Sonochemical Synthesis of Large Two-Dimensional \( \text{Bi}_2\text{O}_2\text{CO}_3 \) Nanosheets for Hydrogen Evolution in Photocatalytic Water Splitting

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Laterally large (≈3 µm), atomically thin 2D \( \text{Bi}_2\text{O}_2\text{CO}_3 \) nanosheets (2D bismuth oxycarbonate, 2D bismutite) are fabricated via sonochemically assisted, template-free synthesis. Keys to the synthesis of the freestanding, laterally large 2D \( \text{Bi}_2\text{O}_2\text{CO}_3 \) nanosheets from bulk Bi powder are choice of suspension medium, controlled reaction temperatures, and several hours processing time. Lateral sizes of 2D \( \text{Bi}_2\text{O}_2\text{CO}_3 \) can be controlled between µm-sized nanosheets and tens of nm sized nanoflakes solely based on the choice of suspension medium. The here introduced 2D \( \text{Bi}_2\text{O}_2\text{CO}_3 \) nano-sheets/-flakes are then hybridized by a simple mix-and-match approach with TiO\(_2\) nanoparticles for testing in suspension-type photocatalytic hydrogen production via water splitting. This introduces the 2D \( \text{Bi}_2\text{O}_2\text{CO}_3 \) as a prospective noble-metal-free catalyst component with TiO\(_2\) for photocatalytic hydrogen evolution, beyond \( \text{Bi}_2\text{O}_2\text{CO}_3 \)'s current use as photocatalyst for organic pollutant degradation. These results enrich the fabrication toolbox of emerging 2D pnictogen oxycarbonates toward large 2D nanosheets and demonstrate the potential of 2D \( \text{Bi}_2\text{O}_2\text{CO}_3 \) as a catalyst component for hydrogen evolution in photocatalytic water splitting.

1. Introduction

2D pnictogens such as 2D antimony (“antimonene”) and 2D bismuth (“bismuthene”) have spurred tremendous interest in electronics, energy applications, and catalysis.[1–5] Likewise, more recently, also 2D pnictogen compounds have come into focus because of their combination of unusual, potentially useful properties in electronics, energy, and catalysis.[6–13] For the case of bismuth, this includes recent work on binary 2D bismuth oxides,[10–13] and 2D ternary and multinary oxygen-containing bismuth compound phases, including 2D Bi-oxyhalides, 2D \( \text{Bi}_2\text{WO}_6 \), 2D \( \text{Bi}_2\text{MoO}_6 \), or 2D \( \text{BiVO}_4 \).[2,3,9,14,15]

Amongst the ternary bismuth compound phases, the bismuth oxycarbonate (BOC) \( \text{Bi}_2\text{O}_2\text{CO}_3 \) phase, also called bismutite and bismuth subcarbonate (\( \text{BiO}_2\text{CO}_3 \)), is of particular interest.[16] \( \text{Bi}_2\text{O}_2\text{CO}_3 \) has an intrinsically layered structure composed of alternating \( \text{Bi}_2\text{O}_2^{2+} \) and \( \text{CO}_3^{2−} \) sub-layers and is a semiconductor with a band gap of ≈3.1–3.5 eV.[16] In nanostructured form \( \text{Bi}_2\text{O}_2\text{CO}_3 \) has been shown to have useful properties in particular toward energy, catalysis, and photocatalysis.[16] In particular for photocatalysis, 2D morphology can offer benefits over other morphologies including intrinsically high specific surface areas and short migration lengths of photogenerated charge carriers to the reaction fronts on the 2D materials’ surfaces. This can reduce recombination losses and thus lead

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to higher activity of 2D forms of common materials.\cite{17} Synthesis of Bi$_2$O$_2$CO$_3$ in atomically thin 2D morphology remains however underdeveloped, in particular in terms of rational control over lateral sizes and thicknesses.\cite{16,18–49} Consequently, it remains unknown if bringing Bi$_2$O$_2$CO$_3$ to 2D form could also open up new photocatalytic applications fields?

Toward filling this gap, we here report a simple method of sonochemically assisted\cite{50,51} template-free synthesis of laterally large, atomically thin 2D Bi$_2$O$_2$CO$_3$ nanosheets. In particular, our synthesis approach readily allows control over lateral 2D Bi$_2$O$_2$CO$_3$ size between unusually large, μm-sized nanosheets and small, tens of nm sized nanoflakes solely depending on suspension medium.

