid leakage (which can be observed by residual air peaks in the GC analysis). To increase the sensitivity, the sample loop size may be increased from $25 \,\mu$ L to 2 mL, but care must be taken to avoid overloading of the precolumn with CO₂. A flow rate between 3.5 and 4.0 standard cubic centimeters per minute (sccm) at a sample loop size of 1 mL was found to be the optimum between high sensitivity and a stable, reproducible gas stream without significant leakage in our



Figure 3. Survey of continuous-flow photocatalytic CO₂ reduction in the presence of ZnSe-BF₄ and various co-catalysts Co(qpy), Ni(cycP), and Co(tppS3N1). (A) H₂ evolution rate, (B) CO evolution rate, (C) total amount of evolved H₂, and (D) total amount of evolved CO. Conditions: 0.5 μ M ZnSe-BF₄, 10 μ M co-catalyst, 0.1 M AA, pH 4.5 (Co(tppS3N1)), pH 5.5 (Ni(cycP) and Co(qpy)), AM 1.5G, 100 mW cm⁻², λ > 400 nm, CO₂ (4.0 sccm), 25 °C.

setup with an excellent limit of quantification of 1.26×10^{-12} mol s⁻¹.

A standard gas mixture for calibration was used containing each 2000 ppm H₂, CO and CH₄ in CO₂ as balance gas. The gas mixture was further diluted with CO₂ (by mixing two gas streams with different flow rates) to reach concentration levels of 2000, 1600, 1200, 800, 400, and 200 ppm, which were used to generate a calibration curve, as depicted in Figure S1. The slope of the linear fit of the curve gives the response factor, for a given sample loop size. The delay of a given gas in the photoreactor to reach the GC was quantified by manually injecting a defined amount of gas into the reactor headspace followed by GC analysis and was found to be <4 min, which is below the time resolution of the GC analysis (Figure S2).

Survey of ZnSe QDs with Molecular Co-catalysts. We studied the capabilities of the continuous-flow system for photocatalysis using state-of-the-art ZnSe QDs as a light absorber in combination with molecular CO₂ reduction cocatalysts based on transition-metal complexes. ZnSe allows for utilization of parts of the visible spectrum of sunlight due to its bulk band gap of 2.7 eV and provides an ample reductive driving force for common molecular catalysts due to its conduction band position at approximately -1.4 V vs normal hydrogen electrode (NHE) (at pH 5.5).¹⁸ Previously, ZnSe QDs have been shown to drive co-catalysts based on the Ni(cyclam) family,¹⁹ and here, we screened a series of molecular co-catalysts based on earth-abundant metals including porphyrins,²⁰ quaterpyridines,²¹ terpyridines,³ and phthalocyanines.^{22,23} See the Experimental Section for the synthesis and characterization of ZnSe QDs and the molecular co-catalysts (Figures S3 and S4). An initial prescreening was conducted to reduce the number of possible combinations and revealed promising activity for Co(quaterpyridine) (Co(qpy)), phosphonic acidmodified Ni(cyclam) (Ni(cycP)), and Co(porphyrins) modified with either four sulfonate groups (Co(tppS4)) or three sulfonate groups and one amine (Co(tppS3N1)) (Figure 1C and Table S1). The latter catalyst is a novel CO₂ reduction cocatalyst and an analogue of the recently reported Co(tppS4), which was shown to be a benchmark molecular co-catalyst for photocatalytic CO₂ to CO reduction in aqueous solution when sensitized with a Ru(2,2'-bipyridine)₃ photosensitizer.²⁰ We introduced an amine moiety into Co(tppS3N1) as this strategy was previously reported to aid coulombic stabilization of CO₂ reduction intermediates²⁴ while preserving the general structure of the molecule.

The photocatalytic activity of the selected co-catalysts Co(qpy), Ni(cycP), and Co(tppS3N1) was subsequently studied with ZnSe QDs under continuous-flow of CO₂ (4 sccm) with our system described above in aqueous ascorbic acid (AA) solution (0.1 M, 3 mL) by irradiating the samples with UV-filtered simulated solar light (λ > 400 nm, AM 1.5G, 100 $mW \text{ cm}^{-2}$; see the Experimental Section for details). The data processing during continuous flow is described in the following and exemplarily shown for photocatalytic CO formation with ZnSelNi(cycP) (Figure S5). The raw data acquired from the GC analysis, \dot{n}_{gas} , is depicted in Figure S5A and gives the product evolution rate. Integration of the formation rate over irradiation time provides the total amount of evolved product. This was achieved by numerical integration of the formation rate using the trapezoidal method for each sample individually (Figure S5B). The three independent replicates of identical conditions were averaged by calculating the mean and standard deviation over irradiation time (see the Experimental Section for details). For visual display, the values of each individual sample are plotted as transparent scatter (50% transparency), whereas the mean is represented as a continuous line (compare also to Figure 3). To display the uncertainty of each experimental condition, the standard deviation is visualized as shaded area surrounding

the mean (mean \pm standard deviation) where the transparency is proportional to the standard deviation. The result appears as a vertical "cloud" of uncertainty and is performed for both product formation rate and total amount of product (Figure S5C,D). This example underscores the excellent data quality and resolution of the data acquired using the continuous-flow methodology, which significantly exceeds many previously reported studies on hybrid photocatalysts.^{3,19} Additionally, the automated sampling technique enables significantly higher throughput of light absorber–catalyst combinations compared to manual sampling because human input is only required for setting up the photoreactors and the tubing, and hereafter, the system operates independently.

