Nanocrystals perovskites photocatalyzed singlet oxygen generation for light-driven organic reactions

Marco Corti¹ · Rossella Chiara¹ · Lidia Romani¹ · Barbara Mannucci² · Lorenzo Malavasi¹ · Paolo Quadrelli¹

Received: 12 July 2021 / Accepted: 16 September 2021 / Published online: 6 October 2021
© The Author(s) 2021

Abstract

Lead halide perovskite nanocrystals were prepared and used as photocatalysts for the in situ $^1\text{O}_2$ generation to perform hetero Diels–Alder, ene and oxidation reactions with suitable dienes and alkenes. The methodology has been reasonably standardized and made applicable to a variety of olefinic substrates. The scope of the method is finely illustrated by the results in all the tested reactions, which allowed to obtain desymmetrized hydroxy-ketone derivatives, unsaturated ketones and epoxides. Some limitations were also observed especially in the case of the alkene oxidations as well as poor chemoselectivity was somewhere observed.

Graphic abstract

$^1\text{O}_2$ generated by lead halide perovskite nanocrystals as photocatalyst in organic reactions.

Keywords Nanocrystals · Singlet oxygen · Diels–Alder cycloadditions · Ene reactions · Oxidation reactions

✉ Lorenzo Malavasi
malalor@unipv.it

✉ Paolo Quadrelli
paolo.quadrelli@unipv.it

Extended author information available on the last page of the article

1 Introduction

Light-driven organic syntheses take an enormous advantage from the development of cheap, effective, and robust, made-easy and long-term stable photocatalysts. The use of external photocatalysts with light and redox properties is generally required for activating most of the organic molecules considering their poor light-harvesting ability in the visible light region. Transition metal complexes [1, 2] and organic dyes [3] are commonly selected to achieve electron transfer (ET) or energy transfer to perform organic reactions. Nevertheless, these photocatalysts suffer from common disadvantages such as high cost, easy decomposition/degradation during the reactions, and poor recyclability. Inorganic semiconductor photocatalysts, such as TiO₂ [4], cadmium sulfide, and other transition metal sulfides and oxides [5] can be used as heterogeneous catalysts but the wide band gap (e.g. for TiO₂ ~ 3.2 eV) makes them only absorb UV or near UV light of the solar spectrum, with low photocatalytic efficiency and quantum yield. In the past 10 years, metal halide perovskites (MHPs) have emerged as one of the leading optoelectronic materials with attracting properties of long carrier lifetime, good band-gap tunability, excellent absorption coefficient, strong nonlinear response, unique carrier bipolar diffusion characteristics, high electron/hole mobility, high tolerance to defects, and facile processing methods [6].

Perovskite-based photocatalysts have fortified their applications in the field of photocatalytic organic reactions and found applications in alcohols and alkene oxidation reactions to aldehydes/ketones, aliphatic and aromatic C–H bond activation to afford alcohols or aldehydes/ketones, aminomethylation of imidazo-fused heterocycles, α -alkylation of aldehyde, carbon–carbon coupling reactions, decarboxylation and dehydrogenation reactions and few others [6].

The ability of MHPs to drive oxygen to be inserted in different ways into an organic molecule, often characterized by a simple carbon skeleton, opens different application opportunities and the generation of Singlet Oxygen (¹O₂) is an interesting way to afford valuable synthons to be used in remarkable approaches to organic molecules. ¹O₂ is photochemically produced by the use of organic molecules (sensitizers) [7] or, alternatively, through classical hydrogen peroxide decomposition promoted by hypochlorite or hypobromite and ozonides decomposition. Moreover, ¹O₂ can also be obtained by thermal decomposition of unstable molecules, such as arene endoperoxides, or by photolysis of oxone [8]. These methodologies are not devoid of problems due essentially to the instability of the organic sensitizers or not completely applicable to the experimental conditions required by specific syntheses.

For these reasons modern chemical literature on ¹O₂ reports the photochemical properties of new catalytic systems that proved to be nicely applicable to the generation of such transient oxygen species [9–12]. ¹O₂ can undergo a variety of reactions; among them the hetero Diels–Alder (HDA) [4 + 2] cycloadditions, the [2 + 2] cycloadditions, the ene reactions and epoxidations are representative of the most relevant categories of methods for the preparation of valuable synthons [13–16].

Recently, we proposed a ¹O₂ generation made-easy method by the catalytic use of oxidized graphitic carbon nitride (g-C₃N₄) under photochemical conditions. g-C₃N₄, a polymeric semiconductor consisting of carbon and nitrogen atoms, is prepared by bulk and hard template pyrolysis of melamine (MLM), or alternatively from other carbon/nitrogen-containing sources [17, 18]. Some HDA and ene reactions were conducted on selected dienes and alkenes showing a general ability of oxidized g-C₃N₄ to promote chemoselective and unselective oxidative processes in strong dependence from substrates nature. The results offered a good panorama of the ability of this type of catalysts to be employed in organic reactions to prepare valuable synthons that can be used in several value-added preparations [19].

Furthermore, triggered by the superior optical properties of MHPs discussed above, we devised novel composite photocatalysts with high visible-light absorption, namely the g-C₃N₄/MHPs systems, which were used for the first time as photocatalysts for the in situ ¹O₂ generation to perform HDA, ene and oxidation reactions with suitable dienes and alkenes. The standardized methodology was made applicable to a variety of olefinic substrates. The reactions afforded desymmetrized hydroxy-ketone derivatives, unsaturated ketones and epoxides. This is the first application of MHP-based composites for in situ ¹O₂ generation [20].