While nanostructured Bi$_2$O$_2$CO$_3$ is a popular photocatalyst for organic pollutant and NO degradation,\cite{16,18–47} it has to date received little attention for photocatalytic solar fuel production such as in photocatalytic hydrogen evolution reaction (HER) from water splitting.\cite{35,36,52} This is despite photocatalytic HER being one of the key technologies to meet the demands of the growing energy crisis in a sustainable way.\cite{53,54} Photocatalytic HER critically hinges on the availability of (cost-)efficient, scalable (heterojunction) catalysts and/or (co-)catalysts and the search for these is an ongoing challenge.\cite{53,54}

To this end, we here hybridize our newly introduced 2D Bi$_2$O$_2$CO$_3$ nano-sheets/-flakes by a simple mix-and-match approach with TiO$_2$ nanoparticles and test these hybrids as heterogeneous photocatalysts in suspension-type photocatalytic HER from water splitting. Our results thereby introduce 2D Bi$_2$O$_2$CO$_3$ as a prospective noble-metal-free catalyst component with TiO$_2$ for photocatalytic HER, beyond the current use of Bi$_2$O$_2$CO$_3$, largely as photocatalyst for organic pollutant degradation.

2. Results and Discussion

2.1. Synthesis of 2D Bi$_2$O$_2$CO$_3$ Nano-Sheets/-Flakes

Our sonochemically assisted synthesis (Figure S1, Supporting Information) first encompasses liquid-phase-exfoliation (LPE)\cite{50,51} type treatment of bulk Bi powder which has a layered, buckled rhombohedral β-Bi/A7 crystal structure\cite{55} and a maximum particle size of up to 150 μm (Figure S2, Supporting Information). To provide energy to the system we employ ultrasonic bath immersion.\cite{50,51} We undertake our sonication with air-tight closed sample vials that are immersed in the temperature-controlled sonication bath. Importantly, we screen five different suspension media ("solvents") for the Bi during our sonochemical treatment, namely water (H$_2$O), methanol (MeOH), isopropanol (IPA), ethanol (EtOH), and (motivated by prior literature\cite{56}) IPA:H$_2$O (4:1) mixture. All solvents are of technical grade and are used without particular purging to remove dissolved gases before synthesis. A wide screening of solvents is often key in LPE and related techniques as 2D materials’ suspendabilities are known to be highly solvent dependent.\cite{58} Important for our recipe development, ultrasonication employs very long processing time (15 h) and very close control of bath temperature during sonication in either “room temperature” (RT, 22–26 °C) or “ice bath” conditions (ICE, 0.1–2.2 °C). Subsequent to sonication, suspensions are centrifuged and then supernatant is collected for further characterization and photocatalytic testing. We note that after the sonication step the suspensions are visibly opaque compared to parent solvents, but that after the centrifugation step the suspensions look virtually as translucent as their parent solvents to the naked eye (Figure S3, Supporting Information). This suggests that concentrations of material in centrifuged suspensions are low. Gravimetric quantification of concentration of solid content via solvent evaporation corroborates this and put concentrations in our suspension to a maximum of ≈50 mg L$^{-1}$ (which is the detection limit of our balance system). A detailed description of our synthesis procedure is given in the Supporting Information.

Figure 1 shows scanning electron microscopy (SEM) images of obtained products from sonication and centrifugation (after drop casting onto SiO$_2$/Si wafer) for MeOH (Figure 1a,b) and H$_2$O (Figure 1d,e) from RT and ICE processing. The SEM images confirm that, despite the visually translucent suspensions, ample solid material is suspended in our sonicated and centrifuged samples. Strikingly, while MeOH (both in ICE and RT) produced small nanoflakes (lateral sizes average ≈80 nm, with a distribution tailing down to ≈10 nm), H$_2$O resulted in large 2D nanosheets of roughly square shapes with lateral sizes.
of several μm (ICE: average 3.5 μm ± 2.6 μm standard deviation; RT: average 2.3 ± 1.3 μm) and an apparently low thickness (as flakes appear electron transparent in the SEM images). We note that in the SEM and atomic force microscopy (AFM) images in Figure 1d–f the 2D nanosheets have restacked during drop casting onto SiO2/Si supports, as common for 2D LPE-type materials.[50] While the H2O preparations are predominately characterized by the large 2D nanosheets, remaining smaller sheet-like objects (<1 μm lateral) in Figure 1d–f are assigned to fragments of such 2D nanosheets either from interrupted lateral growth or post-growth fragmentation. IPA (RT, ICE), EtOH (RT, ICE), and IPA: H2O (RT) lead to small nanoflakes (Figure S4a–e, Supporting Information) akin to MeOH, which for IPA and EtOH also appear to be thicker compared to H2O and MeOH. IPA: H2O (ICE) produces thin square nanosheets with μm lateral sizes (Figure S4f, Supporting Information).