ZnSe-BF₄ QDs in the absence of a co-catalyst are highly active toward the H₂ evolution reaction by reducing aqueous protons (Figure S6) and only form traces of CO from CO_2 as reported previously.^{25,26} Significant amounts of CO are only produced in the presence of co-catalysts, and the best-performing co-catalyst (Co(qpy), Ni(cycP), and Co(tppS3N1)) of the three catalyst families (quaterpyridine, cyclam, porphyrin) were analyzed in detail (see Figure 3 and Table S2). All QD-co-catalyst hybrids were optimized with respect to co-catalyst loading (optimum 20 mol_{co-catalyst} mol_{OD}⁻¹) and pH (4.5 for Co(tppS3N1) and 5.5 for Ni(cycP) and Co(qpy), Figure S7). ZnSelCo(qpy) reaches the maximum CO production rate after approximately 100 min, after which the CO evolution activity declines rapidly and mostly H_2 is generated (Figure 3). In contrast, the ZnSelNi(cycP) system featuring a molecular co-catalyst with phosphonate-anchoring group displays much better longevity, which may be attributed to catalyst immobilization. There is a small induction period for both H₂ and CO evolution, but the generation of CO remains relatively steady over the course of hours and only declines slowly, presumably due to a high quantity of attached/undamaged Ni(cycP) on the surface. Additionally, the initial high rate of Co(qpy) suggests it being the more efficient co-catalyst but less stable under turnover conditions. The time for both catalyst systems needed to reach peak turnover is likely caused by the photophysics of the QDs because it is also visible when the unfunctionalized QDs are used for proton reduction in the absence of a molecular co-catalyst (Figure S6).

In contrast, ZnSelCo(tppS3N1) exhibits a significantly longer induction period for both proton and CO₂ reduction. This is a surprising finding and suggests a strong anchoring of the cocatalyst to the QD surface as otherwise more H₂ evolution would be expected in the initial irradiation time of the experiment due to the high activity of the bare QDs toward proton reduction (Figure S6; see below for a more detailed analysis of the induction period). After approximately 120 min, the hybrid photocatalyst starts to evolve both H₂ and CO with a local maximum rate at approximately 260 min and an absolute maximum after 500 min. It is likely that the evolved H_2 originates not from the ZnSe surface but from the porphyrin co-catalyst itself as H₂ evolution activity is known for Co(tppS4).²⁰ The CO evolution rate peaks eventually and surpasses the two other catalyst assemblies, producing 18.6 \pm 3.3 μ mol of CO (79.7 ± 14.0 mmol of CO g_{ZnSe}^{-1} TON_{Co(tppS3N1)} (CO) of 619) after 1000 min of irradiation. In comparison, ZnSelCo(qpy) and ZnSelNi(cycP) reach a TON_{co-cat} (CO) of 71 and 116, respectively, after the same irradiation time.

All QD-co-catalyst assemblies evolve solely ¹³CO under an atmosphere of isotopically labeled ¹³CO₂, supporting that the

CO originates from CO₂ and no other carbon sources contribute to product generation (Figure S8). No other reaction products (e.g., methane, methanol, formate) were detected via GC and ¹H NMR spectroscopy, respectively. Only traces of CO and mostly H₂ were produced in the absence of a co-catalyst, and no gaseous products were detected in a series of deletional control experiments in the dark or absence of QDs or AA, demonstrating that all components of the photocatalytic system are required (Table S3).

The attachment of the co-catalysts on the QD surface was quantified via UV-vis spectroscopy by comparing the absorption profile of the co-catalyst in solution with the profile of the supernatant after exposure to QDs and subsequent removal of the QDs via centrifugation (Figure S9 and Table S4). The absorption spectra of Co(qpy) are nearly unchanged, confirming its diffusional nature and lack of immobilization. The attachment of Ni(cycP) to ZnSe QDs was previously quantified using ion-coupled plasma optical emission spectroscopy as Ni(cycP) does not feature a distinct UV–vis absorption profile and resulted in immobilization of 7.8% (1.6 mol_{co-cat} mol_{OD}⁻¹).¹⁹ Co(tppS3N1) exhibits a drastically lowered absorption intensity (based on the Soret band at 420 nm), which was translated to an attachment of 84% of the amount of employed co-catalyst (16.8 mol_{co-cat} mol_{QD}⁻¹). Electrokinetic ζ potential measurements confirm that ZnSe-BF₄ exhibits a positive potential (+20 mV), which rationalizes the attachment of negatively charged Co(tppS3N1). This electrostatic assembly also shows a higher attachment than Ni(cycP) with its dedicated phosphonate surface-bound anchoring group. As a result of the different anchoring strategies, the photocatalytic activity of the different catalysts is not strictly comparable, and the selection of catalysts aims to demonstrate the versatility of the continuousflow methodology as well as ZnSe QDs as the light-absorbing platform.