Starting from the encouraging results obtained by the application of bulk MHPs, and upon pursuing our interest in finding new and greener methods for ¹O₂ generation as well as sustainable applications in the synthesis of valuable organic intermediates, we further explored the possible use of MHPs nanocrystals (NCs) for the ¹O₂ generation, to investigate the scope of the method in HDA, ene and oxidation reactions with representative dienes and alkenes. We enlarged the number of substrates used to perform the reactions and found interesting as well as valuable limitations occurring with some of them. The obtained value-added compounds are commonly the synthons for a remarkably high range of synthetic transformations, widely applied in modern organic synthesis and here derive from a sustainable and greener ¹O₂ methodology in organic synthesis taking advantage of easy tunable catalysts.

2 Results

We have prepared lead halide perovskite NCs of general formula MPbX_3 (Table of Fig. 1) where the cation M can be either inorganic (Cesium, Cs) or organic (Formamidinium, FA) and the anion $\text{X} = \text{Cl}, \text{Br}$ or I . Catalysts **C1–4** were prepared according to the reported procedures avoiding the use of toluene that can interfere during the

photochemical reactions and applying centrifugation immediately before suspension in chloroform [21, 22].

Figure 1a reports the emission spectra where the four catalysts show maximum emission wavelengths in the range 450–6870 nm. Catalysts **C1–4** are typical monodisperse nanocrystals and their crystal structure characterization, reported previously, agrees with the current literature with all the prepared NCs showing an orthorhombic unit cell [21]. Transmission electron microscopy (TEM)

Entry	Catalyst	Formula	$\lambda_{\text{max.}}$ (nm)	Ref.
1	C1	$\text{CsPbCl}_3\text{-NCs}^{\text{a}}$	456	21
2	C2	$\text{CsPbBr}_3\text{-NCs}^{\text{a}}$	518	21
3	C3	$\text{CsPbI}_3\text{-NCs}^{\text{b}}$	670	21
4	C4	$\text{FAPbBr}_3\text{-NCs}^{\text{a,c}}$	513	22

Fig. 1 **a** Emission spectra of MHP NCs investigated in the present work; **b** representative TEM image for CsPbBr₃ NCs; **c** photos of the samples under UV lamp. Table of catalysts, emission $\lambda_{\text{max.}}$ values and preparation references.

analysis confirms that all the samples possess a nearly cubic shape with size in the range of 20–30 nm, with a representative example reported in Fig. 1b [22]. Finally, Fig. 1c shows the emission properties under UV illumination of the samples used.

The catalysts were always freshly prepared and used immediately to perform the planned organic reactions.

$^1\text{O}_2$ is known to be a valuable dienophile and enophile whose reactivity has been thoroughly investigated both experimentally [23, 24] and theoretically [25, 26] in the past; the choice of typical $^1\text{O}_2$ HDA cycloaddition reactions with 1,3-cyclohexadiene or freshly distilled cyclopentadiene relies upon the need to optimize the reaction conditions in these catalyzed processes. This starting point aims to evaluate the solvent, reaction time and temperature as well as detection methods for the products to select the best performing catalyst from the table list. To start with, we conducted the first reactions according to the performed experiments, previously set-up in other works for sake of comparison [19, 20]. We used acetonitrile as solvent conducting the irradiation reactions at room temperature for 24 h, starting with the reactions with 1,3-cyclohexadiene whose reduced reactivity in HDA reactions avoids competitive light-promoted polymerization reactions and, eventually, other detrimental oxidation processes.

We precise that, since the NCs are generated in suspensions with other solvents (see Table of Fig. 1), the photocatalyzed reactions were conducted in acetonitrile as the solvent that can be considered as the true reaction solvent, being in large excess. Scheme 1 reports the HDA cycloaddition reaction with 1,3-cyclohexadiene that was conducted with all the four catalysts **C1–4**.

Irradiation was conducted under simulated solar light for 24 h saturating the organic phase with pure oxygen, and leaving the reaction under oxygen atmosphere (using a balloon as the reservoir connected to the photochemical vessel). Table 1 reports the data relative to the different catalysts performances with the yields values. In all the reactions, we verified that the 1,3-cyclohexadiene conversions were quantitative by GC–MS analyses that served also for the detection of the reaction products, here and in the other reported experiments. The characterization of the final products was, in fact, secured by comparison of the

Table 1 Product **2** distribution in photocatalyzed HDA reactions with 1,3-cyclohexadiene

Entry ^a	Catalyst	Product 2 (%)	Other products (%)
1	C1	16	
2	C2	65	
3	C3	31	27 ^b
4	C4	58	

^aThe amount of catalyst is 13% w/w with respect to 1,3-cyclohexadiene

^bCyclohex-2-ene-1,4-diol

mass spectra with data available from literature and from authentic sample analyses [19, 20].

Intermediate **1** represents the primary HDA cycloadduct and was never detected in all the performed experiments. The 4-hydroxycyclohex-2-en-1-one (**2**) was the only reaction product in entries 1–5 and 7 of Table 1, a known compound derived from the reductive cleavage of the peroxide O–O bond and simultaneous oxidation of one of the hydroxy functionalities, simultaneously promoted by the catalyst; the structure was confirmed by comparison with authentic samples (standard) as well as NMR characterization [15].

Catalysts **C1** and **C3** gave from modest to good yields in compound **2**. In the reaction conducted with catalyst **C3**, another product could be detected, the cyclohex-2-ene-1,4-diol, as a mixture of stereoisomers, obtained in 27% yield. The best result was obtained with catalyst **C2** that provided 65% yield of **2**, ameliorating the results obtained with the oxidized g- C_3N_4 (65% of compound **2**) [19]. Catalysts **C4**, that contains an organic cation (FA), gave the hydroxyl-ketone **2** in fair yields (58%).

