Best Practices for Experiments and Reporting in Photocatalytic CO_2 Reduction

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Abstract

Visible light driven conversion of CO_2 to fuels and valuable compounds has experienced tremendous activity in recent years, aiming at storing solar energy into chemical bonds using CO_2 as a renewable feedstock, ultimately at massive scale. Despite these efforts, processes and catalytic systems are still at an early stage of development, with fundamental mechanistic challenges as pre-requisites for device design. In this context, collective efforts currently necessitate the exploration of a variety of approaches. On the other hand, an alignment of practices is required to ensure robustness, precision and accuracy of the results, as well as shared metrics and tools for advancing our understanding of the necessary processes. This perspective aims to provide guidelines and a framework toward these objectives.

Reduction of CO_2 to high value chemicals has the potential to become a technology that can significantly impact future generations and contribute to a net zero carbon economy. The field of electrochemical CO_2 reduction has already proposed the need for catalytic testing under realistic conditions that can be relevant for commercially viable applications.[1] In light-driven

CO_2 reduction, some reports have emerged where semiconductor-based photoelectrodes surpass the solar-to-chemical energy conversion efficiency of natural photosynthesis.[2] In addition, many researchers have pioneered solutions based on photocatalytic CO_2 reduction (e.g. suspension system) as valuable approaches in the last decade.[3,4] For the field to grow in a coherent and rational way, scientists must continue to conduct accurate and precise scientific procedures, to allow meaningful comparisons and to target a reliable and deployable technology. The large number of parameters involved for a single catalytic system in terms of reactor design, light source, reaction conditions and data analysis methods could indeed generate significant discrepancies in the reported performances. It is thus essential to follow common practice guidelines and to report results in a standardized format in order for the scientific community to interpret each other's advancement. In particular, the results and performances must allow the reader to understand the advances and the evolution of the field and to compare them with related technologies considering the various gaps of conditions from one study to another. While performing photocatalytic CO_2 reduction, great care must be taken reporting catalytic efficiencies, selectivities and the origin of the products. In this Perspective, we highlight the main points to be addressed as good practices to share procedures and metrics in the field. For this, it is divided into successive sections addressing the reactions conditions, the identification of reduction products and their origin, the definition of performance metrics and finally the mechanistic aspects.

Setups and protocols

It is essential for the researchers addressing photocatalytic CO_2 reduction to properly understand and deploy the experimental aspects such as the photochemical reactor, the light source and the reaction conditions and then to precisely report their characteristics for the benefit of understanding and comparison.

Photochemical reactor. Because photocatalytic CO_2 reduction is still at an early stage of fundamental development, with a large variety of systems, the quest for a standardized or universal photochemical reactor poses significant challenges. It is indeed the core component for photocatalytic CO_2 reduction, and the commonly employed ones are the gas-liquid and gas-solid cells (Fig. 1a and 1b).[5,6] As a consequence, articles should specify the characteristics of the reactor[7] (for example, by presenting a detailed scheme), the chassis' material composition, the vessel's geometry (square cuvette, cylinder, etc.) and dimensions (including light path length, since light may penetrate the whole reactor), the material of the irradiation window (optical grade glass, quartz, to insure the non-absorbance of the window itself), the introduction method of substrates (flow, preliminary saturation by bubbling, etc.) and product collection, and the running mode (closed batch reactor, single or two compartments, continuous flow, etc.) used for the reported photocatalytic reaction. Flow cells are increasingly employed since they allow continuous processing such as in-line gas quantification.[8]

Reactions conditions. The gaseous (so-called headspace) and liquid volumes of the reactor (on which the performance metrics calculations are closely related), the reaction temperature (with temperature control or not, since illumination commonly induces some heating which can modify reaction kinetics), and pressure must be specified. Special attention must be paid to the increase in solution/reaction media temperature caused by light irradiation (a proper

filtering of IR prevents this effect), especially because the solubility of CO_2 decreases with temperature increase. Researchers should also consider changes in pressure due to the accumulation of gaseous products, which may affect the reactivity through thermodynamic/ kinetic factors. In a typical two-component system, the amount of catalyst and photosensitizer introduced in the cell must be provided, having in mind that nanomolar concentrations of catalyst cast doubt on the reliability of performance metrics. For gas-liquid cell, the molar concentration of dissolved catalyst and photosensitizer or the mass amount of catalyst in suspension are suited. Finally, for gas-solid cell, the mass amount of the catalyst used (deposited on a surface or lying at the bottom of the cell) for the photocatalytic reaction is the common value. When a solid material is employed to support the catalyst, its geometry (porosity, nano-structure, geometric surface area, active surface area) should be described as precisely as possible. The amount of sacrificial electron donor (molar concentration or mass amount) must also be provided since it could constitute the limiting factor of the process, bearing in mind that we must ultimately develop processes free of sacrificial reagent. Finally, the amount of substrate, i.e. CO_2 itself, is needed to determine its conversion yield and to help deciphering the reaction kinetics.

Light source. Since the reaction rate and the energy conversion efficiency for the photocatalytic CO_2 reduction are sensitive to the photon flux and the photon energy (wavelength) distribution, the nature of the light source (Xenon lamp, solar simulator, light-emitting diode (LED), etc.) must be specified, as well as its spectrum, its intensity, and the presence or not of an optical filter (band-pass or cutoff, with the wavelength range). Proper calibration of the light source has to be made, through calibration cells or power meter to ensure a precise knowledge of the irradiation power reaching the sample. In that sense, the distance between the light source and the cell and the light intensity could be provided. For an in depth description of how to perform a light source calibration, one could refer to a recent report.[9] In studies related to solar fuels or sunlight induced processes, a standard illumination at AM 1.5 (1 Sun overall yearly average), corresponding to a light intensity of 100 mW cm^{-2}, is highly recommended as the reference illumination for the community and would allow comparison with photovoltaics. The use of a Xe lamp and LEDs with no appropriate filter or a Hg lamp is discouraged for this purpose since their spectral irradiance sometimes strongly differ from the solar one, even if such sources are still useful elsewhere. The photo-absorption properties (absorption spectra, extinction coefficients) of all components of the system (including the photosensitizer, the sacrificial electron donor/acceptor, any eventual co-substrate and the catalyst itself) are also indispensable to identify the main absorbing species. The energy distribution and intensity of photons are fundamental requirements for understanding the photochemical reaction of interest even if a proper stirring of the solution allows the photon energy to be spread to the whole solution. To illustrate this, Fig. 2 shows photoemission spectra of four typical light sources: a high-pressure Hg lamp (a), a Xe lamp (b), a Xe based solar simulator (c) and a white LED (d) which are becoming more and more popular, including in high grade (AAA or ABA class) solar simulators. The spectra of these conventional light sources are markedly different. Fig. 2(e) shows optical transmission spectra of a cutoff, a wide band-pass, and a narrow band-pass filter. Some white LEDs combine three central wavelengths to produce a white color corresponding to the distribution of human visual sensitivity, which varies depending on the purpose of the LEDs. In particular, the light intensity distribution at wavelengths longer than 500 nm differs greatly depending on the LED.