In Figure 1c,f, we present AFM measurements to ascertain the thickness of the laterally small MeOH ICE and laterally

![Image]( Figure 2. a–c) MeOH ICE studied by overview BF-TEM (a), lattice resolution side-view (b, FT in inset) and lattice resolution top-view (c, FT inset) BF-TEM of nanoflake. d–f) H2O ICE studied by overview (d) and lattice resolution (e, FT in inset, top-view of flake) BF-TEM and top-view SAED (f). g) A structural model of orthorhombic 2D Bi2O2CO3 (powder diffraction file: 04-009-8533) in top-view along [010] (left) and side-view along [001] (middle) and a simulated SAED/FT pattern (middle) for Bi2O2CO3 along [010] zone axis (i.e., top-view) with salient reflections matches to experimental data in (e) and (f) highlighted. For a corresponding SAED/FT simulation of side-view see Figure S6, Supporting Information.)
large \(H_2O\) ICE products. Figure 1c confirms that MEOH ICE results in thin (~2.5–3 nm) but laterally small (~10 nm to \(\approx80\) nm) nanoflakes. In very stark contrast, \(H_2O\) ICE in Figure 1f resulted in approximately square-shaped nanosheets with ultra-high aspect ratios, with lateral sizes of \(\approx3\) \(\mu\)m and atomic-scale thicknesses of only 4–6 nm. Figure S5, Supporting Information, shows that MEOH RT results in correspondingly small nanoflake morphology and that \(H_2O\) RT results in correspondingly large, atomically thin 2D nanosheet morphology.

Figure 2a–c presents a structural characterization of the MEOH ICE products by bright-field (BF) transmission electron microscopy (TEM, overview Figure 2a, lattice resolution side-view in Figure 2b and lattice resolution top-view in Figure 2c with Fourier Transforms [FTs] in insets). TEM confirms the small lateral size, atomic thickness of the nanoflakes and additionally proves their crystalline nature. Figure 2d–f shows corresponding TEM data for the \(H_2O\) ICE products in terms of BF-TEM overview (Figure 2d), lattice resolution TEM in top-view (Figure 2e, FT in inset) and a selected area electron diffraction pattern (SAED) from top-view (Figure 2f). For the \(H_2O\) ICE preparations, TEM confirms the large lateral size, atomic thickness, and approximate square shape, and additionally proves the single crystalline nature of the large nanosheets. Laterally smaller (~1 \(\mu\)m) fragments in Figure 2d are ascribed to interrupted growth or post-growth fragmented nanosheets.

