Conference paper

Juan C. Scaiano* and Anabel E. Lanterna*

A green road map for heterogeneous photocatalysis

https://doi.org/10.1515/pac-2019-0207

Abstract: In the new millennium the well-established paradigms of organic photochemistry have come alive as the basis for a wide range of synthetic methodologies that take advantage of the enhanced redox properties of excited states. While many strategies have been developed using rare, expensive and non-reusable catalysts, the road forward should include catalysts based on more abundant elements and reusable materials. This green road leads to the exploration of heterogeneous systems that can be eventually adapted for flow photocatalysis, and also adopted for the solution of environmental problems such as water treatment and fuel generation using solar radiation. If heterogeneous photocatalysis can play a role in supplying solutions to drug synthesis, energy and potable water supplies, then photochemistry will have an unprecedented societal impact.

Keywords: heterogeneous catalysis; ICPOC-24; photochemistry; photoredox catalysis.

Introduction

The new millennium has seen a dramatic surge in photocatalysis studies with significant emphasis on photoredox catalysis, where electronically excited states undergo electron transfer reactions more rapidly, efficiently and under milder conditions than the corresponding ground states. In the last decade there are numerous examples that elegantly demonstrate how the well-established paradigms of photochemistry, free radical chemistry and catalysis can be combined in remarkable ways for the efficient synthesis of organic molecules [1–5]. Some of these developed new catalytic pathways for old reactions, now performed under milder conditions with increased yields and selectivity, while others have discovered new reactions with broad scope and versatility. The majority of these novel strategies use visible light along with catalysts based on non-recoverable, expensive and sometimes toxic transition metal complexes, frequently based on Ruthenium or Iridium. These photocatalysts have great photoredox properties as they are good electron donors and electron acceptors when they are photoexcited. It is important to highlight that this is not particular for transition metal complexes, but it is a common property of any diamagnetic molecule [6]. Hence, the excited states of diamagnetic molecules are always better electron donors and better electron acceptors than the corresponding ground state, something that is at the root of all excited state electron transfer theories. This can be extended to semiconductors, where HOMO and LUMO are replaced by Valence Band (VB) and Conduction Band (CB), but the concepts that relate to enhanced redox properties remain much the same.

Article note: A collection of invited papers based on presentations at the 24th IUPAC International Conference on Physical Organic Chemistry (ICPOC 24) held in Faro, Portugal, 1–6 July 2018.

***Corresponding authors: Juan C. Scaiano and Anabel E. Lanterna:** Department of Chemistry and Biomolecular Science, Centre for Advanced Materials Research (CAMaR), University of Ottawa, 10 Marie Curie, Ottawa, ON K1N 6N5, Canada, e-mail: titoscaiano@mac.com (J. C. Scaiano); anabel.lanterna@icloud.com (A. E. Lanterna)

An example, where a singlet excited state (D*) behaves as an electron donor – where A is an electron acceptor – is shown in eq. 1.

$$D^{*} + A \rightarrow D^{+\bullet} + A^{-\bullet} \tag{1}$$

For this schematic reaction, the free energy changes for the ground and excited states (ΔG_{eT} and ΔG^{*}_{eT}) are given by eqs. 2 and 3, respectively. Equation 3 is known as the Rehm–Weller equation recognizing their landmark contribution on electron transfer [7].

$$\Delta G_{eT} = E^{0}(D^{\bullet+}/D) - E^{0}(A/A^{\bullet-}) - \boldsymbol{\alpha}\mathbf{e}^{2}/\varepsilon r \tag{2}$$

$$\Delta G^{*}_{eT} = E^{0}(D^{\bullet+}/D) - E^{0}(A/A^{\bullet-}) - E_{S} - \boldsymbol{\alpha}\mathbf{e}^{2}/\varepsilon r \tag{3}$$

where the E^0 values are the electrochemical potentials, E_S is the excited state energy and $\boldsymbol{\alpha}\mathbf{e}^2/\varepsilon r$ is the Coulombic interaction between the ions formed in eq. 1. The last term is frequently negligible, particularly in polar media. In this case the electron donor ability of D* has been enhanced by exactly the value of E_S. Similar equations can be written when the excited state is the acceptor (A*) and for the triplet state (E_T).

The remarkable successes of photocatalysis mentioned above are usually accompanied by shortcomings which, in some cases, defy the values of green chemistry practices. This includes the one-time use of metals with extremely low earth-abundance, expensive, frequently toxic and in many cases requiring long irradiation times. However, these materials can be replaced by earth-abundant elements, and/or using heterogeneous materials that are easily removable and reusable, possess high quantum yields, are compatible with flow photochemistry [8, 9] and can operate at long wavelengths, long enough to avoid product photochemistry.