These variations of the light sources induce differences in the results of photocatalytic reactions so the measured spectra at the reactor is strongly required. More precisely, an expression utilizing energy in one mole of photons (a unit expressed as an einstein) per time unit is an essential metric to evaluate apparent/external/internal quantum efficiencies (see the Setting common performance metrics section). The measurement of the amount of light energy or light energy density reaching the testing vessel can be made by a power meter (before the irradiation window, after the cell), and photon flux inside the reaction cell can be estimated through chemical actinometry.[10] Note that in the case of a heterogeneous or a gas-solid system (Fig. 1), the measurement of the light energy after the cell can be strongly affected by the shielding effect of the particles, with a possible important impact on the apparent quantum yield estimation (see the Setting common performance metrics section). Importantly, the active exposed area of the semiconductor-based photoelectrode or of the photocatalytic material needs to be specified. Ideally, the illumination window corresponds with the irradiated region of the sample and there is no shadowing effect (i.e. a larger area of the semiconductor or of the active material is illuminated with respect to the one that is considered for calculating the photocurrent density). For measurements related to the active area and related issues, please consult the recent report from Alley and coauthors.[9] Finally, note that the illumination can be conducted from the top (as depicted in Fig.1) but also for the side and even from the inside (the source entering the vessel), even if the latter is less relevant in solar conversion.

Identifying the generated products

In this section, we describe the analytical techniques to detect and quantify both gaseous and liquid products from photocatalytic CO_2 reduction as well as to assert the nature and the origin of the carbon products.

Analytical tools. The analysis of CO_2 reduction processes requires careful product identification and quantification, and carbon source verification by rigorous gaseous, liquid and possibly solid phase analysis.[11] In addition, control experiments need to be reported to confirm the role of all components in the photocatalytic system. For example, the absence of CO_2, light, electron donor/acceptor, co-substrate, co-catalyst or absorbing species (i.e. photocatalyst or photosensitizer) should not generate a putative product from CO_2 reduction. Note that replacing an acidic CO_2-purged solution by an inert (typically Ar) atmosphere results in an increased pH value, the blank under inert atmosphere thus being slightly different from the reaction medium under CO_2, which could affect the performance of the catalytic system. Care should also be taken when using a sacrificial agent (which should ultimately be phased out) whose consumption, degradation and accumulation in the reaction medium can generate by-products (for example, highly reducing amine radicals formed upon oxidation of a sacrificial donor) which could interfere with the products of interest. Finally, for photocatalytic materials stability is a fundamental issue; tested photocatalytic materials should be sufficiently stable to allow for CO_2 reduction product detection.

Gas phase. Gaseous products such as CO, CH_4 and ethylene (C_2H_4) are common products from CO_2 reduction and can be readily detected alongside side-products such as H_2, the by-product O_2 from water splitting and N_2 from leaks by gas chromatography (GC) using

manual sampling (typically with syringe) or automated on-line gas analysis (Fig. 3). A proper separation of the peaks is required for a reliable quantification of individual compounds. A non-destructive and low-cost thermal conductivity detector (TCD) can be employed and the sensitivity for most products (e.g., CO and hydrocarbons) can be further enhanced by using a destructive flame ionization detector (FID, with a methanizer) or a dielectric-barrier discharge ionization detector (BID). Internal (or external) gas standards are employed for quantification by establishing a calibration curve within the concentration range of interest. We note that methane is often used as internal standard, which may prevent its detection as a product. GC can be coupled with mass spectrometry (MS, see The carbon origin of products section) for improved product identification. Online analysis with high sensitivity can be performed using membrane inlet mass spectrometry (MIMS).

Liquid phase. In addition to GC and GC-MS, ionic and liquid products such as formate, oxalate, methanol, ethanol and more complex derivatives can be analyzed by NMR (quantitative NMR requiring a proper calibration for relaxation times) via a solvent suppression method,[12] ion chromatography (IC), high performance liquid chromatograph (HPLC) and liquid chromatography coupled to mass spectrometry (LC-MS) as well as capillary electrophoresis (CE). Although gaseous products are commonly the main products, liquid-phase analysis should always be performed to rule out additional products dissolved in solution which would impact the process selectivity.

For all these techniques, the method employed (gas or liquid carrier, flow, type of column, oven temperature, etc.) must be provided as well as individual calibration curves covering the concentration range of products under investigation (in the supporting information). Baselines should also be set accurately to ensure a valid integration of the detected signal. In addition to the m/z peaks obtained by MS, fragmentation patterns are also characteristics of a given compound. The relative intensity of each m/z peak should unambiguously match the proper pattern to avoid any erroneous compound identification. Overall, these patterns must be shown (Fig. 3, inset) since they are strong pieces of evidence to assert the origin of the carbon atom in the observed products.

The knowledge of the detection limit is essential for all techniques to assess the suitability of the technique and the required concentration of catalyst. Product quantification near the limit of detection becomes less reliable and, importantly, exclusion control experiments less meaningful as even a small drop in performance results in the absence of product. Thus, the analytical techniques need to be regularly calibrated and detection limits determined (see Table 1).

Table 1 | Possible analytical techniques for typical CO_2 reduction products.

Compound	Phase	Techniques	Typical detection limit
CO, CH_4, C_2H_4, C_2H_6	(g)	GC, GC-MS	ppm to ppb depending on the detector
Formate, Oxalate, Acetate	(l)	IC, CE, NMR	micromolar

Formaldehyde	(l)	NMR GC-MS	micromolar ppm
Methanol, Ethanol	(l)	HPLC, NMR; GC-MS, LC-MS	micromolar ppm to ppb

GC: Gas Chromatography, GC-MS: Gas Chromatography-Mass Spectrometry, IC: Ionic Chromatography, CE: Capillary Electrophoresis, NMR: Nuclear Magnetic Resonance, HPLC: High-Performance Liquid Chromatography, LC-MS: Liquid Chromatography-Mass Spectrometry.

