Control of monomeric Vo’s versus Vo clusters in ZrO$_{2-x}$ for solar-light H$_2$ production from H$_2$O at high-yield (millimoles gr$^{-1}$ h$^{-1}$)

Yiannis Deligiannakis$^{1,4,5}$, Asterios Mantzanis$^1$, Areti Zindrou$^3$, Szymon Smykala$^3$ & Maria Solakidou$^{1,2}$

Pristine zirconia, ZrO$_2$, possesses high premise as photocatalyst due to its conduction band energy edge. However, its high energy-gap is prohibitive for photoactivation by solar-light. Currently, it is unclear how solar-active zirconia can be designed to meet the requirements for high photocatalytic performance. Moreover, transferring this design to an industrial-scale process is a forward-looking route. Herein, we have developed a novel Flame Spray Pyrolysis process for generating solar-light active nano-ZrO$_{2-x}$ via engineering of lattice vacancies, Vo. Using solar photons, our optimal nano-ZrO$_{2-x}$ can achieve milestone H$_2$-production yield, > 2400 μmol g$^{-1}$ h$^{-1}$ (closest thus, so far, to high photocatalytic water splitting performance benchmarks). Visible light can be also exploited by nano-ZrO$_{2-x}$ at a high yield via a two-photon process. Control of monomeric Vo versus clusters of Vo’s is the key parameter toward Highly-Performing-Photocatalytic ZrO$_{2-x}$. Thus, the reusable and sustainable ZrO$_{2-x}$ catalyst achieves so far unattainable solar activated photocatalysis, under large scale production.

Sunlight energy storage to H$_2$ via photocatalytic water splitting\cite{1,2} bears key advantages, such as high energy-storage capacity of H$_2$ 141.6 kJ g$^{-1}$ versus 0.46–0.72 kJ g$^{-1}$ on Li-batteries\cite{3}. Water photocatalysis to produce H$_2$ is an inherently green-technology, fully compliant with circular economy\cite{4}. Moreover, maximization of photocatalytic efficiency in tandem with minimized costs for industrial-scale production is mandatory. So far, most literature reports on high-performance photocatalysts (HPP) refer to nanomaterials with focus on performance optimization\cite{5}. Except TiO$_2$, industrial-scale and cost-effective production of HPP’s remains at its infancy.

Metal oxides can be HPP’s as long as they fulfill certain key criteria: H$_2$ production and CO$_2$ reduction, are favored by high conduction band (CB) semiconductors. Pristine zirconia (ZrO$_2$) has one of the highest CB-edge energies among metal oxides E$_{CB}$ = − 1100 mV versus NHE. However, its band-gap energy E$_g$ > 5 eV requires highly energetic photons, i.e., λ < 225 nm, which is prohibitive for solar-light harvesting. In this context, pristine ZrO$_2$ despite its established uses in technology, e.g. as refracting coating\cite{6}, thermal coating\cite{7}, gas-sensing\cite{8}, fuel cells\cite{9}, Water–Gas-Shift reaction\cite{10}, so far, has not been established as a high-performance photocatalyst. Historically, Sayama and Arakawa\cite{11} were the first to observe photocatalytic performance of pristine ZrO$_2$ reporting a rather symbolic H$_2$-production yield 72 μmol g$^{-1}$ h$^{-1}$ under X-ray irradiation.

Strategies to ameliorate photocatalytic ZrO$_2$ activity, can include: (i) heteroatom insertion\cite{12-17} into ZrO$_2$ crystal, or (ii) Oxygen-defects’ creation\cite{18-23}. The influence of heteroatoms in ZrO$_2$ has been investigated\cite{18-17}, in photocatalytic dye degradation or O$_2$ evolution. Cerium-doped ZrO$_2$ (Ce-ZrO$_2$) can be photoactive in visible λ > 420 nm light\cite{12}. Erbium-doped ZrO$_2$\cite{14} allowed band-gap tuning towards solar photons, which contributed to improved Methylene-Blue degradation\cite{13}. Nitrogen\cite{15} and carbon 2p-orbitals can enhance photocatalytic dye degradation via generation of intra-bandgap states. However, in all aforementioned cases, the reported