Our imaginary "road map" mentioned in the title of this contribution (Fig. 1) starts with homogeneous photocatalysis, a field that has plenty of room for advances. Starting from replacing transition metal catalysts for some of the many less expensive organic dyes [10–14] that have reduced toxicity or no toxicity at all; to changing to heterogenous systems, where separation and reuse are possible. Although separation is usually trivial, the latter is not necessarily easy to achieve [15]. Additionally, it is important to highlight that the conventional classification between homogeneous and heterogeneous systems is not always clear-cut in the field of catalysis, where intermediate situations are also plausible [16]. In these cases, it is important to use more

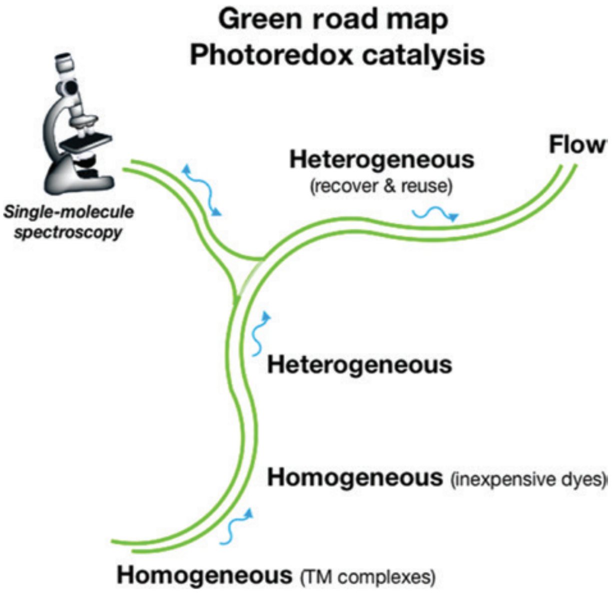


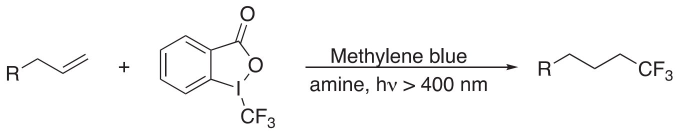
Fig. 1: Suggested green road map for photoredox catalysis.

sophisticated techniques to better describe the catalytic mechanism at the molecular level. We have shown before that single molecule spectroscopy (SMS) techniques can address these concerns and help improve the reactions at the bench level [17, 18]. Finally, the road map ends in flow photocatalysis, the real goal – and essential for environmental applications – presents challenges relating to light penetration, catalyst longevity and its recovery. Despite all this, heterogeneous flow photocatalysis is anticipated to be a major advance. Of course, catalyst powders that can be readily used for batch catalysis are not useful for flow systems, as the catalyst bed must be mechanically stable as the conversion of reagents to products takes place.

This contribution has a disproportionate number of references to University of Ottawa research and reflects this opportunity of highlighting our own work. We recognize that many other have made contributions that in many cases exceed our modest role in this field.

Results and discussion

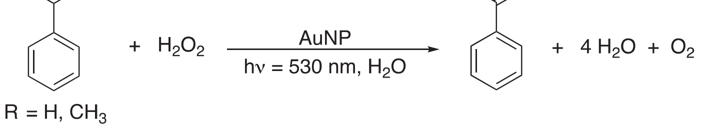
Numerous photoredox catalytic reactions make use of a sacrificial electron donor (SED), frequently a trialkylamine. The fate of the SED-derived radicals was usually ignored, although as we demonstrated [19, 20] they are frequently better electron donors than the acknowledged participants in the redox cycle. This observation, and the understanding that the enhancement of redox properties upon excitation is a very general phenomenon, led us to explore some common organic dyes. In particular, methylene blue (reaction 4) proved to be an inexpensive, readily available substitute for common transition metal complexes [21]. We have also published a database containing the redox and excited state properties of common organic photosensitizers [22]. The concept has been explored by several other groups, and in particular Nicewicz has developed some amazing photoredox catalysts [14, 23]. Nevertheless, in the green road map it is necessary to develop materials that can be used in heterogeneous media, facilitating the recovery and, sometimes, the reuse of the catalysts. Moving forward, we have looked for catalytic processes, normally performed in homogeneous systems, that could be adapted to heterogeneous catalysis, frequently, but not necessarily, photochemical processes. Oxidations, reductions and C–C couplings have been frequent choices, a reflection of their prominent role in organic chemistry and drug development. The following sections deal with the transition from homogeneous to heterogeneous catalysis, with special emphasis on the use of metal oxide semiconductors, up to current efforts to develop photocatalytic flow systems.



(4)

From unsupported to supported catalysts

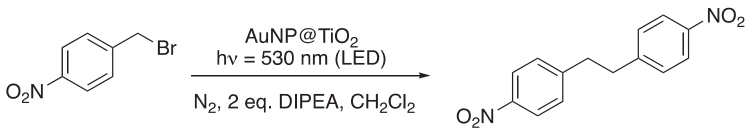
The use of colloidal metal nanoparticles (NP) in photocatalysis has been explored in the past decade, particularly in the case of spherical AuNP that have a maximum absorption band around 520 nm. For example, AuNP can catalyze alcohol oxidations to ketones [24] in their nanoparticle or colloidal form, as in the example of reaction 5.



(5)

Colloidal catalysts can be very efficient, as the active material has excellent surface exposure and mobility, but unfortunately shares some of the problems of homogeneous catalysis as the catalyst becomes extremely difficult to recover and/or reuse. In order to overcome this issue, several efforts were made to support metal NP without losing their catalytic activity [25–27]. Notice that the supports can play two distinct roles, the first is a passive one and fits well with the '*support*' description, that is, catalysts (such as nanoparticles) adhere to the support, thus maintaining their interparticle distance, restricting their mobility, and usually making the catalyst easy to separate through filtration or centrifugation. The second role, frequent while not required, is the case when the support is also an active component of a composite catalyst. This is frequently the case with semiconductors and their mode of action will be discussed later in this contribution.