The carbon origin of the products. To determine the carbon origin of the photocatalytic products, isotope labeling experiments are mandatory and should receive careful attention. Coupling of GC analysis with MS allows for carbon source verification in the product. Experiments conducted under $^{13}CO_2$ should generate ^{13}C products at a comparable rate, which can be identified by their masses (m/z) in MS together with the corresponding typical fragmentation pattern (some soft ionization methods do not induce fragmentation for simple products) which is rarely provided in articles. If the electrons for CO_2 reduction come from water oxidation, $H_2{}^{18}O$ isotope labeling experiment could also be performed to confirm the formation of $^{18}O_2$. The main drawbacks are that GC-MS is quite costly, not always routinely available and can suffer from limitations of overlapping peaks such as ^{12}CO and N_2 (both m/z = 28) thus necessitating a proper separation of all products before the mass analysis.

In addition, nuclear magnetic resonance (NMR) spectroscopy should be employed to confirm that the liquid products originate from CO_2 reduction rather than the decomposition of the organic solvent, other substrates or the photocatalyst itself. For example, it has been shown that organic residues can be present at the surface of the photocatalyst and can then participate in the formation of CO over copper oxide promoted TiO_2 catalysts, as demonstrated by *in-situ* diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy.[14] The ^1H NMR signal of the CH_3 proton peak of methanol is a singlet for $^{12}CH_3OH$ (for ^{12}C, Spin (S) = 0) but is split into a doublet (for ^{13}C, S = 1/2) for $^{13}CH_3OH$,[15] the same behavior being observed with formate and formaldehyde (after derivatization).[16] ^{13}C NMR does not replace, but complements ^1H NMR spectroscopy as ^{13}C NMR spectra are less sensitive, often more challenging to quantify and characteristic peak splitting not observed (e.g., both ^{12}C (with 1.1% natural ^{13}C) and ^{13}C formate show a single peak (S = 0) at the same position in the proton-decoupled ^{13}C NMR spectra). Multi-^{13}C products show characteristic splitting in both ^1H and ^{13}C NMR spectroscopy, with ^{13}C-acetate showing a doublet of doublets and ^{13}C-ethanol a doublet of doublets of quartets and a doublet of doublets of triplets in the ^1H NMR spectrum.[17] The corresponding proton-decoupled ^{13}C NMR spectra show two doublets for both ethanol and acetate.

An alternative for carbon verification in the gas phase is analyzing the headspace by infrared

spectroscopy. Replacing $^{12}CO_2$ by $^{13}CO_2$ results in a red-shift (i.e., toward smaller wavenumber) due to an increased reduced mass of the ^{13}C product (e.g., the CO vibration is shifted from 2142 cm^{-1} to 2095 cm^{-1} from ^{12}CO to ^{13}CO)[18]. The shift in m/z in MS and in wavenumbers in IR spectroscopy therefore supports the origin of the product from the CO_2 substrate. Liquid phase NMR spectroscopy can also be employed for gaseous analytes, for example by transferring the reaction atmosphere into an NMR tube as demonstrated for ethane and ethylene in a deuterated benzene solution.[19]

Identifying the nature of the reactive species

In homogeneous systems using molecular components (photosensitizer, catalyst), molecular structures provide discrete light absorbers and single catalytic sites and can generally be identified with high accuracy through *in-situ* and *operando* spectroscopy. UV-Visible absorption spectroscopy provides a widespread tool to detect the appearance/disappearance of species, providing that their respective signatures do not overlap. It could be used for detecting intermediates such as one-electron-reduced species of photosensitizers and/or catalysts in the system giving insights for identifying mechanisms. In addition, laser flash spectroscopies provide another suitable set of techniques to determine possible reactive intermediates, their evolution and lifetime.[20] However, most homogeneous systems employ an excess amount of photosensitizer, which consequently dominates the absorption and thus prevents any identification of transients. X-ray absorption spectroscopy (XAS) is another powerful tool to determine the chemical state of an element, for example of the metal center of a molecular complex.[21] Cyclic voltammetry (CV) conducted in electrolyte solution with a dissolved catalyst is employed to determine the potential (in V) at which the catalysis occurs (increase in current) and thus to determine the redox active state of the complex.[22] CV can also be conducted on catalytic films.[23] Electrospray ionization-Mass spectrometry (ESI-MS) with or without HPLC can directly determine structure changes of ionic species such as ligand substitution and dimerization.[24] Additionally, special care must be taken to investigate the possible formation of metallic nanoparticles (NPs) from a molecular catalyst, especially when an induction period is observed during catalysis. In that case, the catalysis is no longer homogeneous and the catalyst is not the initially introduced compound (see Post catalysis analysis section).

In heterogeneous systems (such as inorganic semiconductors, functionalized or not with a molecular unit), the identification of the species, state, or site responsible for the catalysis is even more challenging.[25] Thus, even when an identical catalyst composition ratio is described, the amount, distribution, composition distribution, surface structure and defects in the bulk vary depending on the synthesis method, the particle size and the shaping of the material (deposited as films of various porosity and thickness, in suspension as single particle or aggregates) of the semiconductor particles.[26]

Finally, recent studies on photocatalytic CO_2 reduction have also reported hybrid systems[27] combining, through covalent or non-covalent interaction, a molecular catalyst (e.g., a metal complex or a biocatalyst[28]) and a solid support such as TiO_2,[18] dye-sensitized TiO_2,[29]

carbon nitride,[30] graphene related materials,[31] carbon dots, CdS,[32] ZnSe,[33] metal organic frameworks (MOFs)[34] and covalent organic frameworks (COFs)[35]. In these systems in which a positive synergy is expected between the two components,[36] the exact role of each should be clearly identified since bare solid materials could exhibit some catalytic properties even in the absence of a molecular unit, and in that case it may be considered as a co-catalyst for which the activity may be quantified too.

Post catalysis analysis. To help identifying the nature of the catalytic species as well as to evaluate the robustness of the system, post catalysis analysis is required. In particular, in some systems, the initial photocatalyst changes its structure in the early stages of the process and then actually works as a dark catalyst derived from the photocatalyst and/or the photosensitizer. A typical example is $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine), reported as a photocatalyst for CO_2 reduction whereas one bpy ligand detaches upon irradiation in the presence of an electron donor to give $[Ru(bpy)_2(solvent)_2]^{2+}$ that actually is the catalyst.[37] Another example is *fac*-$[Re(bpy)(CO)_3X]$ (X = Cl, Br) that does not work as a photocatalyst alone.[38] In homogeneous systems, changes in UV-Visible absorption spectra, in the cyclic voltammogram or in the ESI-MS signals may be tracked. To rule out the formation of NPs, the mercury poisoning (or mercury drop) test can be conducted to verify the change in performance of the catalytic system in the presence of Hg which would amalgamate with some metal NPs, even if some limitations exist, for example for palladium and platinum.[39] Dynamic light scattering (DLS)[40] and X-ray photoelectron spectroscopy (XPS) analysis of the solution are other techniques able to detect the presence of particles in the reaction media. In heterogeneous systems, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) imaging can provide useful information such as material dissolution or morphology changes, especially for nanoparticles and quantum dots. The comparison of X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma spectroscopy (ICP) data before and after catalysis, including ICP data for the electrolyte, can also reveal some modifications of the system.