---

$^1$Laboratory of Physical Chemistry of Materials and Environment, Department of Physics, University of Ioannina, Ioannina, Greece. $^2$Laboratory of Biomimetic Catalysis and Hybrid Materials, Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece. $^3$Institute of Engineering Materials and Biomaterials, Silesian University of Technology, 18a Konarskiego St, 44-100, Gliwice, Poland. $^4$Institute of Environment and Sustainable Development, University Research Center of Ioannina, 45110 Ioannina, Greece. $^5$email: ideligia@uoi.gr
photocatalytic performances, despite improvement, remain by far inferior versus benchmark photocatalysts, such as TiO$_2$, which routinely achieves H$_2$ photoproduction of the order of several (millimoles H$_2$ g$^{-1}$ h$^{-1}$) in typical lab set ups. So far, the only ZrO$_2$-based photocatalyst passing the threshold of (millimoles H$_2$ g$^{-1}$ h$^{-1}$) is 2.12 mmol H$_2$ g$^{-1}$ h$^{-1}$ by a N-doped ZrO$_2$. 

Without heteroatom doping, generation of reduced states in reducible metal-oxides, such as TiO$_2$, are decisively beneficial for H$_2$ photo yield. Examples include the work of Mao et al., Naldoni et al. and our Flame Spray Pyrolysis (FSP)-made black TiO$_2$. ZrO$_2$ is a notoriously non-reducible oxide, since introduction of Vo’s into the ZrO$_2$ lattice is not favored energetically, thus specific synthesis methods are needed to achieve reduction of the ZrO$_2$ lattice. To this direction, the most significant performance has been reported by Sinha-hamapatra et al. and Zu et al., where defect-rich ZrO$_2$$_{1-x}$ has achieved production of ~ 0.5 mmol g$^{-1}$ h$^{-1}$ H$_2$, in both cases, however, this is still significantly below that of TiO$_2$. 

Regarding material synthesis, none of the so far reported ZrO$_{2-x}$ synthesis methods were designed to be scalable at industrial level. Specifically, previous ZrO$_{2-x}$ synthesis methods include sol-gel, hydrothermal, high pressure/temperature processing. More efficient methods able to overcome the non-reducibility of ZrO$_2$ are magnesiothermic, titaniothermic and lithiothermic where an elementary heterometal M$_0$ atom, i.e. Li$_0$, Ti$_0$, Mg$_0$, is used to reduce ZrO$_2$, and create the desired Vo at high yield. However, all aforementioned synthesis routes include multiple steps and do not always allow facile/reproducible control or tailoring of Vo placement and populations. Particularly, the methods which require heteroatom contact on ZrO$_2$ surface e.g. magnesiothermic, rely on harsh acid washes for removing the leftover hetero-metal oxide, something that mounts questions on how this may impact the state of the catalyst itself.

Herein we have developed a one-step Flame Spray Pyrolysis (FSP) process for synthesis of solar-light active nano-ZrO$_{2-x}$ via engineering of lattice-vacancies, Vo. FSP is eminently suited for synthesis of high crystallinity nano-ZrO$_{2-x}$, however, the synthesis of ZrO$_2$$_{1-x}$ has not been reported by FSP. In principle, ZrO$_2$ can possess two families of reduced states: (i) reduced Zr$^{3+}$ centers, and (ii) oxygen vacancies not-located on Zr atoms (Vo’s). Over last decades, Giamello’s group has provided valuable insights into the complexity of these reduced states. Using Electron Paramagnetic Resonance (EPR) spectroscopy, in combination with quantum chemical calculations, they prove that Zr$^{3+}$ centers can create extra energy states right below the E$_{CB}$ of pristine ZrO$_2$, (~ 4.5–5.0 eV). Based on all existing evidence, these Zr$^{3+}$ centers are expected to have little effect on the photocatalytic activity of zirconia. On the other hand, Vo’s can create mid-gap states but their role in photocatalytic H$_2$ evolution has not been explored systematically. Herein, using FSP we have produced libraries of ZrO$_{2-x}$ nano catalysts with varying concentrations of Vo’s and identified the optimal configuration, towards high photocatalytic H$_2$-production efficiency from H$_2$O. Specific aims of the present work were: (i) to develop a novel industrial-scale FSP method for one-step synthesis of nanosized ZrO$_{2-x}$ with controllable population and placement of the O-vacancies (Vo’s). No heteroatoms were used. (ii) to optimize the ZrO$_2$$_{1-x}$ for highly efficient solar light H$_2$ production, well beyond the current state of the art, i.e., well-above the threshold mmol g$^{-1}$ h$^{-1}$, (iii) to provide a comprehensive understanding of the physicochemical role of Vo, with emphasis on monomeric versus clusters of Vo’s related to the photocatalytic properties. We present a novel anoxic-FSP process that allows in-situ formation of Vo’s during the primary particle formation step. Using solar photons, the optimal nano-ZrO$_{2-x}$ can achieve milestone H$_2$-production yield, > 2400 μmol g$^{-1}$ h$^{-1}$ which is the closest so far to high photocatalytic performance benchmarks. We demonstrate that optimal nano-ZrO$_{2-x}$ can be achieved by controlling the monomeric Vo versus clusters of Vo’s by two routes either during the FSP synthesis or via a short post-FSP oxidation process.