Transmission electron microscopy images of the particles after photocatalysis show the formation of some larger aggregates but retain a nanocrystalline morphology (Figure S10A). The stability of the particles was further confirmed by collecting UV-vis spectra after irradiation of the particles. Increased scattering implies particle agglomeration, but the absorption onset of the ZnSe-BF4 QDs retains unchanged compared to the stock solution, which indicates an unchanged size (Figure S10B). While those analyses do not contain information about the molecular co-catalyst, they demonstrate that the ZnSe particles are stable (within the time frame of the experiments conducted) and retain their key morphological and photophysical properties. Hence, we conclude that the declining photocatalytic activity observed for all QD-co-catalyst hybrids is mainly determined by accumulation of noninnocent oxidation products (DHA),^{27,28} a reduction in overall surface area as a result of agglomeration processes and/or loss and decomposition of the molecular co-catalyst.

In-Depth Study of ZnSelCo(tppS3N1). We subsequently explored the origin of the distinct induction period of Co(tppS3N1) during photocatalysis by comparing it with Co(tppS4). While Co(tppS4) does not exhibit such an induction period, Co(tppS3N1) eventually evolves CO at higher rates and outperforms Co(tppS4) (Figure S11). After 1000 min of continuous irradiation, ZnSelCo(tppS3N1) produces $18.6 \pm 3.3 \ \mu$ mol of CO (79.7 $\pm 14.0 \ m$ mol of CO ($_{2nSe}^{-1}$, TON_{Co} = 619), whereas ZnSelCo(tppS4) generates 7.0 $\pm 0.7 \ \mu$ mol of CO ($30.1 \pm 3.2 \ m$ mol of CO ($_{2nSe}^{-1}$, TON_{Co} = 233). Both molecular co-catalysts attach equally well to the QDs



Figure 4. Investigation of the induction period of Co(tppS3N1). (A) Reduction of Co(tppS4) in the presence of ascorbate as previously reported.²⁰ The reduction of Co^{III} to Co^{III} is accompanied by the removal of an axial H₂O ligand (d⁶ octahedral to d⁷ square-pyramidal). (B) UV–vis absorption spectra of Co(tppS4) and Co(tppS3N1) (1.7 μ M in water) in the presence of AA (0.1 M, pH 4.5) recorded every 1 and 5 min, respectively. "Start" refers to the spectrum in purely aqueous solution in the absence of AA. "Priming" refers to stirring the components in solution prior to irradiation. (C) Priming Co(tppS3N1) in the presence of AA and its influence on the photocatalytic activity using ZnSe-BF₄. The dashed vertical line indicates the catalytic onset of the green and blue traces. Conditions: 0.5 μ M ZnSe-BF₄, 10 μ M co-catalyst, 0.1 M AA, pH 4.5 (Co(tppS3N1)), AM 1.5G, 100 mW cm⁻², $\lambda > 400$ nm, CO₂ (4.0 sccm), 25 °C.

with approximately 86% (Co(tppS4)) and 84% (Co-(tppS3N1)), respectively, of the amount of employed cocatalyst (Table S4). This finding indicates that the affinity of the co-catalyst to the QD surface is not the cause of the different performance. Electrochemical characterization of the two cocatalysts via cyclic voltammetry (CV) did not yield unambiguous results to explain the different activities and induction periods (for details, see Figure S12).

Co(tppS4) was previously shown to occur initially as Co^{III} in aqueous solution and required reduction to Co^{II}, facilitated by AA (independent of light), to enter the catalytic cycle²⁰ (Figure 4A), accompanied by a distinct blueshift of the absorption spectrum. This initial Co^{III} to Co^{II} was monitored via UV–vis spectroscopy by recording a spectrum of the co-catalyst in AA solution at regular time intervals (Figure 4B). The spectrum of Co(tppS4) indeed shows the blueshift of the main absorption feature from 425 to 412 nm (Soret band) within 1 min of addition of AA, presumably due to changes in the metal-toligand charge transfer bands in Co^{II} vs Co^{II} complexes. The shift is followed by a reduction in the intensity of the 412 nm signal accompanied by a broad feature growing at 585 nm, which is presumably caused by a reduced Co species.^{29,30} In comparison, Co(tppS3N1) exhibits only a marginal shift of the main absorption feature at 427 nm upon addition of AA, which is gradually lowered in intensity in subsequent time intervals. A broad growing feature at 580 nm is also visible, likewise to Co(tppS4). Notable is the timescale of both reactions: While Co(tppS4) requires approximately 25 min to reach a steadystate signal, Co(tppS3N1) takes significantly longer (120 min) to reach the steady absorption profile. This period (120 min) matches with the induction period of Co(tppS3N1) under photocatalytic conditions in which no activity is observed (Figure S11).