Setting common performance metrics

The turnover frequency (TOF) and the turnover number (TON) are essential factors in qualifying catalytic performances, especially in homogeneous systems, thus they should always be reported for molecular catalysts. These metrics are more difficult to apply to heterogeneous catalysts and photoelectrodes, since the quantification of catalytically active sites is much more difficult. TOF and TON should be reported whenever possible also in these cases, especially when molecular catalysts are immobilized on a (photo)electrode or photocatalyst surface.

Turnover number. The TON (equation (1)) is defined as the amount of a given product to the amount of (active) catalyst. Since it is generally not possible to determine the precise amount of active catalyst during the reaction, the amount of introduced catalyst is generally employed to provide a conservative estimate. To be meaningful, we recommend that the TON should be reported at the point at which catalytic production stops, i.e., at the time (to indicate) when the generation of a given product reaches a plateau. Reporting TONs for an arbitrary period (for practical reasons) is relatively less useful since the number cannot be used to compare to other

approaches. TONs obtained at the plateau time are thus an indication of photocatalyst durability too.

(1)

In some cases, high TONs have been reported based on very low concentration of catalyst (nM range), leading to a very low absolute yield of CO_2 reduction products. In such cases, not only the real nature of the catalyst becomes doubtful but also performances may be overestimated or simply optimized toward a single metric that is not relevant for device performance.

Note that many studies employing a mixture of a photosensitizer (generally in excess) and a catalyst express TON only in terms of the amount of catalyst. Moreover, employed conditions should be meaningful rather than optimizing a single performance metric such as catalyst TON or turnover frequency (i.e. a vast excess of sensitizer with ultra-dilute catalyst) which is discussed below. However, photosensitizers indeed absorb photons during photocatalytic reaction so TON values related to the sensitizer/catalyst ratio are also critical and should be additionally described in the literature, since it also indicates the durability of photocatalytic reactions.

Turnover frequency. The TOF (equation (2)) is defined as the TON divided by the time over which the TON was determined, and it indicates the photocatalysis rate. Since irradiation times are highly variable, the reported TOF generally is a mean TOF not considering its variation along the process (generally high at the beginning and going lower with time). Some studies reported the TOF_0 or initial TOF, defined as the slope of the product formation starting at t_0, i.e., at maximum rate. Because photon absorption is the rate limiting step for many photocatalytic reactions, TOF depends on the intensity of irradiated light. Therefore, when comparing the TOF values for different reaction conditions, light intensity should be taken into consideration. In particular, evaluation of the TOF response to the irradiation conditions can provide valuable information on the photocatalytic regime.

(2)

Selectivity. Product or catalytic selectivity (CS, equation (3)) is defined as the ratio of the amount of a target product to the sum of amounts of all the products. As a prominent example, the photocatalytic CO_2 reduction reaction frequently competes with the H_2 evolution reaction since a proton source (even traces of water) are present in the reaction medium.

(3)

Product selectivity depends on a variety of factors, from catalyst structure to co-reactants and the stability of intermediates as well as on secondary sphere interactions.[41] Efficiency metrics and selectivity for each product should always be reported with corresponding error bars. The number of repetitions (minimum 3) of the measurements and the deviation from the average, illustrating reproducibility, must be-reported. It is particularly sensitive when the amount of catalyst is low and when the absolute amount of generated product is low.

Quantum yields and energy-conversion efficiency. The quantum yield (QY, equation (4)) - or internal quantum yield (IQY) - is the ratio of the number of electrons used to produce a mol amount of product to the mol amount of absorbed photons (i.e. number of Einstein, see the Light Source section) by the photocatalyst. Apparent quantum yield (AQY, equation (5)) - or external quantum yield (EQY) - is the ratio of the number of photogenerated charge carriers

(i.e., electrons) used to produce a mol amount of product to the mol amount of incident photons to the photocatalyst and is commonly used when the mol number of absorbed photons cannot be precisely determined. It is sometimes called external quantum yield.

(4)

(5)

In both definitions, the number of electrons is employed assuming that they are generated by light absorption. In many systems employing sacrificial electron donor (such as BIH and TEOA)[42], two electrons can be generated from one photon absorption, so in that case the number of electrons should not be used. Since the number of photogenerated electrons per product is generally difficult to determine, we recommend that the mol number of product is used instead of mol number of product × number of photogenerated electrons per product if the number of photogenerated electrons per product is not experimentally clarified, and the definition of QY used in the paper should be clearly described in the experimental section. These quantum yields are essential for scientific discussions. Among them, the AQY is considered significant, especially toward a reactor design and setup for practical uses. Solar-to-chemical (or solar-to-fuel) conversion efficiency, the ratio of solar energy stored in the products from full-spectrum solar energy, is a more significant parameter for technological deployment. The AQY, which can be evaluated by assuming all photons with an energy that photocatalysts can absorb by multiple reflections of light in a reactor, is one reasonable metric to assess. The use of monochromatic light (e.g. photons of a given energy) is required to properly determine the quantum yield whereas commonly used light sources are polychromatic (e.g. solar simulators, but also LEDs which are not monochromatic). Moreover, in most systems, the exact energy of useful photons is not known so quantum yields determination based on polychromatic light are only a crude estimation. Finally, it is essential to be aware that the photocatalytic reaction rate is also dependent on the light intensity. Conditions of adequately low-intensity light tends to result in high quantum efficiency. At the same time, excess light intensity (amount of photons) causes a reduction in photocatalytic reaction rate, for example by increasing charge recombination in the bulk of semiconductor particles.

While the previous metrics are essential for fundamental studies and for the characterization of a catalytic system, solar-to-chemical conversion (SCC) or solar-to-fuel efficiency (SFE) is meaningful when coming to devices not involving a sacrificial agent, such examples still being rare.[43] The general expression for the energy-conversion efficiency is the ratio of the total output power (i.e., chemical energy) divided by the total input power (i.e., solar energy). Various factors must be taken into account when determining this efficiency such as the energy density of the product(s), the application of an electrical bias (electrical power input), the coupling of a photovoltaic unit to an electrochemical one (PV-EC approach)[44] in which the product formation derives from a photovoltage (possibly with a complementary applied potential), etc.