Results
Synthesis of nano ZrO$_{2-x}$ by anoxic-flame spray pyrolysis. The concept of the novel anoxic-FSP process is outlined in Fig. 1. It consists of a single-nozzle FSP reactor with enclosed flame, where a mixture of Dispersion-gas (O$_2$ and CH$_4$) is used to create a reducing reaction atmosphere. In FSP-process, ZrO$_2$ particles are formed in three stages (Fig. 1). First, Zr-precursor droplets are sprayed by the FSP nozzle and combusted to generate the primary particles (PP). Then, primary particles evolve in the high-temperature area of the flame, i.e. up to 2800 K and form nanometric ZrO$_2$ particles via sintering of PP’s. In classical-FSP, used in the majority of lab studies and industry, pure O$_2$ is used as dispersion gas through the spray nozzle, to form the droplets and primary particles. For example, by adjusting the combustion stoichiometry ratio P/D = [fuel/dispersion gas] = 3/3, we obtain fully oxidized, pristine ZrO$_2$. In our anoxic-FSP, combustion of CH$_4$ in the dispersion gas creates reducing agents which, as we show herein, can reduce the primary Zr-particle via formation of Oxygen vacancies (Vo). We also have considered the possibility of the formation of Zr-Hydride states, however, none of our data support this, thus we do not discuss it further.

In this way, we have produced a library of ZrO$_{2-x}$ nanoparticles of varying Vo concentrations, see photos in Fig. 2. Herein we have codenamed the particles according to the dispersion [O$_2$/CH$_4$] ratio used, (see full details in Table S1 in SI). For example, the material codenamed [3/0.1] has been synthesized using a dispersion gas-mixture of [O$_2$ flow = 3.0 l min$^{-1}$ and CH$_4$ flow = 0.1 l min$^{-1}$]. Pristine ZrO$_2$ is codenamed F.O. For Fully Oxidized, while material [1.3/1.7] was the most reduced. As shown in Fig. 2, going from pristine ZrO$_2$ (F.O.) towards more reduced particles, i.e. [3/0.1] to [1.3/1.7], induced a change of particle color from crispy-white to pale grey/yellowish [3/0.1] and dark-gray for [1.3/1.7] material. XPS data (Fig. 2d) shows a progressive increase of Vo’s detected by XPS with the characteristic signal at 532 eV. We have verified that no carbon deposition is evidenced by Raman data (Supplementary Fig. S1), thus the observed color changes in the ZrO$_{2-x}$ materials (Fig. 2), are assigned exclusively to the formation of Vo’s via the anoxic-FSP process. According to XPS, Fig. 2d increased dispersion of CH$_4$ in the FSP process, promotes the formation of Vo’s. No Zr$^{3+}$ states are resolved in Zr-XPS data, i.e., only the Zr$^{4+}$ doublet was detected (181.9 eV, 184.2 eV) (Supplementary Fig. S2a–d).
**Figure 1.** One-step FSP process for ZrO$_{2-x}$ production. The photo at right shows as-produced 500 mg of [1.3/1.7] ZrO$_{2-x}$ particles.