It was then investigated if the induction period observed in photocatalysis can be accelerated/eliminated by priming the cocatalyst in the presence of AA. Therefore, the photocatalyst



Figure 5. Influence of (A) low light intensity, (B) low CO₂ concentration, and (C) O₂ on the photocatalytic CO₂ reduction activity in the presence of ZnSe-BF₄ QDs and various co-catalysts (600 min irradiation). CO selectivity is defined as n (CO)/(n (CO) + n (H₂)). 100% light intensity refers to 100 mW cm⁻². Conditions (if not otherwise stated): 0.5 μ M ZnSe-BF₄, 10 μ M co-catalyst, 0.1 M AA, pH 4.5 (Co(tppS3N1)), pH 5.5 (Ni(cycP) and Co(qpy)), AM 1.5G, 100 mW cm⁻², λ > 400 nm, CO₂ (4.0 sccm), 25 °C. Jitter was added for each data point manually for plots (B) and (C) for clarity and to avoid excessive overlap. Note: the sample ZnSelCo(tppS3N1) at 20% light intensity showed only marginal activity for both H₂ and CO (see the Supporting Information); hence, the CO selectivity constitutes a large standard error.

system was assembled and stirred in the dark in the presence of all components (Prime ZnSelCo(tppS3N1) with AA, Figure 4C, green trace) for 2 h before irradiation. A different sample consisted of only co-catalyst dissolved in AA solution (Prime only Co(tppS3N1) with AA, red trace, Figure 4C), which was left for 2 h prior to addition of ZnSe and irradiation. In comparison to the regular experiment (blue trace, Figure 4C), stirring the fully assembled catalyst system did not affect the induction period. However, when Co(tppS3N1) was prereduced in the presence of AA (and absence of ZnSe), the induction period vanished, and the hybrid catalyst showed an almost instant onset after addition of ZnSe followed by irradiation. This observation supports that the induction period originates from the slow initial reduction of Co^{III} to Co^{II}. It is also observed that there is no local maximum followed by a decrease/increase of the product evolution curves, compared to the samples that were not pre-reduced, which could be related to different types of Co species that initiate at various times

possibly related to a different coordination geometry of Co(tppS3N1) on ZnSe. It can therefore be concluded that Co(tppS3N1) exhibits a different redox behavior when it is in a unique chemical environment (immobilized on the QD surface) compared to when it freely diffuses in the bulk solution. Additionally, the in-depth detection and analysis of the induction period highlight the capabilities of the continuous-flow system with frequent, automated GC sampling.

Performance Evaluation. The external quantum efficiency (EQE) was exemplarily determined for the best-performing photocatalytic system, ZnSelCo(tppS3N1). At 1.5 mW cm⁻² and 400 nm monochromatic illumination, ZnSelCo(tppS3N1) achieved an EQE_{CO} of 5.1 \pm 0.5% (see the Experimental Section for details and Table S5, average over 4 h), which significantly exceeds the previous benchmark on ZnSe QDs (ZnSelNi(cycP), EQE_{CO} = 3.4 \pm 0.3%).¹⁹ The performance reported herein (TON_{co-cat} > 600, EQE_{CO} > 5%) obtained by hybrid ZnSelCo(tppS3N1) is among the highest within reported

colloidal photocatalyst systems that operate free of precious metals in aqueous solution.^{7,19,31} Additionally, the activity translates to a TON (CO) per QD (i.e., sensitizer, approximately 1100 Zn ions per QD) above 10⁴, which underscores the QDs as platform for CO₂ reduction and is in contrast to many homogeneous systems, which often employ much higher concentration of photosensitizer than co-catalyst.²⁰ A higher activity was reported for a mercaptopropionic acidmodified CdS nanocrystal in combination with a dinuclear cobalt catalyst, which reached a $\mathrm{TON}_{\mathrm{co-cat}}$ of 1380 (22 h) with an impressive CO selectivity of 95% in fully aqueous solution.⁷ However, the study did not report the EQE and the light intensity used during photocatalysis, which does not allow for a direct comparison. The Co(tppS4) analogue reached a TON_{co-cat} of 926 (EQE = 0.81%) in homogeneous aqueous solution although only in the presence of large quantities of a precious-metal $[Ru(2,2'-bipyridine)_3]^{2+}$ photosensitizer $(TON_{Ru} \sim 19)$.²⁰ Photosystems consisting of earth-abundant materials have reached high activities (TON_{co-cat} = 155, EQE > 4%) in organic solution, in particular the Co(quarterpyridine) (and its Fe analogue) when linked to mesoporous carbon nitride $(TON_{co-cat} = 500, EQE = 4\%)$.^{6,32} Higher performances have been achieved with precious-metal-based catalysts for CO2 photoreduction to formate. Anchoring a dinuclear Ru complex on Ag-loaded graphitic carbon nitride showed enhanced performance (TON > 2000, up to 98% selectivity, EQE = 0.2%) in water and a TON > 33 000 when organic solvents were used instead.4,33