Deciphering mechanisms

Mechanistic studies for light driven CO_2 reduction can be split into two equally important regimes, (i) Firstly, the photogeneration of the catalytically active state and secondly, the fate of that active state. Each require advanced characterization methods (see Identifying the

generated products section) to ensure that the proposed mechanisms are based on reliable observable data. A major complication here is the wide timescale over which these two regimes occur, typically from the femtosecond timescale (for the initial photoinduced events) to seconds for the following catalytic process steps. Additionally, these component events are critically dependent on the exact composition of the photoactive part of the system and of the catalyst, and how they are interacting. The wide breadth of approaches in the field encompasses, among others, independent homogeneously dissolved photosensitizers and catalysts (one single molecule sometimes playing both roles), molecularly-tethered photosensitizers and catalysts (e.g., molecular dyads, supramolecular assemblies, MOFs and COFs), and semiconductors decorated with NPs and/or molecules (where any component could be the photoactive or catalytic species). Each of these systems requires a unique lens for mechanistic studies and the techniques available to each may vary drastically. Thus, there are few benchmark studies that are consistently carried out by researchers. However, we may identify common guidelines to select appropriate tools and experiments.

The photochemical step(s). Photoexcitation is an ultrafast event and mechanistic investigations of the photoreduction of CO_2 benefit therefore from pulsed laser measurements such as transient absorption (TA, fs to ?s scale) spectroscopy,[45] transient IR spectroscopy,[46] transient electron paramagnetic resonance (EPR) spectroscopy[47] and transient Raman spectroscopy.[48] With advances in instrument design, these techniques are finding a broader range of users. However, common pitfalls need to be considered. First, if the transient signal does not return to baseline after a laser pulse (or several laser pulses), it is likely that one component of the photoactivated system is not stable and calls into question as to whether or not the ensuing photoproduct is important to observe reactivity. The initial and final (after laser excitation) states should be monitored, e.g., with steady-state UV-Visible spectroscopy, and any minor changes carefully considered. Second, for heterogeneous approaches, a major concern is the scattering nature of the materials. Scattered light can often resemble spectra expected for photo-processes and therefore, extreme care must be taken to ensure proper dispersion and particle size control such that one is measuring a true signal. The scatter phenomenon is particularly relevant for approaches where broad spectral losses are expected for the photogenerated state. One method to help with scattering is to focus the laser on a probe area as small as possible. Of course, concerns over the bulk vs. localized nature of the measurement requires the demonstration of consistency over independently prepared samples. Third, for certain techniques, the interpretation of the data requires standards. TA spectroscopy is widely used to demonstrate the existence of the long-lived charge separated states implicated in CO_2 reduction. However, to unequivocally identify charge separated states, standard spectra of the expected oxidized and reduced species must be used to model the transient data. Spectroelectrochemistry can be used to determine spectra for oxidized and reduced species, but if these species are reactive or unstable, it may be difficult to obtain the individual spectra of these species. Additionally, the extinction coefficient for one partner in the charge separated state may be small in the probed spectral region, leading to the assumption that observation of the other partner implies the generation of the charged separated state. Such assumptions are problematic. Fourth, one transient technique (or sometimes multiple transient techniques) cannot always unequivocally determine the mechanism of charge-separated state formation since different pathways result in the same or similar-looking final species. Energy transfer and electron transfer between two molecular species can appear indistinguishable under certain conditions. Oxidative and reductive

quenching of excited states can also be hard to identify, especially if both donor and acceptor are photoactive in the same spectral region. The measurements discussed above have limitations. Each laser pulse induces a very small change in the system and thus, signal averaging over many laser pulses is necessary for appropriate signal-to-noise in the resultant data. Therefore, the system must re-set (or return to the state prior to the laser pulse) within the period between laser pulses. If the system does not re-set, the baseline of each measurement is different, and averaging is near impossible. System reset can often be ensured by allowing recombination of the charge separated state. However, this ultimately means that pulsed laser measurements are rarely carried out under the exact same conditions as catalysis. To elaborate further, many photochemical CO_2 reduction studies are conducted using sacrificial electron donors which are responsible for donating an electron to the photoactivated species. The result is the formation of a purely reduced catalyst that lives much longer and, in turn, drives reactivity. In most circumstances, the purely reduced state is incredibly long-lived even in the presence of CO_2, and generation of the state would result in the aforementioned problematic baseline shift.

The catalytic step(s). The prior discussion leads us to the conclusion that the reduction of CO_2 is the slow step (comparatively). The time scale for catalysis necessitates a completely different approach to mechanistic studies. In the determination of catalytic mechanism, researchers often attempt to isolate stable intermediate species *in situ*, which may also be generated off-cycle. The reactivity of these intermediate species can then be confirmed through independent experiments. For example, if one can generate the hydride of a known catalyst, then addition of CO_2 to the isolated hydride and the observed reactivity can support an operative CO_2 insertion mechanism. In contrast, lack of reactivity indicates insufficient hydricity for the hydride to reduce CO_2 through such a mechanism. Both methods, independent or *in situ* isolation and subsequent characterization are demanding tasks, especially considering the reactive nature of the intermediates. Often, this approach can lead to a more complicated picture than initially expected. For example, isolable-species during the reactivity of $Re(CO)_3(bpy)X$ (bpy = 2,2′-bipyridine, X = halide or solvent) reveal a CO_2 bridged Re dimer and there is still controversy as to the role such a species could display in catalysis.[49] There is a broad literature in the electrochemical study of CO_2 reduction catalysts and researchers often refer to it for insights into photochemical reactivity. Care should be taken when making connections across these two fields. Under electrochemical conditions potential gradients are established that are not present in photochemical approaches. Indeed, the gradients established under electrochemical potential impact the configuration of catalyst at surfaces,[50] and the ions present within the double layer are thought to stabilize critical intermediates[51] and concentrate reactive species.[52] For photochemical reactivity, the additional complication of external compounds (sacrificial donor, Lewis or Bronsted acid or base) cannot be ignored since they all can play various independent roles in the mechanism of CO_2 reduction.[53] Note that theoretical calculations are often conducted in support of the measurements.