**Figure 2.** (a) XRD of FSP-made ZrO$_{2-x}$ materials, (b) TEM images for [3/0.1] and [1.3/1.7] materials, (c) Kubelka–Munk plots DRS UV–Vis spectra. (d) XPS spectra of F.O., [3/0.1], [3/0.2], [2.3/0.7] and [1.3/1.7]. Top-Inset: Photos of the nanopowders.
The DRS-UV/Vis data, (Fig. 2c) show a progressive alteration of the band gaps as evidenced by the absorbance at intra-gap energies of 2.5 to 4.5 eV. All materials exhibit the primary bandgap 5.1 eV (243 nm) typical for monoclinic-ZrO$_2$.\textsuperscript{18,20} Fully oxidized ZrO$_2$ exhibited only the primary bandgap at 5.1 eV with no mid-gap states. Slightly-reduced [3/0.1] exhibited an additional absorbance tail band extending to ~3.1 eV. Low concentration of Vo's, created by 0.1 Lmin$^{-1}$ CH$_4$, (see XPS data Fig. 2d) [3/0.1], allows absorbance of photons near the middle of the primary bandgap, and creates a pale-yellow color, see photo Fig. 2. Increasing dispersion CH$_4$ (materials [3/0.2], [2.3/0.7], [1.3/1.7]) causes a monotonous enhancement of the intra-band absorbances and grey-color intensification (Fig. 2c). Experimentally\textsuperscript{18,20,22,23,30} and theoretically\textsuperscript{29,34} the intra-band absorbances in the range of 2.8–3.5 eV, can be assigned to electrons being injected from the VB$_{\text{maximum}}$ to approximately the middle of the gap, where extra DOS are made available through the introduction of Vo's. For example, by removing one oxygen atom, a doubly occupied (diamagnetic) F-center\textsuperscript{39} can be created inside the bandgap ZrO$_{2-x}$ at 3.3 eV.$^{39}$

**Structural characterization.** XRD (Fig. 2a) shows that our FSP-made Zr-particles consisted of monoclinic (m-ZrO$_2$ in Fig. 2a) and tetragonal (t-ZrO$_2$ in Fig. 2a) phases, at a ratio [t-ZrO$_2$]: [m-ZrO$_2$] = 4:1 and particle sizes 22–29 nm (monoclinic) to 16–20 nm (tetragonal phase) (Table S2). At ambient P, T, ZrO$_2$ has monoclinic (m) structure with Zr$^{4+}$ atoms sevenfold coordinated by O-anions (space group P2$_1$/c). TEM images, (Figs. 2b, 3), show that all ZrO$_{2-x}$ nanomaterials have quasi-spherical shapes, with highly crystalline Miller planes t- [101].
The more reduced ZrO\(_{2-x}\) nanomaterials show some degree of surface distortion, see Fig. 2b. STEM images (Fig. 3a–c) indicate that the particles retain a high degree of crystal quality even at the more reduced ones. In some cases, formation of vacancies could be evidenced in the STEM images, (Fig. 3c). EDX data (Fig. 3) confirm a strong decrease of the Oxygen/Zr ratio in the more reduced [2.3/0.7] and [1.3./1.7] materials. BET analysis (Table S2) shows progressive SSA-decrease upon increase dispersion-CH\(_4\), attributed to increased aggregation of the particles at increased CH\(_4\), i.e. methane creates hotter flames i.e. methane heat of combustion = 50–55 MJ/kg (https://webbook.nist.gov/chemistry).