Influence of Light Intensity, CO₂ Concentration, and Oxygen. The continuous-flow methodology for the photocatalytic experiments allows for the rapid study of different experimental conditions. Lowering the light intensity (I), i.e., changing the flux of available photons and, consequently, electrons generated, can impact the ratio of evolved H₂ vs CO, due to a delicate balance of charge separation/recombination kinetics and turnover rate of the co-catalyst. Lowering the light intensity for the diffusional assembly ZnSelCo(qpy) affects the activity of both proton and CO2 reduction, but CO is less affected than H_2 (Figure 5A, full data set in Figure S13). At a given time point (600 min), H_2 evolution is marginally below a near-linear trend (reduction) in activity, whereas CO deviates from this relation significantly, thus enhancing the overall CO selectivity from 7.9% (I = 100%) close to 5-fold to 39% (I =25%). Nevertheless, the $TON_{Co(qpy)}$ is not improved and saturates between TON < 70 (I = 100%) and TON < 40 (I =20%) (Figure S13). The anchored co-catalyst hybrid ZnSelNi(cycP) also exhibits enhanced CO selectivity, but less pronounced than Co(qpy). The activity at lower light intensities for both H₂ and CO is greatly diminished in the case of the electrostatic assembly ZnSelCo(tppS3N1), (non-primed). This is presumably related to its long induction period. The number of available electrons may not be sufficient to generate the active species within the time frame of this experiment. This finding indicates that the induction period (Co^{III} to Co^{II}) is facilitated by light and proceeds from photogenerated QDs and not from AA, when the co-catalyst is immobilized on the QD surface. This is in line with the experiments from priming the photocatalyst in the dark or in the presence of AA (and absence of QDs). The experiments above demonstrate that excess photogenerated electrons on ZnSe QDs are utilized toward the H₂ evolution reaction. Lowering the light intensity in the case of the weakly anchoring Ni(cycP) and diffusional Co(qpy) allows for higher

proportion of electrons to be transferred to the co-catalyst for CO_2 reduction rather than for competing H_2 evolution.

We then studied the ability of the QD-co-catalyst hybrids to operate under a stream of low concentration of CO₂ (20% in balance gas N₂, similar to flue gas; pH was kept constant in all experiments in regard to the optimized pH determined for each catalyst above) because the supply of concentrated CO_2 for the generation of solar fuels is an obstacle due to the energy costs associated with concentrating atmospheric levels of CO_2 (ca. 415 ppm).³⁴ H₂ evolution is effectively unaffected at 20% CO₂ (within experimental error), whereas the relative CO activity is drastically lowered to 26-38% (Figure 5B, full data set in Figure S14). The loss in CO activity (at 20% CO_2) suggests that the availability of CO₂ is limiting at this concentration. Although photocatalysts were reported to reduce CO₂ with only minimal loss in activity down to 10%,³⁵ those photocatalyst systems achieved this activity via insertion of CO_2 ("capture") into the metal-ligand bond of triethanolamine coordinated to a CO₂reducing Re metal center.

The effect of O₂ on performance is another interesting aspect in colloidal CO₂ photoreduction due to the long-term goal to couple CO₂ reduction with water oxidation (instead of using a sacrificial electron donor), which would produce O_2 as a side product or issues from real-world applications from leakage of atmospheric O_2 into the system.³⁶ This tolerance toward O_2 is particularly challenging because O2 can quench the photoexcited light absorber and photogenerated electrons and is therefore considered parasitic in most cases as it competes with CO_2 reduction. In particular, the formation of singlet O_2 is a feasible pathway and observed for most photosensitizers in the presence of molecular O2.37 Other reactive oxygen species include $O_2^{\bullet-}$ and H_2O_2 , resulting from O_2 reduction and may decompose components of the photocatalytic systems.³⁸ For all studied hybrid photocatalysts, the presence of O₂ led to a diminished photocatalytic activity (Figure 5C, the full data set can be found in Figure S15). While ZnSelCo(qpy) shows 30% relative CO activity in the presence of O₂, ZnSelNi(cycP) shows a reduction to approximately 11%. ZnSelCo(tppS3N1) does not exhibit any activity in the presence of O_2 . The instability of the porphyrin is presumably governed by the formation of singlet O_2 species, which can gradually decompose the molecular unit via a ring-opening pathway, as reported for Co-porphyrin analogues,^{39,40} although the latter catalyst family has also been shown to display some tolerance toward O2 in a different study.²⁰ For Co(qpy), H₂ evolution is suppressed more than CO₂ reduction, thereby enhancing the CO selectivity from 8% (anaerobic) to 16% in the presence of O_2 . For Ni(cycP), the CO selectivity remains unaffected by the presence of O₂. This observation may be explained by the diffusional nature of Co(qpy), which leaves the QD surface accessible for O_2 reduction from the ZnSe conduction band. Nevertheless, O₂ is detrimental to all photocatalyst systems studied here and is presumably related to the formation of reactive oxygen species.