Concluding remarks

The creativity exerted by chemists to activate and catalytically convert CO_2 to fuels and

various compounds with visible light as main (if not exclusive) energy source has led to fast progress at lab scale. However, due to the complexity of the multi-component catalytic systems driving the reactions and the multiple photophysical, photochemical and chemical elementary steps jointly controlling the efficiency and rate, mechanistic understanding remains limited, even for the most studied CO_2-to-CO conversion processes. This understanding requires not only patience and rigor, but also shared practices in reporting results and describing set up and reactors, in assessing performances and ensuring reproducibility, and finally in deploying spectroscopic and analytical tools to contribute to mechanistic investigation (Fig. 4). Such a Perspective will not only strengthen our community in terms of ensuring a robust and trustable set of knowledge and rational optimization of processes, but it may ultimately lead to scientific breakthroughs that will be necessary for designing efficient and scalable devices.

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Authors contributions

J.B. and M.R. built up the article based on the contribution of all the authors who also contributed to the discussion, reviewing and editing of the manuscript.

Competing interests

The authors declare no competing interests.

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Figures captions

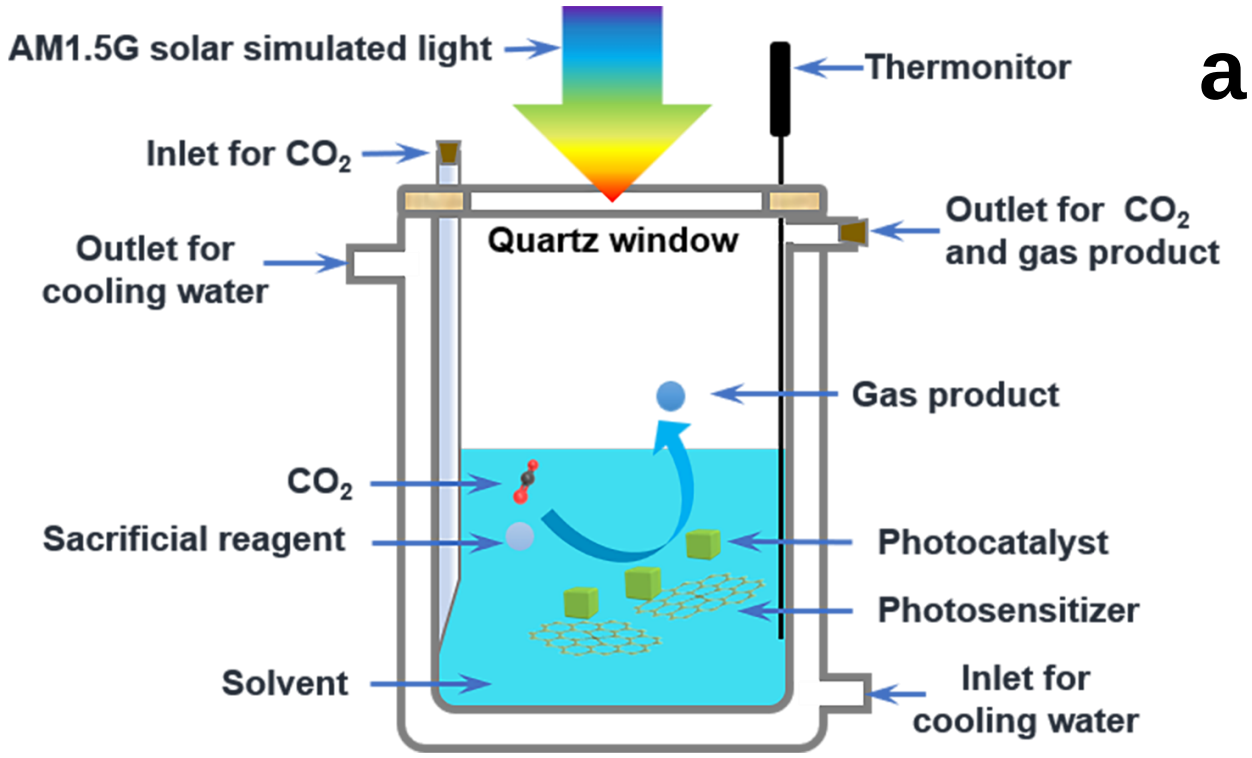
Fig. 1 | Scheme of a typical photochemical reactor. (a) gas-liquid system in which the photocatalyst and the photosensitizer can be both in homogeneous and/or in heterogeneous phase, the sacrificial reagent (electron donor) being homogeneous. (b) gas-solid system in

which both photosensitizer and photocatalyst are lying at the bottom of the vessel.

Fig. 2 | Emission spectra of various light sources. (a) high-pressure mercury lamp, (b) xenon lamp, (c) solar simulator, (d) light-emitting diode (white light of 3-peak type) and (e) optical filters: wide-bandpass filter (390-800 nm), narrow-band pass filter (centered at 555 nm), and short wavelength cutoff filter (Hoya L42, 420 nm threshold).

Fig. 3 | Typical gas chromatogram and mass spectra of gaseous products from CO_2 reduction. (a) gas chromatogram of a mixture of H_2, O_2, N_2, CO and CH_4 obtained in a photochemical experiment with $^{13}CO_2$ as the substrate. (b) fragmentation pattern of the mass spectra obtained on the blue $^{13}CH_4$ peak asserting the identity of the species.

Fig. 4 | Flowchart for properly conducting light-driven CO_2 catalytic reduction. Main steps to be performed and reported in photocatalytic CO_2 reduction studies. LED, light-emitting diode; T, temperature; P, pressure; GC, gas chromatography; GC-MS, gas chromatography-mass spectrometry; NMR, nuclear magnetic resonance; HPLC, high performance liquid chromatography; TON, turnover number; TOF, turnover frequency.