In our own examples, reaction 6 shows how the surface plasmon excitation of supported AuNPs in the presence of an di-isopropylethyl amine (DIPEA) leads to the C–C coupling of a variety of substituted benzyl bromides at room temperature with good yields in a free radical-mediated reaction [28]. This is an unusual example where C–C formation is truly a diffusional process which is helped by high light intensity, a wise selection of the solvent –a truly inert solvent–, and a SED reactive enough to undergo electron transfer, yet, not so reactive as to scavenge the benzylic radicals that mediate the reaction.

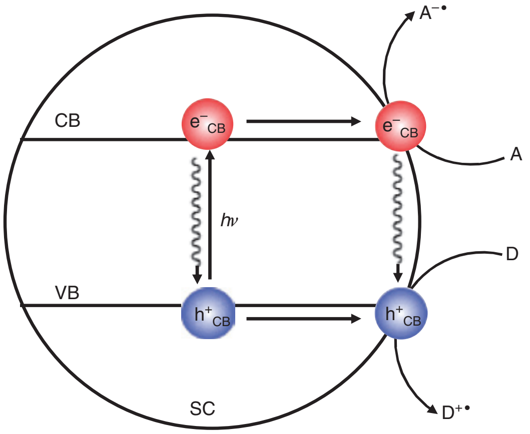


(6)

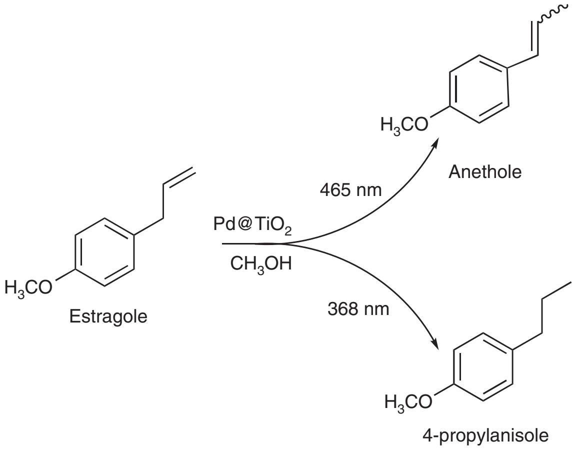
Note that in reaction 6, the AuNP are supported on TiO_2, a very useful semiconductor that plays an important role in this reaction, as well as on many other electron transfer reactions. It is important to highlight that the use of a semiconductor as a "support" material should rarely be regarded as a passive support in photocatalytic processes without proper control reactions.

Use of semiconductors in heterogeneous photocatalysis

The excitation of a semiconductor can generate electron-hole pairs (usually referred as excitons) that can catalyze photoredox reactions, indeed replacing traditional transition metal complexes [29, 30]. TiO_2, in its anatase form, is by far the most studied material for heterogeneous photocatalytic applications. Although, TiO_2 only absorbs light below 400 nm (UVA irradiation), we have reported on the formation of electron-transfer complexes where the reagents can indeed change the band gap energy of the semiconductor allowing for absorption at longer wavelengths [31]. The mechanism of action of TiO_2 can be separated into two main



Scheme 1: Generation of electron-hole pair in a semiconductor (SC) upon illumination. Electrons and/or holes need to reach the semiconductor surface to enable reactions with electron acceptor (A) or electron donors (D) molecules, respectively. Notice wavy arrows indicate the electron-hole recombination, the main deactivation path for the semiconductors redox activity.

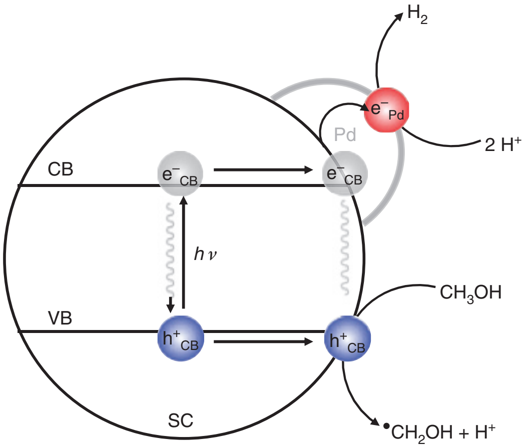


Scheme 2: Photocatalytic hydrogenation and isomerization of estragole.

sections: (i) the excited electron in the CB makes the excited TiO_2 a good reducing agent, (ii) current research in our group suggests that the hole in the VB acts as a good oxidizing agent and is a great electrophilic center, capable of generating carbon centered radicals from fairly inactivated molecules. The two roles can be conceptually differentiated, but in real practice their performance is intimately coupled. Scheme 1 shows the general mechanism for photoredox reactions catalyzed by a semiconductor (SC).

A very important consequence of the photoredox activity of the semiconductors is that when used as "supports" they can generate a hybrid photocatalyst capable of showing distinct behavior in the UV-Visible region; where the outcome of reactions can be controlled by the excitation wavelength, atmosphere and solvent. Scheme 2 shows a clear example where supported PdNP on TiO_2 can furnish different products under different irradiation conditions. Thus, using estragole as a substrate, Pd@TiO_2 as catalyst and methanol as solvent, the excitation wavelength can be used to control the outcome, hydrogenation upon 368 nm irradiation or isomerization under 465 nm light [32].

In the case of hydrogenation the reaction requires UVA light that is absorbed by the TiO_2 support, a clear example of an active support. Wavelengths below 400 nm promote an electron from the VB into the CB, creating the electron-hole pair. In the case of "*decorated*" TiO_2 (e.g. by PdNP here) the CB electron moves to the nanoparticle, causing a delay of the otherwise ultrafast electron-hole recombination (Scheme 3). This delay gives the electron increased opportunities to react, for example, to generate H_2 as in the example of Scheme 3. At the same time, the hole reacts with methanol in this case, or in general with a SED, thus neutralizing the hole (Scheme 4).