Based on the above-illustrated results we also investigated the behavior of cyclopentadiene to probe the scope of the reaction with a highly reactive diene, testing all the prepared catalysts. Scheme 2 shows the structures of the products obtained from the reaction of photogenerated $^1\text{O}_2$ with freshly distilled cyclopentadiene. Due to the high reactivity of this diene and the known tendency to dimerize, we verified that the reaction conversion was complete although affected by an important amount of cyclopentadiene

Scheme 1 HDA cycloaddition reaction of 1,3-cyclohexadiene and $^1\text{O}_2$ used as benchmark reaction to test the efficiency of all the catalysts

Scheme 2 HDA cycloaddition reaction of cyclopentadiene and $^1\text{O}_2$

polymerization material. The composition of the reaction mixtures is reported in Table 2 as it was found by GC–MS analyses. The experimental conditions clearly activate a very fast cyclopentadiene dimerization that is responsible for the reaction outcome as shown in Scheme 2.

The primary HDA cycloadduct **3** was neither isolated nor detected in the final reaction mixtures from independent experiments. Compound **4a** that derives from the peroxide bond reductive cleavage was detected only in the reaction with catalysts **C3** just in 3% yield and **C4** in 7% yield (Table 2). For the first time in this type of experiments we could detect the presence of oxidation products directly obtainable from the HDA cycloaddition reaction of the $^1\text{O}_2$ to cyclopentadiene. This is furtherly demonstrated by the presence of the oxidized diketone **4b** (6% yield) in the reaction mixture obtained from catalyst **C1**. All the reported products are known in literature and the structures are consistent with the reported data [27–37]. Looking at the other products, catalyst **C1** is the worst in terms of the capability to functionalize the cyclopentadiene (monomer or dimer) scaffold. Catalysts **C2** and **C3** showed somewhat a similar behavior; compound **5a** was obtained in 22% yield; analogously compound **5f** was obtained in 22% yield but only in the case of catalyst **C2**. Compounds **5b–d** complete the composition of the reaction mixture with variable amounts.

Catalyst **C4** displayed a variable composition of the reaction mixture regarding the functionalization of the cyclopentadiene dimer. Poor yields were generally obtained for compounds **5**. The best result corresponds to product **5f**, obtained in 13% yield. It must be emphasized that in all the experiments above reported the catalyst was simply filtered at the end of each reaction and disposed. Freshly prepared catalysts were employed for new reactions and repetitions.

The presence of large amounts of dicyclopentadiene oxidized compounds **5a–f** in the reactions shown in Scheme 2, prompted us to perform control experiments trying to reduce as much as possible the competing cyclopentadiene dimerization/oxidation processes, thus orienting the catalyzed reactions on the cyclopentadiene monomer, only. Scheme 3 shows the results obtained by conducting the same reaction with freshly distilled cyclopentadiene at $-78\text{ }^\circ\text{C}$ (dry ice bath) in the presence of catalyst **C4** that gave the best results in terms of cyclopentadiene monomer oxidation.

The other experimental conditions, aside from the reaction temperature, were the same as before but the results are remarkably different. Besides the presence of 49% of cyclopentadiene dimer, the oxidation processes of this latter were reduced with respect to the reaction at room temperature, at least in terms of a variety of compounds. In parallel, cyclopentadiene monomer undergoes the HDA cycloaddition

Table 2 Product distribution in photocatalyzed HDA reactions with cyclopentadiene

Entry	Catalyst ^a	4a (%)	4b (%)	5a (%)	5b (%)	5c (%)	5d (%)	5e (%)	5f (%)
1	C1	–	6	–	–	–	4	–	–
2	C2	–	–	22	4	5	12	–	22
3	C3	3	–	22	–	11	6	–	–
4	C4	7	6	5	–	3	–	4	13

^aThe amount of catalyst is 13% w/w with respect to cyclopentadiene

Scheme 3 HDA cycloaddition reaction of cyclopentadiene and $^1\text{O}_2$ at -78°C

reaction; the detected products are the diketone **4b** (7%) (see also entry 4 of Table 2) and the 4-hydroxy-cyclopentenone **4c**, obtained in 18% yield, as a mixture of stereoisomers. This means that the natural orientation of cyclopentadiene to dimerize is hard to constrain; if this powerful side reaction could be forbidden, the reaction non the monomer would lead to better and valuable results.

We pointed out that $^1\text{O}_2$ is not only a powerful dienophile but it undergoes ene reactions with alkenes through a complex mechanism finely elucidated by Houk in his theoretical investigations [25]. In our previous works we also evidenced that simple g- C_3N_4 catalyzed processes or its composites with MHPs promoted oxidation reactions with several olefins to afford in some cases valuable synthons for organic chemistry applications [19, 20]. For these reasons oxidations of alkenes and ene reactions represent the second task of

our investigations with the new catalysts of Fig. 1 that gave the best results from the HDA cycloaddition reaction with 1,3-cyclohexadiene, i.e. **C2** and **C4**.

We started with cyclic alkenes that were found prone to give valuable oxidized products in the presence of in situ generated $^1\text{O}_2$ and Scheme 4 reports the structures of the obtained compounds along with their yields, from the selected catalysts.

Both the catalysts **C2** and **C4** gave nice and in some cases comparable results. The reactions with cyclopentene and cycloheptene (the odd-membered rings) display a good chemoselectivity leading to the corresponding α,β -unsaturated ketones as major products. The reaction of cyclopentene with catalyst **C2** affords the chloro-cyclopentanol **6b** whose formation can be attributed to the presence of chloride anion as impurity deriving from the catalyst preparation; the ether

Scheme 4 Oxidation products from cyclic alkenes in $^1\text{O}_2$ photocatalyzed reactions. ND, not detected

6c was also detected in the reaction with catalyst **C4**, only, presumably deriving from rearrangement of the corresponding peroxide derivative. In the reaction with cycloheptene, the epoxide **8a** was also obtained in comparable amounts in both the catalyzed reactions.