To identify the crystal structure of the nanoflakes and nanosheets from the lattice resolution TEM and SAED data, we consider that the starting educt is Bi, and that reactions to \(Bi_2O_3\) and \(Bi_2O_2C\) via oxygen and carbon from MEOH and \(H_2O\) decomposition in sonication and via dissolved oxygen and carbonate ions \(CO_3^{2-}\) from dissolved \(CO_2\) in the solvents are likely reaction pathways during our long sonication processes. Interestingly, comparing against multiple Bi, \(Bi_2O_3\) and \(Bi_2O_2C\) database structures (see extended discussion in Supporting Information), we consistently find that the best match to our experimental top-view TEM/SAED data (Figure 2c,e,f) is orthorhombic \(Bi_2O_2C\) viewed along the \(\{010\}\) zone axis (Figure 2g, left) (Please note that instead of the orthorhombic unit cell alternatively often a tetragonal unit cell is used to describe \(Bi_2O_2CO_3\). We discuss our results using this tetragonal notation in the Supporting Information). Our nanoflakes and nanosheets are thus layered orthorhombic \(Bi_2O_2CO_3\) with the alternating \(Bi_2O_3\) and \(CO_3^{2-}\) sub-layers parallel to the substrate (Figure 2g, middle, orthorhombic \(Bi_2O_2CO_3\) with \(\{010\}\) or \(\{001\}\) texture). Beyond structure identification from top-view images, for the MEOH ICE we also obtained lattice resolved side-view images of the 2D flakes (Figure 2b). These confirm their atomically thin “few-layer” nature and we measure lattice fringes in the side view of \(\approx0.68\) nm, which is also in excellent agreement of the layer distance in orthorhombic \(Bi_2O_2CO_3\) of \(\approx0.68\) nm (corresponding to \(\{010\}\) plane family, see also side-view SAED/FT simulation in Figure S6, Supporting Information). Thus our side-view TEM data also corroborates 2D \(Bi_2O_2CO_3\) with \(\{010\}\) texture. Our TEM-based structural phase assignment is also backed up on a larger scale by Bragg-Brentano X-ray diffractometry (XRD) measurements of nanosheets drop-cast onto \(SiO_2/Si\) wafers (Figure S7, Supporting Information). The measured XRD patterns are highly consistent with \(Bi_2O_2CO_3\) with \(\{040\}\) (and equivalently \(\{010\}\)) texture. Notably, XRD is inconsistent with other possible candidate phases; most importantly excluding all \(Bi_2O_3\) polymorphs (see Supporting Information for extended discussion). Furthermore, XRD does not indicate the presence of any other phases, thus confirming phase purity of the 2D \(Bi_2O_2CO_3\) nanosheets from our synthesis procedure. The phase purity is also corroborated by the number of flakes/sheets observed at lattice resolution in TEM (7 for MEOH, 15 for \(H_2O\) which are all consistently best indexed to 2D \(Bi_2O_2CO_3\) along \(\{010\}\) zone axis. Similarly, we find that MEOH RT and \(H_2O\) RT synthesis products are best matched by 2D \(Bi_2O_2CO_3\) (Figure S8, Supporting Information). Our phase assignment therefore suggests that during 15 h sonication, the Bi has not only transformed to 2D nano-flake/-sheet morphology but concurrently got oxidized and bridged/intercalated by \(CO_3^{2-}\) to form 2D \(Bi_2O_2CO_3\). We will discuss a suggested mechanism for this process below.

Additional characterization data of our 2D \(Bi_2O_2CO_3\) nanoflakes/-sheets is presented in Figures S9–S13, Supporting Information. Energy dispersive X-ray spectroscopy (EDX) mapping in SEM (Figure S9, Supporting Information) clearly shows the homogeneous presence of Bi, O, and C in \(H_2O\) ICE nanosheets, fully consistent with the 2D \(Bi_2O_2CO_3\) assignment. X-ray photoelectron spectroscopy (XPS) measurements of the \(H_2O\) ICE samples (Figures S10–S12, Supporting Information) confirm Bi 4f, O 1 s, and C 1 s signatures consistent with \(Bi_2O_2CO_3\) and exclude the presence of metallic Bi. Photo-luminescence (PL) measurements of \(H_2O\) (ICE) nanosheets and MEOH (ICE) flakes on \(SiO_2/Si\) in Figure S13, Supporting Information, reveal a PL emission peak at \(\approx550\) nm (for \(532\) nm excitation), consistent with prior reports of PL signatures of \(Bi_2O_2CO_3\). Combined, TEM/SAED, XRD, EDX, XPS, and PL all corroborate the assignment of our \(H_2O\) nanosheets and MEOH nanoflakes to 2D \(Bi_2O_2CO_3\).