Scheme 3: Pd-decorated semiconductors are expected to delay the electron-hole recombination by trapping the electron, facilitating the reduction and oxidation of molecules as illustrated with H^+ and methanol, respectively.

$$\mathrm{TiO_2} \xrightarrow{h\nu = \mathrm{UV}} \mathrm{h^+} + \mathrm{e^-}\ (\text{@CB/Pd}) \qquad (7)$$

$$\mathrm{CH_3OH} \longrightarrow {}^{\bullet}\mathrm{CH_2OH} + \mathrm{H^+} + \mathrm{e^-}\ (\text{@hole}) \qquad (8)$$

$$^{\bullet}\mathrm{CH_2OH} \longrightarrow \mathrm{CH_2O} + \mathrm{H^+} + \mathrm{e^-}\ (\text{@CB/Pd}) \qquad (9)$$

$$2\mathrm{H^+} + 2\mathrm{e^-}\ (\text{@CB/Pd}) \longrightarrow \mathrm{H_2} \qquad (10)$$

$$\mathrm{CH_3OH} \xrightarrow{\text{Overall reaction}} \mathrm{CH_2O} + \mathrm{H_2} \qquad (11)$$

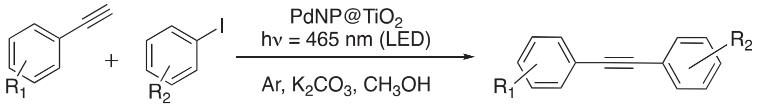
Scheme 4: Methanol decomposition upon irradiation of decorated TiO_2.

Note that the $^{\cdot}CH_2OH$ radical can also donate an electron to the CB/Pd system, forming CH_2O and a second proton needed to generate H_2. Overall, reactions 7–11 show the events that lead to methanol decomposition into formaldehyde and H_2 [33].

While in a substrate-free system electrons and protons yield H_2, these CB/Pd hosted transients can be used for reduction of some substrates, including alkenes as in Scheme 2. Visible wavelengths that excite the PdNP, but not the TiO_2, are ineffective in reduction reactions. Isomerizations as in Scheme 2 can be performed at wavelengths absorbed by PdNP and in the case of Pd@TiO_2 are restricted to visible wavelengths. Here PdNP is believed to behave as a H-atom shuttle facilitating the isomerization which in this case is energetically favorable as the double bond moves from non-conjugated to conjugated with the aromatic system.

For these two examples, Pd@TiO_2 catalyst can be readily recovered after reaction and reused several times. Note that reusability in batch reactions is a desirable characteristic for all catalysts, but very specially in those that may find applications suitable for flow photochemistry.

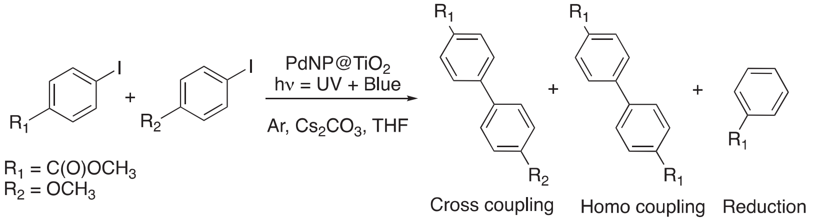
In another example, the same catalyst is active for the Sonogashira coupling between an aryl iodide and an alkyne under visible light irradiation (reaction 12); however, it becomes useless under UV irradiation. Under these conditions, TiO_2 absorption outcompetes the absorption of the PdNP masking their catalytic activity. If the same reaction is run in the presence of a passive support, such as nanodiamonds, the reaction can be photocatalyzed under UV or visible light irradiation with the same efficiency [34].



(12)

In this case, Pd@TiO_2 shows excellent performance, however, its reusability is limited and by the third use the yields drop to less than 3 %. Detailed catalyst characterization shows that after three uses at least 97 % of the Pd is retained in the catalyst. The deterioration of the catalyst is attributed to changes in the oxidation state of Pd and can be easily corrected with reductive treatments, or using a recently published strategy that we describe as *catalytic farming*, where reaction rotation is used to improve catalyst performance in the same way in which farmers use crop rotation to retain or restore soil nutrients [15]. It is important to highlight here that the loss of catalytic activity needs to be studied for each catalytic system and that different catalysts may need different recovery processes. We deliberately prefer to use the term deterioration rather than 'poisoning' of the catalyst, as the latter conveys a message inconsistent with the sustainability approach in this article, while 'deterioration' is more compatible with the recovery that we aim for.

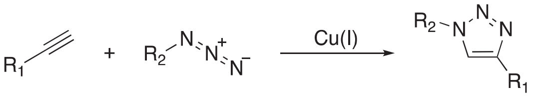
Our second example of C–C coupling involves the Ullman reaction (reaction 13), where photocatalysis allows the reaction to proceed under remarkably mild conditions [35]. The reaction is moisture tolerant, but requires an inert atmosphere, as the catalytic process involves free radical reactions. The reaction requires UVA light, that is, light absorption by TiO_2, but as we discovered accidentally the addition of visible light can alter the course of reaction in interesting ways. Solvent screening showed the reaction is solvent-dependent, thus the use of tetrahydrofuran (THF) as solvent is essential. This likely reflects that ethers are excellent solvents for these reactions and among common ethers THF is the best hydrogen donor.