Raman spectra (Fig. 4b) exhibit the vibrational modes from both monoclinic and tetragonal crystal phases\(^{40–43}\) (Fig. S4 and Table S3) and absence of carbon peaks (Fig. S1). In ZrO\(_{2-x}\) materials, certain Raman modes are shifted (see Fig. 4b(I–III) and Table S4). More particularly, material [3/0.1] exhibits upshift of + 4 cm\(^{-1}\) at 313 cm\(^{-1}\) mode (Table S4). Material [2.3/0.7] exhibits downshifts of − 5 cm\(^{-1}\), − 2 cm\(^{-1}\), − 4 cm\(^{-1}\) at 313 472 cm\(^{-1}\), and 643 cm\(^{-1}\) respectively (Table S4). Material [1.3/1.7] exhibits downshift of up to 22 cm\(^{-1}\). Such downshifts can be attributed to tensile stress\(^{44}\) effectively lengthening the bonds, see Fig. 4a, i.e. due to loss of oxygen atoms from the lattice. Raman downshifts prevail in the t-ZrO\(_2\) phase; thus, the tetragonal phase is more responsive in the reductive atmosphere in anoxic-FSP. This can be explained by the existence of two different/non-equivalent Zr-O bond conformations in t-ZrO\(_2\),\(^{44}\) corresponding to 4-coordinated Zr(O\(_4\))\(_{2}\) and 3-coordinated Zr atoms (O\(_3\))\(_{2}\) respectively\(^{46}\). For comparison, the t-ZrO\(_2\) matrix consists solely of O\(_{4}\) Zr atoms while the m-ZrO\(_2\) matrix consists of both O\(_{4}\) and O\(_{3}\)\(_{2}\). Accordingly, the present Raman data indicate that removal of oxygen from the ZrO\(_2\) matrices is also non-equivalent, thus is easier to extract oxygen from an O\(_{4}\) site rather than an O\(_{3}\) site by 0.1 eV\(^{22}\), therefore it is easier to reduce t-ZrO\(_2\).

Photocatalytic H\(_2\) production at (millimole gr\(^{-1}\) h\(^{-1}\)). Figure 5a presents the photocatalytic H\(_2\) production from H\(_2\)O, for all our ZrO\(_{2-x}\) materials, under Xenon-illumination. In each panel in Fig. 5a the as-prepared photocatalysts are marked as “a.p”. The time indication in each bar, refers to the post-FSP oxidation-time at 400 °C (see also XRD data in Fig. S3 in S.I.). First, we discuss the as-prepared ZrO\(_{2-x}\) materials i.e., see the first bar in each column group in Fig. 5a. Pristine, (F.O.) ZrO\(_2\) was practically non-photoactive in H\(_2\) production, with a yield of 20 μmol g\(^{-1}\) h\(^{-1}\).

In contrast, a slightly reducing FSP atmosphere, i.e., as-prepared [a.p. 3/0.1], enables an impressive amelioration of H\(_2\) evolution of 1700 μmol g\(^{-1}\) h\(^{-1}\). This demonstrates that anoxic-FSP can provide as-prepared ZrO\(_{2-x}\) material exhibiting millimoles per gram per hour H\(_2\) production. Further increase of O\(_2\)/CH\(_4\) ratio impacted negatively the H\(_2\) photogeneration with a tendency towards a steady production near 500 μmol g\(^{-1}\) h\(^{-1}\) of H\(_2\) for
Figure 5. (a) Photocatalytic H₂ production from H₂O by as-prepared and oxidized ZrO₂-c catalysts under full-solar Xenon-light irradiation. (b) H₂ production by [2.3/0.7] ZrO₂-c catalyst under various oxidation times (400 °C). (c) Comparison of photocatalytic H₂ production by the best performing ZrO₂-c catalysts under full-solar Xenon-light versus visible 405 nm LED irradiation. (d) XPS spectra, (e) EPR spectra, indicating the evolution of the Vo's under oxidation of [2.3/0.7] ZrO₂-c. (f) Schematic DOS configuration and excitation under visible 405 nm, see full DFT data in S.I. Fig. S10.
the highly reduced as-prepared materials (see the first bar in each group in Fig. 5a). Soft oxidation by calcination at 400 °C under ambient O₂, exerted a dramatic influence on the H₂-photoproduction: a characteristic bell-shaped dependence was observed for the [3.0/0.2] and [2.3/0.7] materials. The optimum oxidation time was 90 min for [2.3/0.7] ZrO₂−x, which achieved a remarkable yield of 2428 μmol H₂ g⁻¹ h⁻¹. The best performance of the [3.0/0.2] ZrO₂−x material was 1500 μmol H₂ g⁻¹ h⁻¹ (Fig. 5a). Table S5 summarizes a comparison of FSP-ZrO₂−x versus other pertinent ZrO₂−x materials reported in the literature (see also Fig. S7).