CONCLUSIONS

A continuous-flow setup for CO_2 reduction photocatalysis was developed to study semiconductor-metal complex systems, which enables automated, high-frequency measurements of multiple samples in parallel while retaining a high sensitivity. The capabilities of the continuous-flow methodology were exemplified using a state-of-the-art light-absorbing platform based on ZnSe-BF₄ QDs, which was shown to drive a range of molecular co-catalysts based on Ni or Co for visible-light-driven

CO₂ reduction. The QDs were thereby able to supply photogenerated electrons to molecular co-catalysts that are either of diffusional nature, possess a phosphonate-anchoring group, or assemble on the surface through electrostatic interactions. The different anchoring strategies were compared and quantified with the electrostatic assembly leading to nearquantitative immobilization. A novel CO₂ reduction catalyst, a Co-tetraphenylporphyrin featuring three sulfonate groups and one amine group (Co(tppS3N1)), thereby exhibited the benchmark photocatalytic activity in combination with ZnSe-BF₄, evolving 18.6 μ mol of CO (79.7 mmol of CO g_{ZnSe}^{-1}) and reaching a TON_{Co} (CO) of 619 after 1000 min of irradiation with a CO selectivity of >40%. This photocatalytic activity is the highest obtained using ZnSe QDs and among the highest in colloidal photocatalytic CO2 reduction using earth-abundant materials in aqueous solution. The distinct induction period of this benchmark photocatalyst was assigned to slow $\mathrm{Co}^{^{1\!\mathrm{II}}}$ to $\mathrm{Co}^{^{\mathrm{II}}}$ reduction as a prerequisite to enter the catalytic cycle and could be accelerated by priming (pre-reducing the co-catalyst in AA solution in the dark). All photocatalyst systems were studied under low light intensities, low CO₂ concentration, and aerobic conditions, which was shown to affect the ratio of H₂ evolution vs CO formation. The screening method presented here allows for faster, more reliable, and accurate analysis of photocatalytic systems for aqueous CO₂ reduction and further demonstrates the underexplored potential of rationally assembled semiconductor-metal complex hybrids constructed from abundant elements for demanding photocatalytic transformations at high performance.

EXPERIMENTAL SECTION

Materials. Zinc stearate (purum, Sigma-Aldrich), octadecene (90% techn., Sigma-Aldrich), and selenium powder (99%, Sigma-Aldrich) for the ZnSe QD synthesis; L-ascorbic acid (99%, Sigma-Aldrich), trimethyloxonium tetrafluoroborate (\geq 97.0%, Sigma-Aldrich), and organic solvents were used as received. Anhydrous solvents were supplied from Acros Organics. All aqueous experimental solutions were prepared with ultrapure water (DI water; Milli-Q, 18.2 M Ω cm). ¹³CO₂ (>99 atom % ¹³C) was purchased from Sigma-Aldrich.

Physical Characterization. Powder X-ray diffraction was conducted using an X'Pert PRO by PANalytical BV instrument using Cu K_a irradiation. Transmission electron microscopy images were collected using a Thermo Scientific (FEI) Talos F200X G2 instrument, operating at an accelerating voltage of 200 kV. Samples were prepared by drop-casting a dilute QDsolution on holey-carbon-coated Cu grids followed by evaporation of the solvent. Gas-phase infrared spectra of the photoreactor headspace were recorded on a Thermo Scientific Nicolet iS50 FT-IR spectrometer in transmission mode. UV-vis spectra were recorded on an Agilent Cary 60 UV-vis spectrophotometer using quartz glass cuvettes (1 cm path length). ζ -Potential measurements of ZnSe-BF₄ (0.5 μ M, in water) were conducted using a Malvern Zetasizer Nano ZS90 instrument at 25°C. High-resolution mass spectra were recorded using a Thermo Scientific Orbitrap Classic mass spectrometer. Elemental analysis was carried out by the Microanalysis Service of the Yusuf Hamid Department of Chemistry, University of Cambridge, using an Exeter Analytical CE-440 Elemental Analyzer. Inductively coupled plasma optical emission spectroscopy was carried out by the Microanalysis Services, Yusuf Hamied Department of Chemistry, University of Cambridge, using a Thermo Scientific iCAP 7400 spectrometer. The

samples were digested in HNO_3 and diluted with ultrapure water to 1–10 ppm analyte. Blank samples of diluted HNO_3 were recorded as background. ¹H NMR spectra (to investigate the potential production of formate) were recorded on a Bruker 400 MHz Avance III HD Smart Probe Spectrometer with water pre-saturation (64 scans).

Synthesis and Characterization of ZnSe QDs. Ligand-free ZnSe-BF₄ QDs were prepared as reported previously.¹⁹ The mean particle size was determined from transmission electron microscopy images (d = 4.65 nm) and the particles feature a good visible-light absorption onset ($\lambda_{max} = 412$ nm). To calculate the QD concentration in the stock solution, the Zn²⁺ and Se²⁻ concentration determined by ion-coupled plasma optical emission spectroscopy was divided by the number of Zn atoms per QD based on the mean particle diameter and the bulk density of ZnSe (5.262 g cm⁻³). The full characterization of the QDs can be found in Figure S3.

Synthesis and Characterization of Molecular Cocatalysts. Ni(cycH) and Ni(cycP),^{41,42} Co(pcS4)⁴³ and Co(pcTMA4),²³ Ni(terpyS) and Ni(terpyP),³ and Co-(tppS4)²⁰ and Co(qpy)²¹ were prepared and characterized according to literature procedures.