Less chemoselectively, the reactions with cyclohexene and cyclooctene (the even-membered rings) gave a plethora of products the most important of which were surely the α,β -unsaturated products **7a, b** in the reaction with cyclohexene that represent more than 60% of the reaction mixture when catalyst **C2** is used. Compounds **7c, d** were also detected in the same reaction.

Catalyst **C4** substantially broadens the variety of products but in modest yields. In the case of cyclooctene reactions, the epoxide **9a** is the major product with both the catalysts (42%) and the reactions are accompanied by other product in a range of yields 7–17%, confirming a poor

chemoselectivity, in general. All the detected products are known compounds whose characterization is reported in literature, taken as reference [38–46].

The investigations in this field continued with a variety of acyclic alkenes, ranging from the highly C=C double bond substituted, such as tetramethyl ethylene (TME) and trimethyl ethylene (tme), *cis*- and *trans*-disubstituted olefins up to a monosubstituted one (e.g. 1-octene) (Scheme 5).

The **C2** and **C4** catalyzed reactions were quite unsatisfactory. The ene adduct **10**, quantitatively prepared in previous works [19], could not be obtained here and compound **11** was obtained in **C2** catalyzed reaction in 16% yield; the presence of bromide in compound **11** is due to the catalyst structure. Only catalyst **C4** allows for the introduction of the novelty regarding the disubstituted alkenes, such as *cis*-2-hexene and *trans*-4-nonene, that however did not give remarkable results both in terms

Scheme 5 Oxidation products from acyclic alkenes in $^1\text{O}_2$ photocatalyzed reactions. ND, not detected

of chemoselectivity and yields. The oxidation of the *cis*-2-hexene afforded mainly α,β -unsaturated carbonyl compounds (**12a–c**) while the epoxides **12d, e** clearly derive from the epoxidation reactions of **12b, c**. On the contrary, the monosubstitute 1-octene underwent oxidative pathways to afford in fair yields the diol **14a** and the ketoacid **14b** when the catalyst **C2** was used. With catalyst **C4** novel compounds were also formed, one of them **14f** in 33% yield. The structures were confirmed upon comparison with known products reported in the literature [47–58].

The studies were extended to some aromatic alkenes, such as allyl benzene, indene and 9,10-dihydroanthracene. Similarly as before, the reactions were performed by using **C2** and **C4** catalysts that gave the best performances in HDA cycloadditions, under the typical set-up experimental conditions above reported (Scheme 6).

Indene gave a selective reaction outcome with catalyst **C2**, affording the diol **15b** as single product in fair yield (39%). The reactions with catalyst **C4** were quite unselective and afforded in fair yields a mixture of ketones and alcohols, one of them, **15a** (7%) directly obtainable from the ene reaction of indene with $^1\text{O}_2$.

The dihydroanthracene afforded the anthraquinone **16a** in excellent yields with both the catalytic systems. The **C2**-catalyzed reaction is accompanied by the formation of the anthracen-9(10*H*)-one (**16b**) in 7% yield and of the anthracene (**16c**) from complete reduction of the starting material in up to 28% yield. Catalyst **C4** shows a brilliant 100% yield of compound **16a**.

Finally, we investigated the oxidation of allylbenzene. A poor chemoselective process results from the yields of the obtained products **17a–g** with both the catalytic systems. The primary ene adduct **17a** was obtained using catalyst **C2**, only. The cinnamaldehyde (**17b**) and the corresponding alcohol **17c** are the major products along with the hydroxyl-ketone **17d** in the same catalyzed reaction. Minor amounts of **17f, g** complete the mix of the products. The reaction catalyzed by **C4** did not give the same performances since low yields and low chemoselectivity characterized the outcome. All the compounds reported in Scheme 6 are known in literature [19, 20, 59–66].

In all the reported experiments, blank trials were performed to verify that the absence of the catalysts would not activate any of the oxidative reaction pathways shown in the present work.

Scheme 6 Oxidation products from aromatic compounds in $^1\text{O}_2$ photocatalyzed reactions. ND not detected

Scheme 7 Photooxidation reactions of Type I and Type II pathways

To summarize, lead halide perovskite NCs (see Fig. 1) were prepared and used as photocatalysts in HDA, ene and general oxidation reactions of dienes and alkenes as well as representative aromatic systems. HDA cycloaddition reaction with 1,3-cyclohexadiene and cyclopentadiene were used to define the best catalysts to conduct photooxidative processes with the other substrates. Catalysts **C2** and **C4** were found to give the best results with HDA in the presence of 1,3-cyclohexadiene, affording compound **2** up to 68% yield. In spite of the new catalysts employed, cyclopentadiene suffers of its spontaneous tendency to dimerize and even polymerize under the experimental conditions, offering a variety of oxidized compounds of the dimer itself. Interesting results were obtained with cyclic alkenes of different ring size. The oxidation reactions are not completely chemoselective, especially in the case of cyclohexene and cyclooctene, but α,β -unsaturated ketones are often the main products of the reactions along with the epoxides. As already reported in previous studies [19, 20], the results of acyclic alkenes do not offer significant chances of applicability of the methodology for this type of molecules; we have not found yet a catalyst structurally fitted to interact positively with linear olefins in order to give valuable oxidized compounds. Finally, aromatic compounds such as indene, dihydroanthracene and allyl-benzene were easily oxidized by the selected catalysts. In particular, catalysts **C4** gave quantitatively the anthraquinone **16a**. Indene is mainly oxidized to the corresponding diol and the allyl-benzene offer a wide selection of oxidized compounds.