(13)

The cross-coupling to homocoupling ratio was 0.5 with just 368 nm light, while it became 4.0 when 465 nm light was combined with the 368 nm light under conditions of two-color simultaneous irradiation. Interestingly, 465 nm light by itself causes no chemical change at all. The reaction is mediated by THF radicals reducing the aryl iodides, with the free THF radicals generated by reaction of THF with the TiO_2 photogenerated hole. That is, the same chemistry as in Scheme 3, with THF replacing methanol. The scope of the study includes 12 different reactions with moderate to excellent yields. The catalyst from reaction 13 shows excellent reusability, although the ratio of cross coupling to homocoupling underwent a modest deterioration after multiple uses. In addition, the Ullmann reaction proved to be a good way to restore the catalyst performance after use in Sonogashira C–C coupling reactions [15].

In a different approach, we have also used copper-decorated TiO_2 ($Cu_xO_y@TiO_2$) to photocatalyze C–N heterocycloadditions, reaction 14 [36]. In this case, we used the photoredox properties of the semiconductors (TiO_2, Nb_2O_5 or copper oxides) to generate Cu(I) – the known catalyst for click reactions – on demand.



(14)

To the best of our knowledge, our report is the first example of heterogeneous photocatalysis applied to the formation of triazoles through the well-known click chemistry reaction. In contrast to the previous examples, the photoredox mechanism behind this reaction only involves the heterogeneous materials in the reaction mixture. Thus, Cu(II) can be readily reduced to Cu(I) upon UV excitation of the TiO_2, the so-formed species catalyze the click chemistry reaction and the presence of oxygen (the reaction evolves better under air conditions comparing to inert atmosphere such as Ar) contributes to the system by re-oxidation of the Cu species formed, closing the catalytic cycle (see Scheme 5). An amine can be added to accelerate the process, as it is discussed in the next section.

$$TiO_2 \xrightarrow{h\nu = UV} h^+ + e^- (@CB) \qquad (7)$$

$$Cu(II) \xrightarrow{+e^-} Cu(I) \qquad (15)$$

$$Cu(I) \xrightarrow{+e^-} Cu(0) \qquad (16)$$

$$Cu(0) \xrightarrow{+\ O_2} Cu_2O \qquad (17)$$

$$Cu_2O \xrightarrow{+\ O_2} CuO \qquad (18)$$

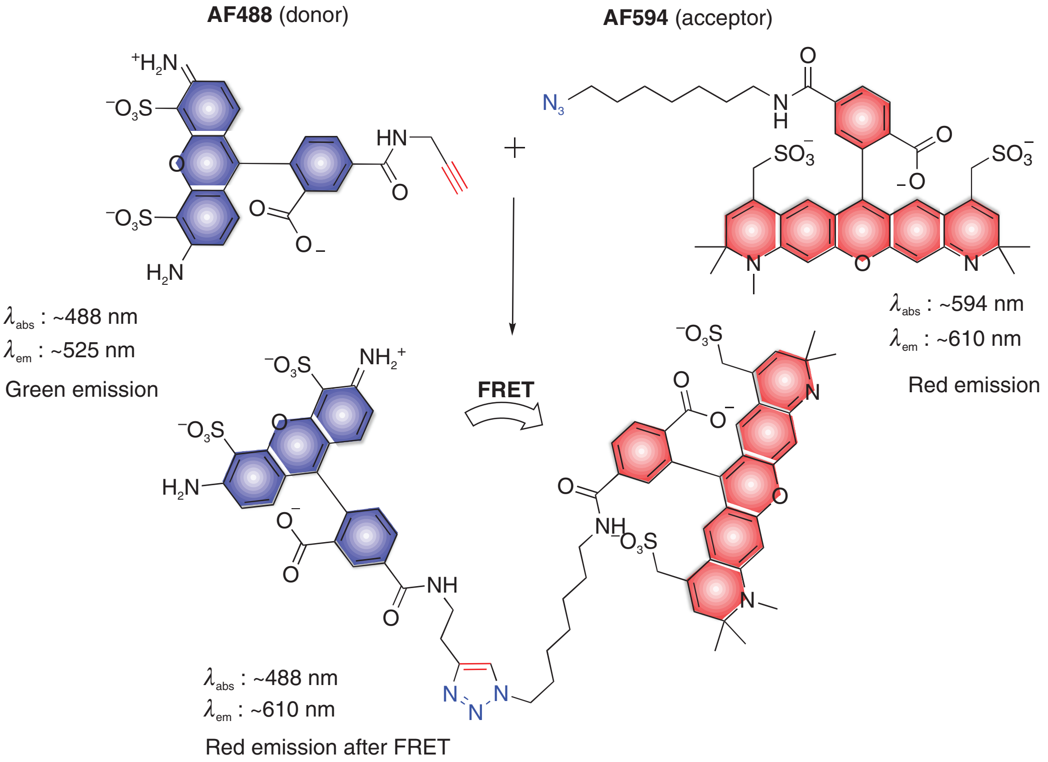
Scheme 5: Catalytic cycle for the *in situ* photochemical generation of Cu(I) species upon UV exposure of $Cu_xO_y@TiO_2$ under air.