We note however that we observe a strong solvent dependence not only in terms of resulting 2D \(Bi_2O_2CO_3\) nano-flake/-sheet morphology as between MEOH versus \(H_2O\), but also in terms of resulting phase when comparing with IPA, EtOH, and IPA: \(H_2O\) solvents. While for MEOH and \(H_2O\), we obtain 2D \(Bi_2O_2CO_3\) nano-flakes/-sheets, as described above, for IPA (RT, ICE) amorphous nanoflakes are obtained, and for EtOH amorphous (ICE) or Bi(001) (RT) nanoflakes are obtained (Figure S14, Supporting Information). In turn for IPA: \(H_2O\) (RT) again 2D \(Bi_2O_2CO_3\) nanosheets are obtained, while for IPA: \(H_2O\) (ICE) amorphous nanoflakes result (Figure S15, Supporting Information). This underlines an active role of the solvent in the transformation, oxidation, and carbonate bridging/intercalation of initial Bi into the 2D \(Bi_2O_2CO_3\) nano-flakes/-sheets, with best results toward crystalline 2D \(Bi_2O_2CO_3\) in \(H_2O\) for large nanosheets and MEOH for small nanoflakes, respectively.

Comparing to prior literature, the observation of 2D \(Bi_2O_2CO_3\) is surprising: Recent work by Pumera et al. found for a similar sonication scheme to ours and also in water, not 2D \(Bi_2O_2CO_3\) but large metallic \(\beta\)Bi[42-1] nanosheets to be produced while MEOH resulted in small metallic \(\beta\)Bi(001) nanoflakes. In fact, Pumera et al. explicitly excluded bismuth oxidation in their study. Key differences were however the excitation energy source (tip sonication vs bath sonication here) and in particular a much shorter sonication time (maximum 60 min vs 15 h here). Pumera et al. suggested for their
60 min sonications result in H2O not only physical exfoliation of the parent Bi powder to take place but due to Bi’s low melting point (≈271 °C), Bi melting under the tip sonicator, dissolution effects, and then crystallite growth in suspension to partake in large nanosheet formation.[13,33] In contrast, in MeOH for 60 min, Pumera et al. suggested fragmentation (rather than crystallite growth as in H2O) to be the dominant mechanism for small nanoflake formation. While Pumera et al.’s maximum 60 min processing times resulted in metallic β-Bi nano-sheets/-flakes, we suggest that for our much longer 15 h processing, in addition to the crystallite growth/fragmentation mechanisms suggested by Pumera et al. also concurrent oxidation and carbonate bridging/intercalation processes of the Bi in H2O and MeOH take place. Compared to many prior reports on Bi2O2CO3 synthesis,[16] we notably do not employ a dedicated source of oxygen or carbonate ions in our synthesis but only Bi as dedicated precursor in the various solvents. We thus suggest that the sources of the required oxygen and carbon for our proposed mechanism are coming from solvent decomposition under ultrasound and dissolved atmospheric oxygen and carbonate CO32– ions from dissolved atmospheric CO2 in the solvents (see also Supporting Information), which is a precursor in situ formation pathway also consistent with prior reports.[17–19,31,39] Thus bismuth oxy carbonate nano-sheets and -flakes are produced under our conditions in H2O and MeOH, respectively. This oxidation and carbonate bridging/intercalation process was arrested in the Pumera et al. work due to their shorter processing time.

In prior reports on 2D Bi2O2CO3, lateral sizes of atomically thin 2D Bi2O2CO3 were largely limited at ≈1 µm,[16,18–49] while our work increases lateral nanosheet sizes to ≈3 µm. Our report therefore so far establishes a controllable synthesis route for laterally large (≈3 µm), atomically thin 2D Bi2O2CO3 nanosheets (H2O ICE and RT) and for laterally small (≈80 nm), atomically thin 2D Bi2O2CO3 nanoflakes (MeOH ICE and RT), importantly solely based on the choice of solvent.