The catalyst with the higher H₂ yield, [2.3/0.7]-90, is highly recyclable, (Fig. S5a), retaining 100% of its activity after two reuses and > 96% after four reuses. XRD (Fig. S5b), shows that the [2.3/0.7]-90 crystal remains intact after 4-uses. Concurrently, DRS-UV/Vis (Fig. S5c), demonstrates that its light-absorption profile remains also intact. As we discuss hereafter, optimization of monomeric Vo-concentration is determinant for photocatalytic activity. In [2.3/0.7]-90, the monomeric Vo’s is optimized, see EPR and XPS data in Figs. 5d,e. However, further oxidation of Vo’s tends to delimit the photocatalytic activity. In [2.3/0.7]-90 material, the monomeric vacancies are not altered, neither the ZrO₂−x crystal. Thus, the ZrO₂−x provide a robust reusable photocatalyst.

Discussion

The data in Fig. 5a demonstrate that there are two options to achieve high-photocatalytic performance ZrO₂−x materials: either (i) to be prepared at low O₂/CH₄ ratio e.g. [3.0/0.1], or (ii) after a soft post-FSP oxidation of more reduced materials e.g. [2.3/0.7]. Very-high O₂/CH₄ ratio [1.3/1.7] results in highly-reduced ZrO₂−x which cannot be improved by post-FSP oxidation.

The origins of these trends can be understood by considering the types and populations of the Vo’s in ZrO₂−x. Figure 5b,d,e indicate a correlation of the H₂ production rates for the [2.3/0.7] ZrO₂−x catalysts, with the Vo’s detected by XPS, Fig. 5d, and EPR Fig. 5e. The XPS and EPR data show a clear decrease in the population of Vo of the [2.3/0.7] material upon oxidation at 400 °C. Importantly, theoretical simulation of the EPR signals, Fig. 6, allows distinction between Vo-clusters versus monomeric Vo's. For example, in [a.p. 2.3/0.7] Vo clusters prevail, while in [3.0/0.1], monomeric Vo’s prevail, as we can see from percentages in Fig. 6c. Oxidation progressively eliminates Vo clusters towards monomeric Vo’s. This is also evident from the progressive elimination of the deep-grey color, and the changes in the UV–Vis spectra (Fig. 58 in SI). Taking this information into account, the bell-shaped H₂ production trend in Fig. 5b, indicates that a high concentration of O-vacancies, forming Vo clusters, is detrimental to the photocatalytic activity of ZrO₂−x. Fewer Vo’s are better suited for optimal photocatalytic activity (see trend in Fig. 5a, for [2.3/0.7]). However, further oxidation of Vo’s tends to delimit the photocatalytic activity. This teaches us that a quantitative control of the Vo’s clusters versus monomeric Vo is necessary, to achieve high-performance photocatalytic ZrO₂−x, see full trend in Fig. 6c. We consider that this factor was also of pertinence in the magnesiothermically reduced ZrO₂−x materials.22 Although not noticed by these authors, inspection of their EPR spectra, shows that these correspond to Vo clusters, which concurs with their limited H₂ production of 506 μmol H₂ g⁻¹ h⁻¹, resembling our as-prepared [2.3/0.7] material.

The data under visible 405 nm LED irradiation (Fig. 5c), indicate that significant part of photocatalytic H₂ production, at least 70% versus the solar-light photons, can be excited by visible 405 nm photons (3.1 eV). Taking into account the DRS-UV/Vis data, (Fig. 2c) this can be attributed to the occurrence of the mid-gap states, (Fig. S1). Theoretical DFT calculations (Fig. S10) show that in ZrO₂−x, few oxygen vacancies can create mid-gap states, located at energy distances around 3.0 eV from both the VB-top and ~2 eV from the CB-bottom. Thus, in ZrO₂−x the 3.1 eV photons (405 nm LED) are able to excite two consecutive electron transitions, (Fig. 5f). Increased anoxicity, i.e., as in material [2.3/0.7], enhances the DOS band-tailing (see S.I. Figs. S10 and 5f). This would increase the probability of two-photon electron photoexcitation via VB → Vo, and Vo → CB. These electrons are favorably transferred to the Pt particles, which act as electron collectors i.e. work function of Pt, q = +0.9 eV versus NH₄⁶, is favorable for acceptance of electrons from the highly-excited electrons in the CB.