Co(tppS3N1). The free base ligand, tppS3N1 (41.7 mg), was prepared as described in the literature^{44,45} and added to a 125 mL, three-neck flask containing 10 mL of methanol, and the resulting solution was stirred at 60 °C under nitrogen for 10 min. A solution of cobalt(II) acetate tetrahydrate (57.1 mg) in 5 mL of methanol and 15 mL of chloroform was then added, and the progress of the stirred reaction was monitored by thin-layer chromatography and UV-vis spectroscopy. After 8 h of reaction, the flask was opened to air and the solvent removed under reduced pressure with a rotatory evaporator, and the red solid residue was purified by column chromatography on silica gel (gradient of methanol and methanol/acetic acid (9:1) as eluent) to remove the excess Co salt. The crude product was then passed through an ion-exchange resin (Dowex 50W-X8, H⁺ form, 50-100 mesh), followed by filtration over Celite using MeOH $(3\times)$. The product was precipitated with an excess of acetonitrile and collected as a dark purple solid and dried in vacuo (yield 84%). Mass spectrometry (MS) (electrospray ionization (ESI), positive mode) (m/z) calcd for $[C_{44}H_{27}N_5O_9S_3Co]^{2+}$: 462.0157; found 462.0174. Elemental analysis for C44H26CoN5Na3O9S3·9H2O: C, 45.76; H, 3.84; N, 6.06; found: C, 45.67; H, 3.51; N, 5.81.

Sample Preparation for Photocatalysis. A ZnSe-BF₄ stock solution (64.1 μ M in dimethylformamide (DMF), 23.4 μ L) and a co-catalyst solution (5.0 mM in H₂O, typically 6 μ L) were added to a Pyrex glass photoreactor (Chromacol 10-SV, Fisher Scientific) containing a magnetic stirrer bar. The mixture was diluted with AA (0.1 M in water, pH adjusted to 4.5-6.5 with NaOH and NaHCO₃) to a total solution volume of 3 mL. Specifically, pH 4.5 (after saturating with CO_2) was achieved by adjusting the pH of the 0.1 M AA solution with NaOH to 4.5. A final pH of 5.5 (after saturating with CO₂) was achieved by adjusting the pH of the 0.1 M AA solution with NaOH to 6.5, which decreases to 5.5 upon purging with CO₂. A final pH of 6.5 was achieved by neutralizing the pH of the 0.1 M AA solution and adding 0.1 M NaHCO₃ buffer, which gives a pH of 6.5 upon saturation with CO₂. The photoreactor was then sealed with a rubber septum and pierced with two needles (inlet and outlet).

Constant-Flow Setup with Automated Product Quantification. The inlet of the photoreactor was connected to a MFC (Brooks GF040) supplying a stream of CO_2 (CP grade,

BOC, humidified with a water saturator) with a flow rate of 4.0 sccm. The flow rate at the GC outlet was verified prior to the experiment with an Alicat gas flow meter to avoid gas leakage. The outlet of the photoreactor was connected to a flow-selection valve controlled by a Shimadzu Tracera GC-2010 Plus GC for product quantification of the gaseous reaction products (see below). Six samples (two triplicates of identical conditions) were typically analyzed in parallel. Upon purging with a constant stream of CO2, the solution pH decreased to 5.5 due to saturation with CO₂ (pH 6.5 prior to purging) or remains at 4.5 (pH 4.5 prior to purging). The photoreactor was purged for a further 45 min in the dark and sampled via online GC quantification. The first two injections of each sample were used to determine a "background" peak, which was subtracted from further injections. The photoreactor was then placed in a water bath maintained at 25 °C, stirred, and irradiated by a solar light simulator (Newport Oriel, AM 1.5G, 100 mW cm⁻²). The six samples were evenly distributed within the light simulator to account for possible variations of the light intensity depending on the position in the simulator. UV irradiation was filtered with a 400 nm cutoff filter (UQG).

GC Setup. The Shimadzu Tracera GC-2010 Plus GC used a barrier discharge ionization detector, kept at 300 °C, and was equipped with a HayeSep D $(2 \text{ m} \times 1/8 \text{ in. OD} \times 2 \text{ mm ID}, 80/2 \text{ mm ID})$ 100 mesh, Analytical Columns) precolumn and an RT-Molsieve 5A (30 m \times 0.53 mm ID, Restek) main column to separate H₂, O₂, N₂, CH₄, and CO while preventing CO₂ and H₂O to reach the Molsieve column. He carrier gas (grade 5.0, BOC) was purified (HP2-220, VICI) prior to entering the GC. The column temperature was kept at 85 °C. The gaseous flow from the flow-selection valve was passed through a loop (volume 1.0 mL) and injected approximately every 4.25 min into the GC. Six samples were analyzed in parallel, with each individual sample being injected every 25.5 min. The GC calibration was performed with a known standard for H₂, CO, and CH₄ (2040 ppm H₂/2050 ppm CO/2050 ppm CH₄ in balance gas CO₂, BOC) by diluting the mixture with pure CO_2 .