AM1.5G solar simulated light
Thermonitor
a
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Outlet for CO_2 and gas product
Quartz window
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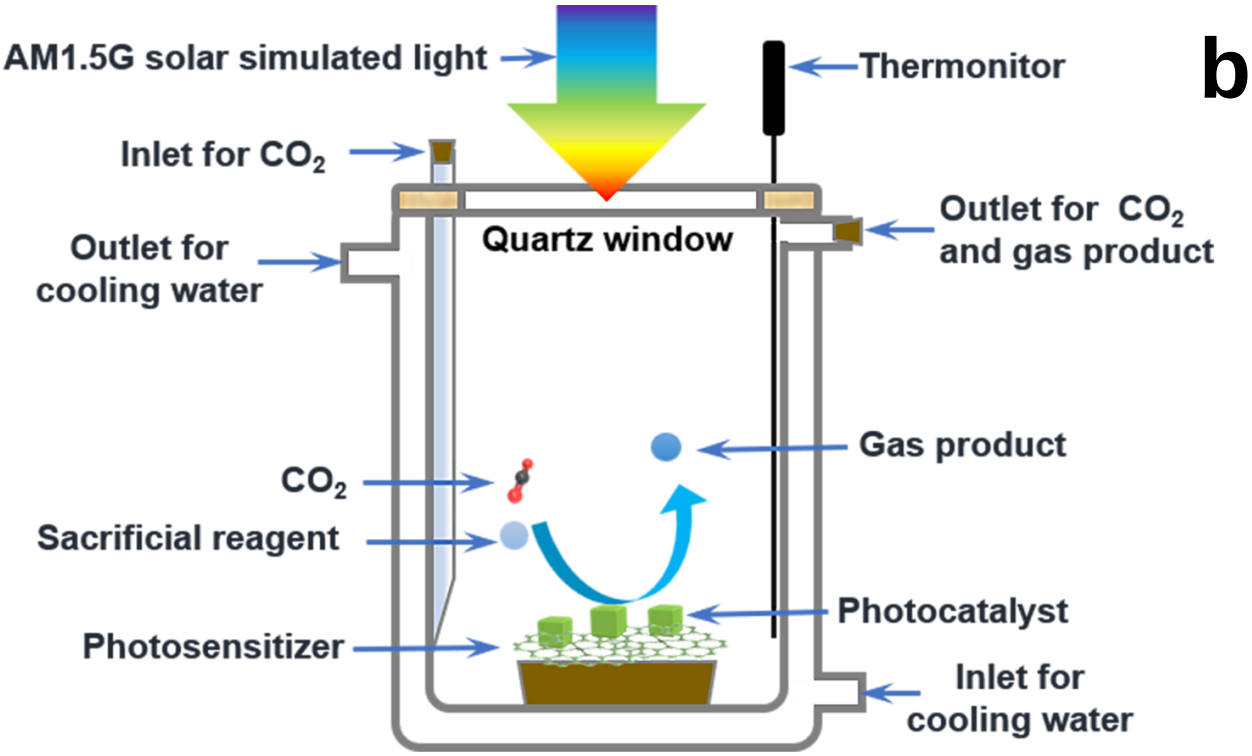
Gas product
CO_2
Sacrificial reagent
Photocatalyst
Photosensitizer
Solvent
Inlet for cooling water


AM1.5G solar simulated light
Thermonitor
b
Inlet for CO_2
Outlet for CO_2 and gas product
Quartz window
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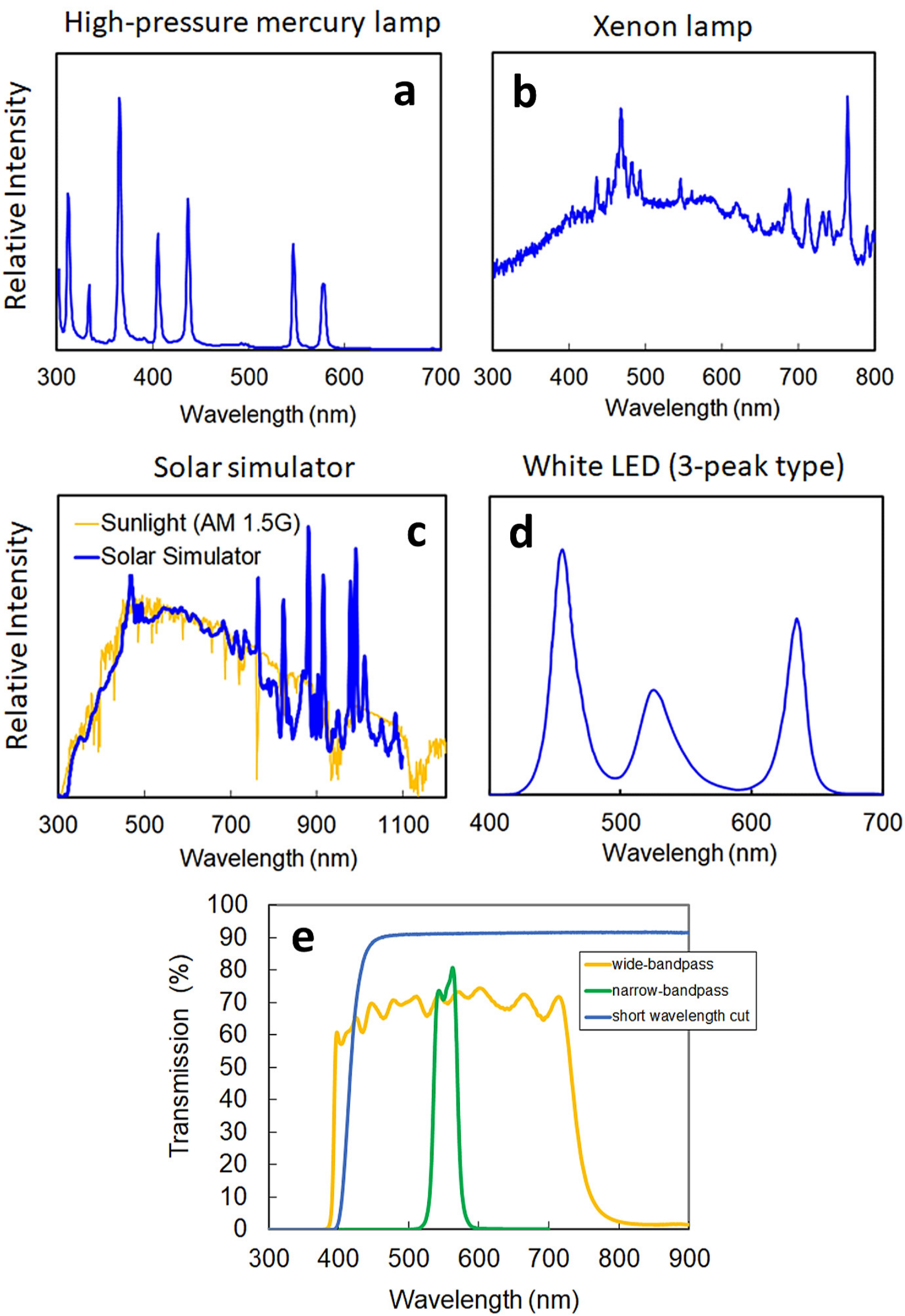
Gas product
CO_2
Sacrificial reagent
Photocatalyst
Photosensitizer
Inlet for cooling water