3 Discussion and conclusions

Lead halide perovskite NCs proved to be valuable photocatalysts for in situ 1O_2 generation; easy-made 1O_2 can be more conveniently employed in C–O bond formation reactions in the presence of a variety of olefinic compounds. The catalysts used in the present work display remarkable

fluorescence properties (Fig. 1) that make them fit to be used in solar-light-driven processes in a sustainable manner.

These features have been thoroughly investigated and their application in organic synthesis is constantly growing. These catalyst make easier the possibility to run photooxidation reactions of Type II according to the Scheme 7 that sketches the differences between photooxidations of Type I and Type II [67]. In the first case, radicals or radical ions are photogenerated by suitable triplet state sensitizers and oxygen is captured to give the products (Type I); for example, the lack of 1O_2 ene reactions in some cases and other non 1O_2 products such as in indene are candidates for Type I reactions derived from oxygen radicals and oxygen radical ions [68–70]. In the second case, the sensitizer promotes the 1O_2 formation that undergoes oxidation reactions with variable substrates (Type II). In the present cases, sensitizers can be avoided and the low cost and easy procedures to prepare the tested catalysts offer a valuable and cheap alternative to perform photooxidation reactions.

The obtained results open, however, some questions and problems to be solved. First problem is the possibility to design, on the basis of the results obtained from these and previous investigations, more selective and in particular chemoselective catalysts. This problem is, in some cases, solved on the substrate side, i.e. the substrate structure is prone to be easily oxidized affording single products, such in the case 1,3-cyclohexadiene or 9,10-dihydroanthracene. In other, we are in the presence of a totally absence of selectivity or even any possibility to run a reaction. The design of such a catalysts implies also to face the problem of their stability and photochemical properties that must be suited for performing organic reactions. Second problem is the scale up in organic processes to make these methodologies applicable to the production of valuable synthons not easily obtainable with other approaches. The possibility to conduct photooxidations on a large scale could be extremely important to change the habit to use toxic reagents, such as heavy metals, to perform oxidations on total carbon organic molecules. Strictly linked to this problem is the third, which is essentially

technological, i.e. the possibility to industrialize the method making the catalyst recoverable in some way and/or linkable on a solid support that would make easier and easier their use in organic synthesis. Last point is the extension to other substrates that could be oxidized. At the moment, we have limited our reaction spectrum to the classical $^1\text{O}_2$ processes, such as HDA and ene reactions. Within the oxidation reaction box, many other interesting processes can find a relevant place for disrupting traditional approaches into sustainable ones. On the mechanism side, Type II pathway reasonably fits with the nature of the obtained products. Competitive radical routes cannot be excluded in part and other investigations are required for a definitive answer. Moreover, organic reaction other than $^1\text{O}_2$ involving processes awaits their contribution to novel photocatalytic methodologies.

In conclusion, we can affirm that lead halide perovskite NCs are interesting and valuable photocatalysts for the in situ generation $^1\text{O}_2$ to perform HDA, ene and oxidation reaction with suitable dienes and alkenes. The methodology has been reasonably standardized and made applicable to a variety of olefinic substrates. The scope of the method has been finely illustrated by the results in all the tested reactions, which allowed for the obtaining of desymmetrized hydroxy-ketone derivatives, unsaturated ketones and epoxides. Notable limitations were also observed especially in the case of the alkene oxidation as well as the poor chemoselectivity somewhere observed. These tuned-up oxidative properties of suitably modified catalysts offer a remarkable improvement in determining a change in the approach to $^1\text{O}_2$ generation methods that may open other ways to perform organic reactions through greener and sustainable ways.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s43630-021-00106-x>.

Acknowledgements Financial support by University of Pavia, MIUR (PRIN 2015, CUP: F12F16001350005) are gratefully acknowledged. We also thank “VIPCAT—Value Added Innovative Protocols for Catalytic Transformations” project (CUP: E46D17000110009) for valuable financial support. Thanks are also due to the project “Scent of Lombardy” (CUP: E31B19000700007) for financial support.

Author contributions Equal contribution.

Funding Open access funding provided by Università degli Studi di Pavia within the CRUI-CARE Agreement.

Declarations

Conflict of interest The authors declare no competing financial interest.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source,

provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Prier, C. K., Rankic, D. A., & MacMillan, D. W. C. (2013). Visible light photoredox catalysis with transition metal complexes: Applications in organic synthesis. *Chemical Reviews*, 113, 5322–5363.
- Twilton, J., Le, C., Zhang, P., Shaw, M. H., Evans, R. W., & MacMillan, D. W. C. (2017). The merger of transition metal and photocatalysis. *Nature Reviews Chemistry*, 1, 52.
- Srivastava, V., & Singh, P. P. (2017). Eosin Y catalysed photoredox synthesis: A review. *RSC Advances*, 7, 31377–31392.
- Cheng, H. J., & Xu, W. T. (2019). Recent advances in modified TiO_2 for photo-induced organic synthesis. *Organic and Biomolecular Chemistry*, 17, 9977–9989.
- Hao, H. M., & Lang, X. J. (2019). Metal sulfide photocatalysis: Visible-light-induced organic transformations. *ChemCatChem*, 11, 1378–1393.
- Zhang, M., Sun, W., Lv, H., & Zhang, Z.-H. (2021). Syntheses and applications of perovskite-based photocatalysts in light-driven organic reactions. *Current Opinion in Green and Sustainable Chemistry*, 27, 100390.
- Klan, P., & Wirz, J. (2009). *Photochemistry of organic compounds* (pp. 404–451). Wiley.
- Bonnett, R. (1995). Photosensitizers of the porphyrin and phthalocyanine series for photodynamic therapy. *Chemical Society Reviews*, 24, 19–33.
- Frimer, A. A. (1985). *Singlet oxygen* (Vol. I). CRC Press.
- Denny, R. W., & Nickon, A. (2011). Sensitized photooxygenation of olefins. *Organic reactions* (Vol. 20, pp. 133–336). Wiley.
- Foot, C. S., Valentine, J. S., Greenberg, A., & Liebman, J. F. (Eds.). (1995). *Active oxygen in chemistry* (p. 105). Chapman & Hall.
- Ogilby, P. R. (2010). Singlet oxygen: There is indeed something new under the sun. *Chemical Society Reviews*, 39, 3181–3209.
- Adam, W., Bosio, S. G., & Turro, N. J. (2002). Highly diastereoselective dioxetane formation in the photooxygenation of enecarbamates with an oxazolidinone chiral auxiliary: Steric control in the [2 + 2] cycloaddition of singlet oxygen through conformational alignment. *Journal of the American Chemical Society*, 124, 8814–8815.
- Clennan, E. L., & Pace, A. (2005). Advances in singlet oxygen chemistry. *Tetrahedron*, 61, 6665–6691.
- Alberti, M. N., & Orfanopoulos, M. (2010). Unraveling the mechanism of the singlet oxygen ene reaction: Recent computational and experimental approaches. *Chemistry: A European Journal*, 16, 9414–9421.
- de Souza, J. M., Brocksom, T. J., McQuade, D. T., & de Oliveira, K. T. (2018). Continuous endoperoxidation of conjugated dienes and subsequent rearrangements leading to C–H oxidized synthons. *Journal of Organic Chemistry*, 83, 7574–7585.
- Wang, Z., Hong, X., Zong, S., Tang, C., Cui, Y., & Zheng, Q. (2015). BODIPY-doped silica nanoparticles with reduced dye leakage and enhanced singlet oxygen generation. *Science and Reports*, 5, 12602. <https://doi.org/10.1038/srep12602>