Data Analytics. The data were processed and visualized using the statistical programming language R with the tidyverse library.^{46,47} First, the flow rates were corrected by subtracting a "background" peak obtained in the dark prior to irradiation (we noticed a marginal CO background peak depending on the residual amount of oxygen present in the sample stream—a feature of the gas chromatograph and not the sample). Second, the momentary product evolution rate (\dot{n}_{gas}) corresponding to each injection was calculated using the following formula.

$$\dot{n}_{\rm gas} = \frac{p \times \dot{V} \times \frac{\text{area GC}}{f_i}}{R T}$$

where *p* is the pressure in the photoreactor (ambient pressure, 101 325 Pa), \dot{V} is the flow rate (4.0 sccm), *R* is the universal gas constant, *T* is the temperature (298 K), and f_i is the response factor for each gas determined by the calibration procedure. Third, the total amount of evolved product was calculated using trapezoidal integration of the product evolution rates. The three independent replicates of identical conditions were averaged by calculating the mean and standard deviation over irradiation time and sample. For visual display, the actual values for each sample are plotted as transparent scatter, whereas the mean is represented as a continuous line. In addition, the standard deviation is visualized by the shaded area surrounding the mean where the transparency is proportional to the standard

deviation. Specifically, the calculated standard deviation is used to compute a Gaussian density for that standard deviation, plotting a cloud with the opacity proportional to the density. This appears as a vertical "cloud" of uncertainty.⁴⁸ The maximum of the uncertainty cloud is set to 1 standard deviation.

Isotopic Labeling Studies. For ¹³C isotopic labeling, photocatalysis experiments were performed as described above, but with accumulating products in the headspace under steady-state conditions and using ¹³CO₂ as the headspace gas. After 1000 min (16.7 h), the photoreactor headspace was transferred to an evacuated gas infrared cell (SpecAc, 10 cm path length, equipped with KBr windows) and a high-resolution gas-phase transmission spectrum was collected.

EQE Determination. Photocatalysis samples were prepared with a modified procedure using a flat-sided quartz cuvette (1 cm path length, airtight) as the photoreactor in batch mode. Co(tppS3N1) was first dissolved in AA solution (1.2 mL, 0.1 M, pH adjusted to 4.5). After 2 h, the ZnSe-BF₄ QD stock solution was added to give a 0.5 μ M concentration, and the sample was purged with CO₂ (containing 2% CH₄ as internal standard). The sample was preirradiated for 200 min with a solar light simulator to approach the highest activity. The cuvette was then purged again with CO₂/CH₄ (2%) and irradiated with monochromatic light ($\lambda = 400 \pm 5$ nm, A = 0.80 cm²) using an LOT Quantum Design MSH 300 monochromator. Aliquots of headspace gas were taken periodically and analyzed by gas chromatography. The EQE was calculated according to the formula

EQE (%) =
$$\frac{2n \times N_{\rm A} \times h \times c}{t_{\rm irr} \times \lambda \times I \times A} \times 100$$

where *n* is the amount of produced CO, N_A is Avogadro's constant, *h* is Planck's constant, *c* is the speed of light, t_{irr} is the irradiation time, λ is the irradiation wavelength, *I* is the irradiation intensity, and *A* is the irradiated area. The factor 2 in the numerator is used because two electrons (and consequently two photons) are required for the conversion of CO₂ to CO.

Electrochemical Characterization. CV was performed in a one-chamber electrochemical cell using a glassy carbon working electrode. The cell was assembled by placing the working electrode together with a Ag/AgCl reference and a Pt mesh counter electrode into a solution of the co-catalyst (1.0 mM) dissolved in 0.1 M aqueous NaClO₄ (1 mL total volume). (Note, NaClO₄ can be explosive, and care needs to be taken when handling it. A stock solution should never be left to dry.) The cell was sealed and purged with CO₂ for 15 min. CV scans were recorded at room temperature using a BioLogic VSP potentiostat with a scan rate of 100 mV s⁻¹. The potentials were converted from Ag/AgCl/KCl(sat'd) to normal hydrogen electrode (NHE) by adding +0.2 V.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c02921.

Results from prescreening of various molecular CO_2 reduction co-catalysts (Table S1); results of the photocatalytic CO_2 reduction experiments and photocatalytic control experiments (Tables S2 and S3); quantification of co-catalyst attachment (Table S4); external quantum efficiency determination (Table S5); calibration curve of the GC and raw gas chromatograms (Figure S1); continuous-flow photocatalysis method development (Figure S2); characterization of ZnSe-BF₄ QDs (Figure S3); overview of screened molecular co-catalysts (Figure S4); data processing and visualization for evolved CO (Figure S5); photocatalytic H₂ evolution (Figure S6); co-catalyst optimization (Figure S7); ¹³C isotopic labeling (Figure S8); co-catalyst attachment quantification (Figure S9); postcatalysis characterization (Figure S10); benchmarking the photocatalytic CO₂ reduction activity (Figure S11); CV scans (Figure S12); influence of light intensity on photocatalytic CO₂ reduction (Figure S13); influence of low CO₂ concentration on photocatalytic CO₂ reduction (Figure S13); influence of O₂ on photocatalytic CO₂ reduction (Figure S14); and influence of the presence of O₂ on photocatalytic CO₂ reduction (Figure S15) (PDF)

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Notes

The authors declare no competing financial interest.

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