Quantitative analysis of Vo-clusters versus monomeric Vo’s, by EPR and XPS. Numerical EPR simulations, dashed lines Fig. 6a, show that monomeric Vo’s were characterized by an inhomogeneous lineshape with linewidth ΔH_monomer = (9.4 ± 0.1) Gauss and a rhombic g_monomer-tensor, (Table S5). Vo clusters are characterized by a Lorentz line-shape and ΔH_cluster = (4.6 ± 0.1) Gauss and isotropic g_cluster-tensor, (Table S6).

The structural significance of this is: for isotropic EPR signals with low g-anisotropy, a Gaussian line-shape is the fingerprint of the so-called inhomogeneously-broadened S = 1/2 states⁴⁷,⁴⁸ which is indicative of isolated Vo’s, with no-interactions⁴⁷,⁴⁸. Physically, this indicates that in the ZrO₂−x, particles produced under low CH₄-flow e.g. [3.0/0.1], monomeric isolated VoEPR⁴⁷ centers. The Lorentz line-shape of the Vo clusters indicates that it originates from Vo centers with spin-exchange and/or fast dipolar interactions. In ZrO₂−x, this Lorentz line-shape indicates formation of Vo-clusters upon increasing dispersion-Ch₄.

Comparing the XPS data for surface-Vo’s Fig. 6d) versus the quantitative data for total-paramagnetic Vo’s, (Fig. 6c and Table S7 in SI), derived from the EPR spectra (Fig. 6b) and their deconvolution in monomer/cluster (see example for [1.3/1.7] in Fig. S9 in SI), we notice a correlation: highly reduced ZrO₂−x have higher surface-Vo’s, and total paramagnetic Vo’s. Figure 6e provides an overview plot, which shows that optimization of H₂ photocatalysis can be achieved via optimization of Vo-clusters versus monomeric Vo’s by two routes: (i) control of FSP anoxicity, or (ii) by soft post-FSP oxidation. This demonstrates that our novel anoxic-FSP process allows facile synthesis of solar-light active nano-ZrO₂−x via engineering of lattice-vacancies, Vo. Control of monomeric Vo clusters of Vo is the key-parameter toward Highly-Performing-Photocatalytic ZrO₂−x. The anoxic-FSP process presented here, should be easily adaptable to existing industrial-scale FSP reactors. This offers an efficient technology that can be adopted in the future and provide new tools for the design of other families of photocatalytic nanomaterials via control of oxygen vacancies.
Methods

Synthesis of nanomaterials by FSP. Precursor solution was prepared by dissolving Zirconium (IV) Propoxide (70 wt% in 1-propanol) in xylene and acetonitrile in a 2.2/1.0 ratio at a concentration of 0.25 M. Then, the solution was fed through a capillary at 3 ml min⁻¹ and dispersed to a self-sustained oxygen/methane (4–2 L min⁻¹) pilot flame to initiate combustion. An important distinction must be made which leads to the innovation of the presented work. ZrO₂−ₓ materials were prepared by modifying the dispersion feed. While keeping the 3 ml min⁻¹ dispersion constant, methane gas (CH₄) was fed along with the traditional dispersion gas (O₂). The resulting high temperatures and hydride formation through the decomposition of methane lead to the formation of ZrO₂−ₓ. Furthermore, the protocol of methane injection ensures the formation of bulk defects as the particle is influenced at its early stages of flight, at the primary particle stage. Finally, the pressure drop was fixed at 1.5–2.0 bar, and an additional 10 L min⁻¹ O₂ sheath was used to aid in particle collection which was made possible by a vacuum pump (Busch V40) and by a glass microfiber filter (GF 6 257, Hahnemühle, Dassel, Germany).
Characterization techniques. Powder X-Ray Diffraction (XRD) data were collected at room temperature using a Bruker D8 Advance 2theta diffractometer with copper radiation (Cu Ka, λ = 1.5406 Å) and a secondary monochromator operating at 36 kV and 36 mA. Crystal size is calculated by the Scherrer formula. X-Ray photo-electron spectroscopy (XPS) data were collected by a surface analysis ultrahigh vacuum system (SPECS GmbH) equipped with a twin Al–Mg anode X-ray source and a multichannel hemispherical sector electron analyzer (HSA Phoibos 100). The base pressure was 2 × 10⁻⁹ mbar. A monochromatized Mg Kα line at 1253.6 eV and analyzer pass energy of 20 eV were used in all XPS measurements. The binding energies were calculated with reference to the energy of C1s, peak of contaminant carbon at 284.5 eV. The peak deconvolution was calculated using a Shirley background.