Single molecule spectroscopy: departing from the most travelled path

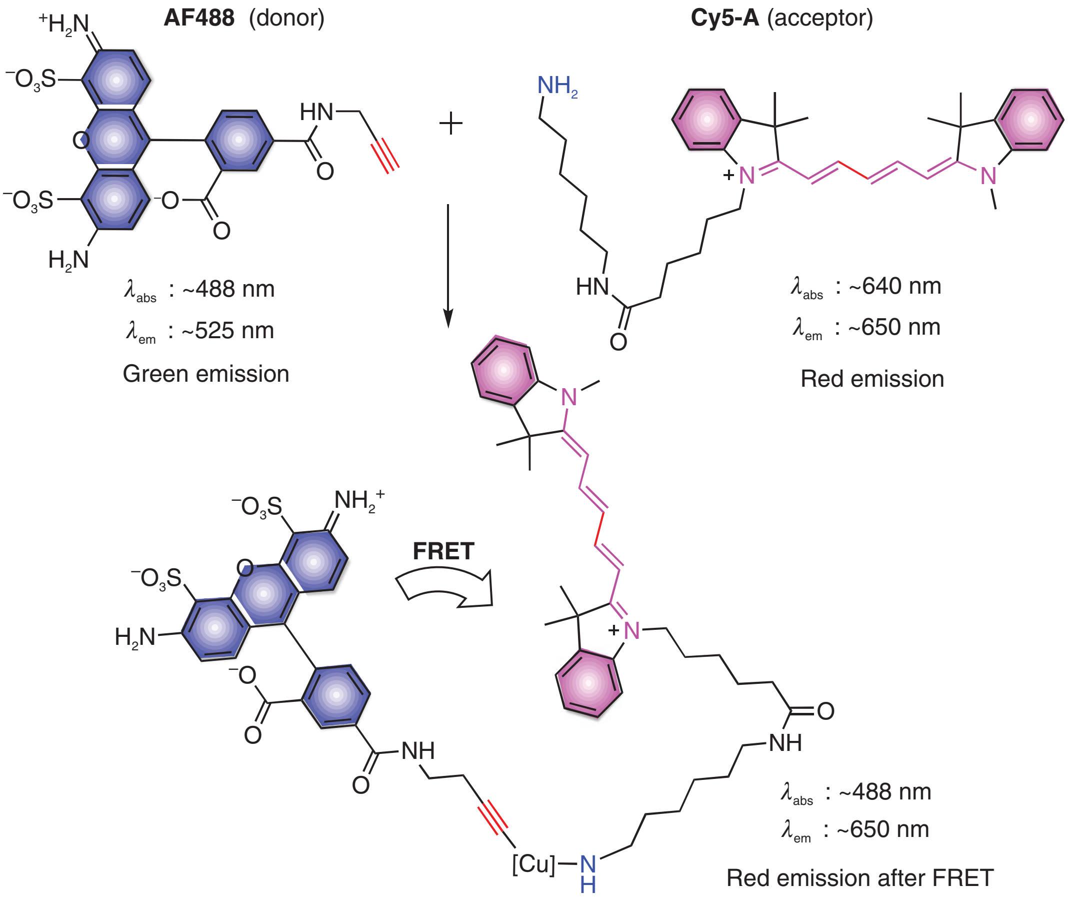
The microscope path on the left side of Fig. 1 reflects our attempts to use single molecule spectroscopy (SMS) to learn about intimate details of the catalytic process and to try to translate that information into real changes at the bench level [18]. As we entered this field a few years back, SMS had become a challenging but standard technique where many others had travelled this trail developing the tools, strategies and protocols that enabled our work. In the context of this review, the click reaction between an alkyne and an azide (reaction 14) provided an excellent system to see to what extent the less travelled path, from the microscope to the bench, offered a viable tool for the organic chemistry laboratory. In 2017 we wrote a *Perspective* discussing in some detail the validity of this strategy [16]. The reaction can be performed thermally or photochemically [36] and works well as long as Cu(I) is available to catalyze the process. For example, Cu-on-charcoal a very useful catalyst first described by Lipshutz and Taft [37] is a convenient and commercially available catalyst for click chemistry. Our SMS studies established that only 0.003 % of the surface of the commercial catalyst was active [38]. With this information it was possible to treat the catalyst improving its performance by over an order of magnitude [17]. Therefore, besides proving that the Cu-on-charcoal catalyst is inefficient at the single molecule level –in spite of its good overall activity at the bench scale we managed to show that bench scale treatments of the catalyst can indeed increase the number of multiple events on one catalytic site, by following the reaction at the SM level [17].

The simplicity of reaction 14 hides some of the complexity of SMS experiments. How can one tell that the reaction has occurred? For this, one needs a ‘reporter’ that in the case of SMS it usually is a burst of fluorescence that only occurs if the reaction takes place. In our case, we chose Förster resonance energy transfer (FRET) as the process that acts as a reaction reporter. The alkyne is attached to a high energy chromophore (AlexaFluor488 – AF488 – in Scheme 6). In the absence of reaction, excitation of AF488 yields fluorescence only from AF488. However, when reaction takes place, chromophores AF488 and AlexaFluor594 – AF594 – are held in close proximity and thus fluorescence from AF584 can be detected upon AF488 excitation following intramolecular FRET, thus reporting on the occurrence of the click reaction.

Some of the challenges intrinsic to SMS include work at concentrations between 0.01 and 1 nM and the use of very robust chromophores, capable of resisting excitation 10^6 times or higher before degrading. Translating SMS knowledge into bench applications at concentrations between 1 mM and 1 M include the challenge of bridging at least 6 orders of magnitude in concentration between the two environments.



Scheme 6: Reaction reporters used for the SMS studies of reaction 14.



Scheme 7: Reaction reporters used for the SMS studies of the amine role in reaction 14.