18. Lakhi, K. S., Park, D. H., Al-Bahily, K., Cha, W., Viswanathan, B., Choy, J. H., & Vinu, A. (2017). Mesoporous carbon nitrides: Synthesis, functionalization, and applications. *Chemical Society Reviews*, 46, 72–101.
19. Camussi, I., Mannucci, B., Speltini, A., Profumo, A., Milanese, C., Malavasi, L., & Quadrelli, P. (2019). g-C₃N₄—Singlet oxygen made easy for organic synthesis: Scope and limitations. *ACS Sustainable Chemistry and Engineering*, 7, 8176–8182.
20. Corti, M., Chiara, R., Romani, L., Mannucci, B., Malavasi, L., & Quadrelli, P. (2021). g-C₃N₄/metal halide perovskite composites as photocatalysts for singlet oxygen generation processes for the preparation of variable oxidized synthons. *Catalysis Science and Technology*, 11, 2292–2298.
21. Protesescu, L., Yakunin, S., Bodnarchuk, M. I., Krieg, F., Caputo, R., Hendon, C. H., Yang, R. X., Walsh, A., & Kovalenko, M. V. (2015). Nanocrystals of cesium lead halide perovskites (CsPbX₃, X = Cl, Br, and I): Novel optoelectronic materials showing bright emission with wide color gamut. *Nano Letters*, 15, 3692–3696.
22. Levchuk, I., Osvet, A., Tang, X., Brandl, M., Perea, J. D., Hoegl, F., Matt, G. J., Hock, R., Batentschuk, M., & Brabec, C. J. (2017). Brightly luminescent and color-tunable formamidinium lead halide perovskite FAPbX₃ (X = Cl, Br, I) colloidal nanocrystals. *Nano Letters*, 17, 2765–2770.
23. Clennan, E. L. (2000). New mechanistic and synthetic aspects of singlet oxygen chemistry. *Tetrahedron*, 56, 9151–9179.
24. Singleton, D. A., Hang, C., Szymanski, M. J., Meyer, M. P., Leach, A. G., Kuwata, K. T., Chgen, J. S., Greer, A., Foote, C. S., & Houk, K. N. (2003). Mechanism of ene reactions of singlet oxygen. A two-step no-intermediate mechanism. *Journal of the American Chemical Society*, 125, 1319–1328.
25. Leach, A. G., & Houk, K. N. (2002). Diels–Alder and ene reactions of singlet oxygen, nitroso compounds and triazolinediones: transition states and mechanisms from contemporary theory. *Chemical Communications*, 1243–1255.
26. Leach, A. G., & Houk, K. N. (2002). The ene reactions of nitroso compounds involve polarized diradical intermediates. *Journal of the American Chemical Society*, 124, 14820–14821.
27. Koch, H., Pirsch, J., & Benedikt, A. (1963). Notiz zur Darstellung von cyclopenten-3,4- und -3,5-diol. *Monatshefte für Chemie und verwandte Teile anderer Wissenschaften*, 94, 1093–1097.
28. Chang, C.-C., Lee, J.-F., & Cheng, S. (2017). Highly catalytically active micro/meso-porous Ti-MCM-36 prepared by a grafting method. *Journal of Materials Chemistry A*, 5, 15676–15687.
29. Alvarez, C., Pelaez, R., & Medarde, M. (2007). New dicyclopentadiene-based scaffolds. *Tetrahedron*, 63, 2132–2141.
30. Schnurpfeil, D. (1983). Dicyclopentadienoxidation. I. Unkatalysierte Flüssigphasenoxidation von Dicyclopentadien. *Journal fuer Praktische Chemie/Chemiker-Zeitung*, 325, 481–488.
31. Terashima, S., & Yamada, S. (1977). Novel use of meso-compound for the preparation of optically active compounds: synthesis of optically active prostaglandin intermediates from CIS-2-cyclopentene-1,4-diol. *Tetrahedron Letters*, 18, 1001–1004.
32. Zhu, J., Klunder, A. J. H., & Zwanenburg, B. (1995). A facile approach to norbornene-annulated cyclopentenones, a novel class of tricyclodecadienones. *Tetrahedron*, 51, 5117–5132.
33. Dolls, P. P. M. A., Arnouts, E. G., Rohaan, J., Klunder, A. J. H., & Zwanenburg, B. (1994). Nucleophilic additions to tricyclodecadienone epoxides. The Payne rearrangement of α,β -epoxycyclopentanols contained in a rigid tricyclic system. *Tetrahedron*, 50, 3473–3490.
34. Wiel, J.-B., & Rouessac, F. (1976). A new approach to the synthesis of the prostanoids. *Journal of the Chemical Society, Chemical Communications*, 446–447.
35. Ingelbrecht, H., Kumar, A., Menon, A. R., Nadkarni, P., & Pawar, R. (2007). US 2007/0049767.
36. Jeanmart, S., Taylor, J. B., Parsons, R. W., Mathews, C. J., & Smith, S. (2013). Synthesis of novel heterocyclic acetyl coenzyme-A carboxylase inhibitors via a Claisen rearrangement. *Tetrahedron Letters*, 54, 3378–3383.
37. Skumov, M., & Balbolov, E. (2000). Oxidation of dicyclopentadiene catalyzed by palladium(II) acetate and p-benzoquinone in the presence of inorganic acid. *Catalysis Letters*, 69, 103–107.
38. Sankaralingam, M., Lee, Y.-M., Nam, W., & Fukuzumi, S. (2017). Selective oxygenation of cyclohexene by dioxygen via an iron(V)-oxo complex-autocatalyzed reaction. *Inorganic Chemistry*, 56, 5096–5104.
39. Ponoras, A. A., & Zaim, O. (1986). Synthetic elaboration of diosphenols. Replacement of hydroxyl by halogen. *Journal of Organic Chemistry*, 51, 4741–4743.
40. Yu, J., Zhou, Y., Lin, Z., & Tong, R. (2016). Regioselective and stereospecific copper-catalyzed deoxygenation of epoxides to alkenes. *Organic Letters*, 18, 4734–4737.
41. Amanchi, S. R., Khenkin, A. M., Diskin-Posner, Y., & Neumann, R. (2015). Bismuth-substituted “Sandwich” type polyoxometalate catalyst for activation of peroxide: Umpolung of the peroxo intermediate and change of chemoselectivity. *ACS Catalysis*, 5, 3336–3341.
42. Zhang, J., Wei, W.-J., Lu, X., Yang, H., Chen, Z., Liao, R.-Z., & Yin, G. (2017). Nonredox metal ions promoted olefin epoxidation by iron(II) complexes with H₂O₂: DFT calculations reveal multiple channels for oxygen transfer. *Inorganic Chemistry*, 56, 15138–15149.
43. Dulcere, J. P., & Rodriguez, J. (1982). Epoxidation with H₂O₂/Vilsmeier reagent system. *Tetrahedron Letters*, 23, 1887–1888.
44. Raina, S., Bhuniya, D., & Singh, V. K. (1992). A mild method for conversion of epoxides into α -chloro ketones. *Tetrahedron Letters*, 33, 6021–6022.
45. Bhat, G. A., Verma, S., Rajendran, A., & Murugavel, R. (2018). Thermolabile organotitanium monoalkyl phosphates: Synthesis, structures, and utility as epoxidation catalysts and single-source precursors for TiP₂O₇. *Inorganic Chemistry*, 57, 7644–7654.
46. Allinger, J., & Allinger, M. N. L. (1959). Conformational analysis. V. 2-bromocyclooctanone. *Journal of the American Chemical Society*, 81, 5736–5740.
47. Göksu, H., Dalmizrak, D., Akbayrak, S., Gültekin, M. S., Ozkar, S., & Metin, O. (2013). One-pot synthesis of 1,2/3-triols from the allylic hydroperoxides catalyzed by zeolite-confined osmium(0) nanoclusters. *Journal of Molecular Catalysis A: Chemical*, 378, 142–147.
48. Collette, T. W., Richardson, S. D., & Thruston, A. D., Jr. (1994). Identification of bromohydrins in ozonated waters. *Applied Spectroscopy*, 48, 1181–1192.
49. Camarena-Díaz, J. P., Iglesias, A. L., Chávez, D., Aguirre, G., Grotjahn, D. B., Rheingold, A. L., Parra-Hake, M., & Miranda-Soto, V. (2019). Rh^(III)Cp* and Ir^(III)Cp* complexes of 1-[(4-methyl)phenyl]-3-[(2-methyl-4'-R)imidazol-1-yl]triazene (R = *t*-Bu or H): Synthesis, structure, and catalytic activity. *Organometallics*, 38, 844–851.
50. Oswald, M. F., Raw, S. A., & Taylor, R. J. K. (2004). Tandem oxidation processes for the preparation of functionalized cyclopropanes. *Organic Letters*, 6, 3997–4000.
51. Pillai, U. R., & Sahle-Demessie, E. (2004). Epoxidation of olefins and α,β -unsaturated ketones over sonochemically prepared hydroxyapatites using hydrogen peroxide. *Applied Catalysis A: General*, 261, 69–76.
52. Kamata, K., Hirano, T., Kuzuya, S., & Mizuno, N. (2009). Hydrogen-bond-assisted epoxidation of homoallylic and allylic alcohols with hydrogen peroxide catalyzed by selenium-containing dinuclear peroxotungstate. *Journal of the American Chemical Society*, 131, 6997–7004.