Raman HORIBA-XploRA Plus spectrometer, equipped with an Olympus BX41 microscope. A 785 nm diode laser was used as an excitation source, and the laser beam was focused on the sample with the aid of the microscope. Before measurement, each powder material was softly pressed between two glass plates to form a pellet-like structure. Brunauer–Emmett–Teller (BET) adsorption–desorption isotherms were recorded at 77 K using a Quantachrome NOVA touch LX2. Outgassing was performed at 80 °C for 5 h under vacuum, before the measurements. The absorption data points in the relative pressure P/P₀ range of 0.1–0.3 was used to calculate the specific surface area (SSA).

Electron paramagnetic resonance spectroscopy. The X-band electron paramagnetic resonance (EPR) spectra of ZrO₂/ZrO₂-x materials were recorded with a Bruker ER200D spectrometer at 77 K, equipped with an Agilent 5310A frequency counter. The spectrometer was running under a custom-made software based on LabView. Adequate signal-to-noise ratio was obtained after 15–20 scans, with a microwave power fixed at 20 mW. The EPR instrumental conditions were as follows: microwave frequency = 9.53 GHz and modulation amplitude = 10 Gpp.

Theoretical analysis of the EPR spectra. The experimental EPR spectra were simulated using the EasySpin software. A $S = \frac{1}{2}$ spin Hamiltonian was used $\hat{H} = \beta \hat{B} \cdot \hat{S}$ where $\beta$ is the Bohr magneton, $\hat{B}$ is the applied magnetic field, $\hat{g}$ is the spectroscopic $g$-tensor and $\hat{S}$ the spin angular momentum. The X-band electron paramagnetic resonance (EPR) spectra were recorded with a Bruker ER200D spectrometer at 77 K, equipped with an Agilent 5310A frequency counter. The spectrometer was running under a home-made software based on LabView. Adequate signal-to-noise ratio was obtained after 30–50 scans. The EPR instrumental conditions were as follows: microwave frequency = 9.55 GHz, modulation frequency = 50.00 kHz, and modulation amplitude = 10 Gauss peak-to-peak.

Photocatalytic H₂ evolution procedure. The photocatalytic hydrogen reactions were realized into a double wall Pyrex reactor, cooled with tap circulation ($T = 25 ^\circC$). Light source was a Solar Simulator (Scientech, Class AAA, model SciSun-150) with average irradiation intensity of 180 W m⁻² equipped with a xenon lamp of 150 W and Air Mass filter (1 sun, AM1.5G). As Visible light source was used a Led lamp FireEdge™ FE410 (λ = 405 nm) supplied by Phoseon company, which power intensity was set to be 180 W m⁻², using a power meter (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). Each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlabs Inc., USA). In each experiment, 50 mg of the catalyst was suspended into 150 ml water/methanol mixture (Thorlas...
50. Stathi, P., Solakidou, M. & Deligiannakis, Y. Lattice defects engineering in W-, Zr-doped BiVO₄ by flame spray pyrolysis: Enhancing photocatalytic O₂ evolution. *Nanomaterials* **11**, 501 (2021).

**Acknowledgements**
This research was funded by the Hellenic Foundation for Research and Innovation (H.F.R.I) under the “First Call for H.F.R.I Research Projects to support Faculty members and Researchers and the procurement of high-cost research equipment grant” (Grant HFRI-1888).

**Author contributions**
A.M.; Particle synthesis and characterization, writing-original draft, A.Z.; Particle synthesis, Writing-original draft, M.S.; Photocatalytic experiments, Writing—review and editing, S.S. TEM analysis, Y.D.; Conceptualization, Supervision, Funding acquisition, Writing—review and editing.

**Competing interests**
The authors declare no competing interests.

**Additional information**

**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1038/s41598-022-19382-3.

**Correspondence** and requests for materials should be addressed to Y.D.

**Reprints and permissions information** is available at [www.nature.com/reprints](http://www.nature.com/reprints).

**Publisher’s note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

[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/](http://creativecommons.org/licenses/by/4.0/).

© The Author(s) 2022