Furthermore, click reactions are normally performed in the presence of an amine as it is believed that they facilitate the complexation between the alkyne and the copper active site (Cu-acetylide complex). However, we found no evidence of the role of the amine in heterogeneous systems. Therefore, we decided to use SMS studies to establish the role of the amine in reaction 14. Using the same approach described before, the system presented in Scheme 7 was used to monitor the role of the amine. We were able to show that the amine extends the time the alkyne resides on the catalyst surface, thus prolonging the time available for reaction [39]. Additionally, the amine takes part of the Cu-acetylide complex formed as we proved the amine and alkyne reporters are in close proximity – dye-labelled experiments suggest the proximity between the amine and the alkyne is close enough to enable FRET (Scheme 7).

Beyond TiO_2: on the way to flow-friendly catalysts

In the context of Fig. 1, we have travelled most of the green road, to the point of developing strategies towards recover and reuse, but all of it with batch systems using powder-like catalysts; while an essential step in catalyst development, these materials are impractical for use in flow systems. Flow photochemistry will present a range of challenges including the restriction of light penetration through moderately absorbing solutions, light scattering by catalysts, and in the case of passive supports the preference for supports that have desirable optical properties, for example glass will be preferred over carbon fibers. The catalyst needs to be mechanically robust, so that it is not released or fractured during the flow. Catalyst durability is expected to correlate with the ability to reuse in the case of batch reactions.

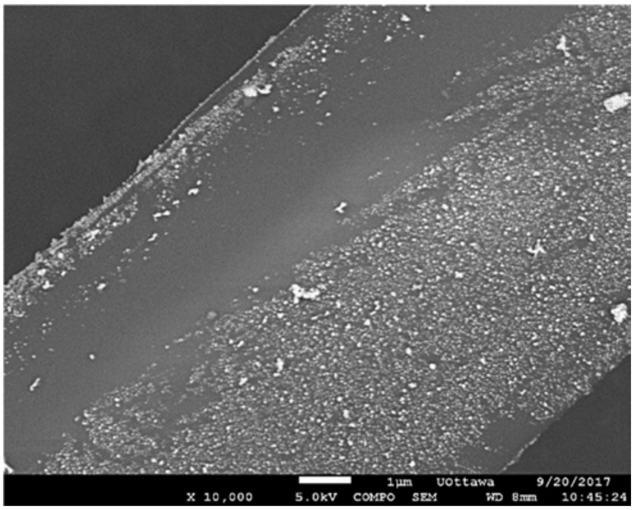


Fig. 2: SEM image of AuNP-functionalized glass fiber.

We foresee three types of strategies in designing catalysts for heterogeneous flow photocatalysis applications: (i) derivatization of the surface of flow chamber materials, for example make glass surfaces catalytic by suitable derivatization. This approach is likely to be feasible and simple to implement, but unlikely to provide enough catalytic surface, in other words, the surface to volume ratio is likely to be low. (ii) Derivatization of porous solids with a high surface area per gram. For this it will be important to design or select materials that allow liquid flow easily and that are suitable for significant light penetration, as in this case the advantages would be lost if catalysis occurs only on exterior surfaces. (iii) Use of fibrous or cloth-like materials is the third option and the one we have explored using commercial fiberglass as a support [40]. We anticipated that this support would be a passive one, although to our surprise in a few cases the role of the support was important beyond catalyst immobilization.

By using glass wool as a support (Fig. 2) we were able to show that this inexpensive and widely available material performs well as a catalyst support with different metal and metal oxide nanoparticles, based on Pd, Co, Cu, Au and Ru, and used as heterogeneous catalysts for a range of thermal and photochemical organic reactions including reductive de-halogenation of aryl halides, reduction of nitrobenzene, C–C couplings and N–C heterocycloadditions (click chemistry). Typical fibers were about 10 μm in diameter and provided much more active surface than simple glass plates [40].

Conclusions

Major developments in flow chemistry have expanded to include flow photochemistry, but have had virtually no impact in heterogeneous photocatalysis, in particular in strategies that can be scaled-up to address energy and environmental problems. Photochemistry poses unique challenges as they relate to light penetration that can frustrate any linear approach to scale-up and is compounded by light transmission and scattering effects. In this sense the development of robust photocatalytic processes with the right optical and photochemical properties is essential. Covering 75 % of the road map in Fig. 1 places us at the doorstep of the major challenges that heterogeneous flow photochemistry will pose. Over 100 years ago Ciamician predicted a bright future for solar photochemistry [41]; if we can reach the destination in Fig. 1, then his prediction may prove correct and have a major societal impact.

Acknowledgements: First and foremost, we are pleased to acknowledge the contributions from our coworkers, whose names appear in the references. May the Ottawa references serve to recognize the contribution of numerous coworkers who contributed their work, their ideas and their inexhaustible enthusiasm for research. Without their talent, work, persistence, humor and enthusiasm this contribution would not exist. This work was supported by the Natural Sciences and Engineering Research Council of Canada, the Canada Foundation for Innovation, the Canada Research Chairs Program, and Canada's International Development Research Centre, Grant Number: International (IDRC).