53. Luggren, P. J., Apesteguia, C. R., & Di Cosimo, J. I. (2016). Conversion of biomass-derived 2-hexanol to liquid transportation fuels: Study of the reaction mechanism on Cu–Mg–Al mixed oxides. *Topics in Catalysis*, 59, 196–206.
54. Sharpless, K. B., & Lauer, R. F. (1973). Mild procedure for the conversion of epoxides to allylic alcohols. First organoselenium reagent. *Journal of the American Chemical Society*, 95, 2697–2699.
55. Petrova, K. V., Jalluri, R. S., Kozekov, I. D., & Rizzo, C. J. (2007). Mechanism of 1, ^N2-etheno-2'-deoxyguanosine formation from epoxyaldehydes. *Chemical Research in Toxicology*, 20, 1685–1692.
56. Atienza, C. C. H., Diao, T., Weller, K. J., Nye, S. A., Lewis, K. M., Delis, J. G. P., Boyer, J. L., Roy, A. K., & Chirik, P. J. (2014). Bis(imino)pyridine cobalt-catalyzed dehydrogenative silylation of alkenes: Scope, mechanism, and origins of selective allylsilane formation. *Journal of the American Chemical Society*, 136, 12108–12118.
57. Lebeuf, R., & Nardello-Rataj, V. (2019). Dual catalytic role of molybdate ions for direct conversion of photo-oxidized fatty acid methyl esters into keto or hydroxy derivatives. *ACS Sustainable Chemistry and Engineering*, 7, 3034–3041.
58. Dewkar, G. K., Narina, S. V., & Sudalai, A. (2003). NaIO₄-mediated selective oxidative halogenation of alkenes and aromatics using alkali metal halides. *Organic Letters*, 5, 4501–4504.
59. You, B., Li, S., Tsona, N. T., Li, J., Xu, L., Yang, Z., Cheng, S., Chen, Q., George, C., Ge, M., & Du, L. (2020). Environmental processing of short-chain fatty alcohols induced by photosensitized chemistry of brown carbons. *ACS Earth and Space Chemistry*, 4, 631–640.
60. Jiang, D., Hu, W., Chen, M., Fu, Z., Su, A., Yang, B., Mao, F., Zhang, C., Liu, Y., & Yin, D. (2020). Visible-light-triggered quantitative oxidation of 9,10-dihydroanthracene to anthraquinone by O₂ under mild conditions. *ChemSuschem*, 13, 1785–1792.
61. Raghuvanshi, K., Zhu, C., Ramezani, M., Menegatti, S., Santiso, E. E., Mason, D., Rodgers, J., Janka, M. E., & Abolhasani, M. (2020). Highly efficient 1-octene hydroformylation at low syngas pressure: From single-droplet screening to continuous flow synthesis. *ACS Catalysis*, 10, 7535–7542.
62. Wusimana, A., & Lu, C.-D. (2015). Selective oxidation of benzylic, allylic and propargylic alcohols using dirhodium(II) tetraamidinate as catalyst and aqueous *tert*-butyl hydroperoxide as oxidant. *Applied Organometallic Chemistry*, 29, 254–258.
63. Ju, M., Guan, W., Schomaker, J. M., & Harper, K. C. (2019). Sequential reduction of nitroalkanes mediated by CS₂ and amidine/guanidine bases: A controllable Nef reaction. *Organic Letters*, 21, 8893–8898.
64. Lacasse, M.-C., Poulard, C., & Charette, A. B. (2005). Iodomethylzinc phosphates: powerful reagents for the cyclopropanation of alkenes. *Journal of the American Chemical Society*, 127, 12440–12441.
65. Kumari, A., Singh, S. K., Singh, R. B., Bhunia, S., & Ghosh, P. (2020). A concise synthesis of 2-benzoyl-1-indanones and 1-indanones from 2-aryl-1-tetralones. *Synthetic Communications*, 50, 2313–2318.
66. Nicolaou, K. C., Huang, X., Snyder, S. A., Rao, P. B., Bella, M., & Reddy, M. V. (2002). A novel regio- and stereoselective synthesis of sulfamides from 1,2-diols using burgess and related reagents: A facile entry into β -amino alcohols. *Angewandte Chemie International Edition*, 41, 834–838.
67. Baptista, M. S., Cadet, J., Di Mascio, P., Ghogare, A. A., Greer, A., Hamblin, M. R., Lorente, C., Nunez, S. C., Ribeiro, M. S., Thomas, A. H., Vignoni, M., & Yoshimura, T. M. (2017). Type I and type II photosensitized oxidation reactions: Guidelines and mechanistic pathways. *Photochemistry and Photobiology*, 93, 912–919.
68. Burns, P. A., & Foote, C. S. (1974). Chemistry of singlet oxygen. XIX. Dioxetanes from indene derivatives. *Journal of the American Chemical Society*, 96, 4339–4340.
69. Burns, P. A., Foote, C. S., & Mazur, S. (1976). Chemistry of singlet oxygen. XXIII. Low temperature photooxygenation of indene in aprotic solvent. *Journal of Organic Chemistry*, 41, 899–907.
70. Easton, N. R., Jr., Anet, F. A. L., Burns, P. A., & Foote, C. S. (1974). Carbon-13 nuclear magnetic resonance studies on polyepoxides derived from singlet oxygen addition to indene. *Journal of the American Chemical Society*, 96, 3945–3948.

Authors and Affiliations

Marco Corti¹ · Rossella Chiara¹ · Lidia Romani¹ · Barbara Mannucci² · Lorenzo Malavasi¹ · Paolo Quadrelli¹

¹ Dipartimento di Chimica e INSTM, Università degli Studi di Pavia, Viale Taramelli 12, 27100 Pavia, Italy

² Centro Grandi Strumenti, Università degli Studi di Pavia, Via Bassi 21, 27100 Pavia, Italy