High-pressure mercury lamp
a
Relative Intensity
300
400
500
600
700
Wavelength (nm)
Xenon lamp
b
300
400
500
600
700
800
Wavelength (nm)
Solar simulator
Sunlight (AM 1.5G)
Solar Simulator
c
Relative Intensity
300
500
700
900
1100
Wavelength (nm)
White LED (3-peak type)
d
400
500
600
700
Wavelengh (nm)
e
Transmission (%)
100
90
80
70
60
50
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30
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10
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wide-bandpass
narrow-bandpass
short wavelength cut
300
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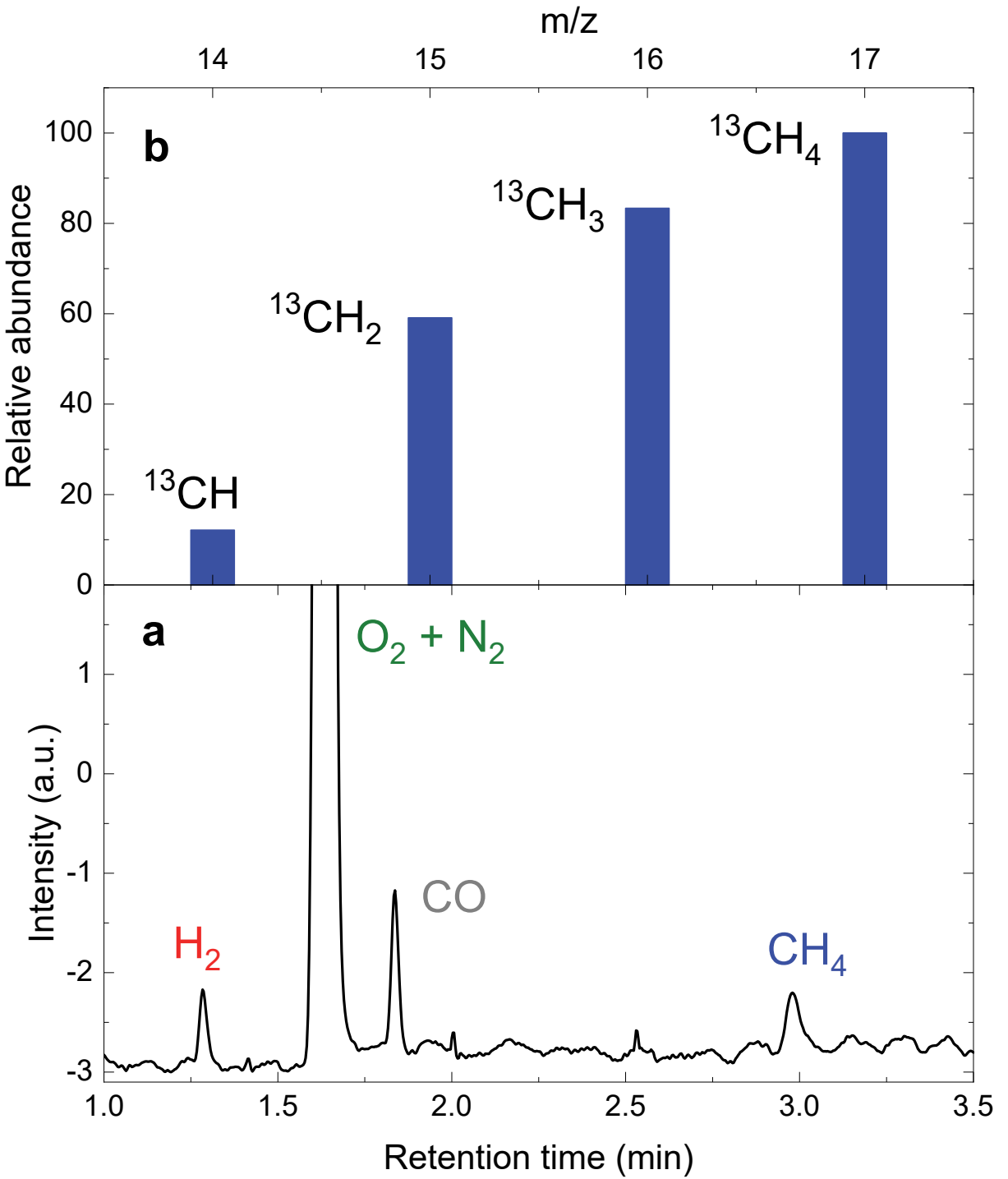
Wavelength (nm)


m/z
14
15
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b
Relative abundance
100
80
60
40
20
0
^{13}CH
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$^{13}CH_4$
a
Intensity (a.u.)
1
0
-1
-2
-3
$O_2 + N_2$
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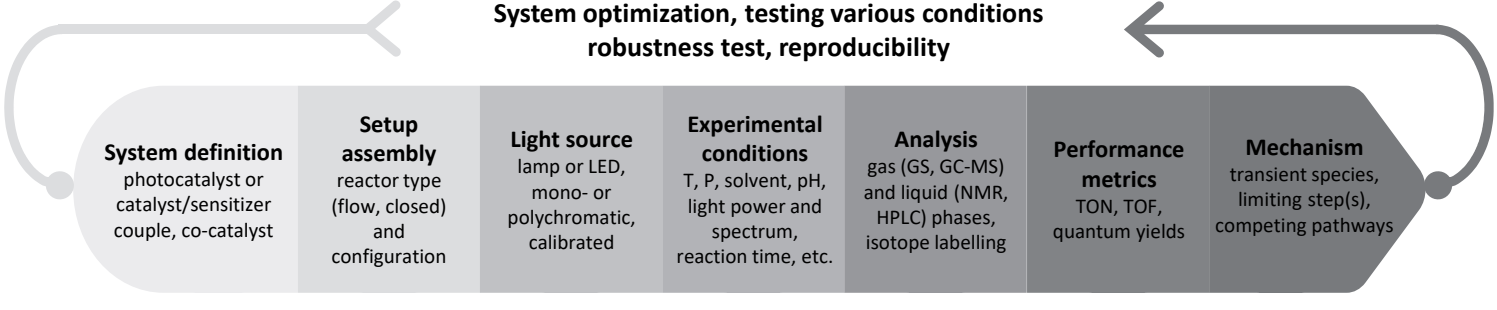
Retention time (min)


System optimization, testing various conditions
robustness test, reproducibility
System definition
photocatalyst or catalyst/sensitizer couple, co-catalyst
Setup assembly
reactor type (flow, closed) and configuration
Light source
lamp or LED, mono- or polychromatic, calibrated
Experimental conditions
T, P, solvent, pH, light power and spectrum, reaction time, etc.
Analysis
gas (GS, GC-MS) and liquid (NMR, HPLC) phases, isotope labelling
Performance metrics
TON, TOF, quantum yields
Mechanism
transient species, limiting step(s), competing pathways