References

[1] C. K. Prier, D. A. Rankic, D. W. C. MacMillan. *Chem. Rev.* **113**, 5322 (2013).
[2] N. A. Romero, D. A. Nicewicz. *Chem. Rev.* **116**, 10075 (2016).
[3] K. L. Skubi, T. R. Blum, T. P. Yoon. *Chem. Rev.* **116**, 10035 (2016).
[4] T. P. Yoon, M. A. Ischay, J. Do. *Nature Chem.* **2**, 527 (2010).
[5] J. W. Tucker, C. R. J. Stephenson. *J. Org. Chem.* **77**, 1617 (2012).
[6] N. J. Turro, V. Ramamurthy, J. C. Scaiano. *Modern Molecular Photochemistry of Organic Molecules*, University Science Publishers, New York, NY (2010).
[7] D. Rehm, A. Weller. *Isr. J. Chem.* **8**, 259 (1970).
[8] J. W. Tucker, Y. Zhang, T. F. Jamison, C. R. J. Stephenson. *Angew. Chem. Int. Ed.* **51**, 4144 (2012).
[9] J. D. Nguyen, B. Reiss, C. Dai, C. R. J. Stephenson. *Chem. Commun.* **49**, 4352 (2013).
[10] D. A. Nicewicz, T. M. Nguyen. *ACS Catal.* **4**, 355 (2013).
[11] S. P. Pitre, C. D. McTiernan, H. Ismaili, J. C. Scaiano. *J. Am. Chem. Soc.* **135**, 13286 (2013).
[12] S. P. Pitre, C. D. McTiernan, H. Ismaili, J. C. Scaiano. *ACS Catal.* **4**, 2530 (2014).
[13] S. P. Pitre, C. D. McTiernan, J. C. Scaiano. *Acc. Chem. Res.* **49**, 1320 (2016).
[14] A. Joshi-Pangu, F. Lévesque, H. G. Roth, S. F. Oliver, L.-C. Campeau, D. Nicewicz, D. A. DiRocco. *J. Org. Chem.* **81**, 7244 (2016).
[15] A. Elhage, A. E. Lanterna, J. C. Scaiano. *Chem. Sci.* (2019).
[16] J. C. Scaiano, A. E. Lanterna. *J. Org. Chem.* **82**, 5011 (2017).
[17] B. W. Wang, J. Durantini, M. R. Decan, J. Nie, A. E. Lanterna, J. C. Scaiano. *Chem. Commun.* **53**, 328 (2017).
[18] J. C. Scaiano, A. E. Lanterna. *J. Org. Chem.* **82**, 5011 (2017).
[19] H. Ismaili, S. P. Pitre, J. C. Scaiano. *Catal. Sci. Technol.* **3**, 935 (2013).
[20] J. C. Scaiano. *J. Phys. Chem.* **85**, 2851 (1981).
[21] S. P. Pitre, C. D. McTiernan, H. Ismaili, J. C. Scaiano. *ACS Catal.* **4**, 2530 (2014).
[22] S. P. Pitre, C. D. McTiernan, J. C. Scaiano. *ACS Omega* **1**, 66 (2016).
[23] K. A. Margrey, D. A. Nicewicz. *Acc. Chem. Res.* **49**, 1997 (2016).
[24] G. L. Hallett-Tapley, M. J. Silvero, C. J. Bueno-Alejo, M. González-Béjar, C. D. McTiernan, M. Grenier, J. C. Netto-Ferreira, J. C. Scaiano. *J. Phys. Chem. C.* **117**, 12279 (2013).
[25] L. C. Liu, A. Corma. *Chem. Rev.* **118**, 4981 (2018).
[26] L. Cisneros, P. Serna, A. Corma. *Angew. Chem. Int. Edit.* **53**, 9306 (2014).
[27] M. Stratakis, H. Garcia. *Chem. Rev.* **112**, 4469 (2012).
[28] A. E. Lanterna, A. Elhage, J. C. Scaiano. *Catal. Sci. Technol.* **5**, 4336 (2015).
[29] M. A. Fox, B. Lindig, C. C. Chen. *J. Am. Chem. Soc.* **104**, 5828 (1982).
[30] C. Hu. *Modern Semiconductor Devices for Integrated Circuits*, Prentice Hall, Upper Saddle River, NJ (2010).
[31] S. P. Pitre, T. P. Yoon, J. C. Scaiano. *Chem. Commun.* **53**, 4335 (2017).
[32] A. Elhage, A. E. Lanterna, J. C. Scaiano. *ACS Catal.* **7**, 250 (2017).
[33] A. S. Hainer, J. S. Hodgins, V. Sandre, M. Vallieres, A. E. Lanterna, J. C. Scaiano. *ACS Energy Lett.* **3**, 542 (2018).
[34] A. Elhage, A. E. Lanterna, J. C. Scaiano. *ACS Sust. Chem. Eng.* **6**, 1717 (2018).
[35] N. Marina, A. E. Lanterna, J. C. Scaiano. *ACS Catal.* **8**, 7593 (2018).
[36] B. Wang, J. Durantini, J. Nie, A. E. Lanterna, J. C. Scaiano. *J. Am. Chem. Soc.* **138**, 13127 (2016).
[37] B. H. Lipshutz, B. R. Taft. *Angew. Chem. Int. Edit.* **45**, 8235 (2006).
[38] M. R. Decan, S. Impellizzeri, M. L. Marin, J. C. Scaiano. *Nat. Commun.* **5**, (2014).
[39] B. W. Wang, A. E. Lantema, J. C. Scaiano. *ACS Catal.* **7**, 8487 (2017).
[40] A. Elhage, B. W. Wang, N. Marina, M. L. Marin, M. Cruz, A. E. Lanterna, J. C. Scaiano. *Chem. Sci.* **9**, 6844 (2018).
[41] G. Ciamician. *Science* **36**, 385 (1912).