2.2. Photocatalytic Testing of 2D Bi2O2CO3 Nano-Flakes/-Sheets

Nanostructured Bi2O2CO3 has been prior reported to have interesting properties as photocatalyst for predominantly organic pollutant degradation.[16] To expand on this, in the remainder of this report we investigate the here introduced 2D Bi2O2CO3 nanosheets and nanoflakes as heterogeneous (co-)catalysts in suspension-type photocatalytic HER from water splitting under ultraviolet (UV) excitation. To date, Bi2O2CO3 has predominantly been screened as a photocatalyst for organic pollutant degradation and NO removal.[16,18–34,47–49] To this end, not only monolithic Bi2O2CO3, alone but also various mixed-dimensionality hybrids of Bi2O2CO3 with metals, metal oxides, sulfides, Bi-compounds, and carbon-nitride (g-C3N4) have been investigated.[16,22–24,26,27,36,44,52,60–62] Only very little work has however thus far focused on photocatalytic HER from Bi2O2CO3,[16] namely only hybrids consisting of Bi2O2CO3 nanoplates/PT.[35] Bi2O2CO3 nanoparticles/g-C3N4/PT.[34] and Bi2O2CO3 nanoparticles/Bi.[36] Further, despite the archetypical importance of TiO2 as photocatalyst,[53,54] only very few reports on potentially synergetic performance from Bi2O2CO3/TiO2 hybrids exist.[56,60] Few prior examples are Bi2O2CO3 nanoflowers hybridized with TiO2 nanoparticles on graphene sheets[60] and Bi2O2CO3 nanoplates hybrids with TiO2 nanoparticles and carbon networks,[61] whereby both hybrids showed higher photocatalytic activity in organic dye degradation than their separate components. Notably however, another study reported reduced photocatalytic dye degradation activity from hybridizing Bi2O2CO3 to TiO2 compared to neat TiO2.[62] In either case, no work has as of yet hybridized atomically thin 2D Bi2O2CO3 with TiO2 or studied Bi2O2CO3/TiO2 hybrids for photocatalytic HER, as we do here.

For photocatalytic HER measurements via water splitting a sacrificial agent, which is often an alcohol, is commonly used as a hole scavenger.[63–69] One of the most commonly used systems in photocatalytic HER is a 1:1 H2O:MeOH mixture.[63,64] Therefore for the 2D Bi2O2CO3 nano-flakes/-sheets exfoliated in MeOH and H2O, respectively, the respective other solvent was added toward obtaining 2D Bi2O2CO3 nano-flakes/-sheets in 1:1 H2O:MeOH mixture. This consistency of sacrificial agent concentration ensures direct quantitative comparability of HER results for MeOH and H2O preparations (within limits of the estimated maximum solid content concentrations of maximum of ≈50 mg L−1). To elucidate possible roles of the 2D Bi2O2CO3 in photocatalysis, HER measurements were undertaken for 1) neat 2D Bi2O2CO3 nano-flakes/-sheets and 2) 2D Bi2O2CO3 nano-flakes/-sheets hybridized with TiO2 nanoparticles (Degussa P25, average particle size ≈25 nm). TiO2 nanoparticles are archetypal photocatalysts, but are comparatively inactive toward HER, thus commonly requiring a HER cocatalyst such as expensive Pt.[53,54,63] Thereby combination of 2D Bi2O2CO3/TiO2 to hybrids allows to assess if 2D Bi2O2CO3 can aid HER as a photocatalyst component. Notably most of the few prior reports on HER with Bi2O2CO3 hybrids had Pt as additional co-catalyst present in the hybrids,[35,52] thus masking potential intrinsic Bi2O2CO3 performance toward HER. See Supporting Information for details of sample preparation and setup for HER testing.

Figure 3a shows that for neat, small 2D Bi2O2CO3 nanoflakes (MeOH ICE), we observe no appreciable photocatalytic HER response above noise level. This suggests that under our conditions, our 2D Bi2O2CO3 nanoflakes are not active as a monolithic photocatalyst for HER. When however hybridizing our 2D Bi2O2CO3 nanoplates (MeOH ICE) with TiO2 nanoparticles, we notably get a significant HER response upon UV illumination (Figure 3a). Most importantly, this HER response is significantly larger than the response from neat TiO2 alone (Figure 3a). This suggests that our small 2D Bi2O2CO3 nanoflakes here significantly aid the photocatalytic HER with TiO2. We note that photocatalytic measurements at lower 2D Bi2O2CO3 concentrations (3.8-times lower 2D Bi2O2CO3 concentration compared to Figure 3a) with the same amount of TiO2 result in similar H2 evolution rates (Figure S21, Supporting Information), suggesting that our measurements probe within the plateau region of optimal rate with respect to the 2D Bi2O2CO3, as recommended by Qureshi et al. for photocatalytic measurements standards.[62] TEM of the MeOH ICE 2D Bi2O2CO3 nanoflake/TiO2 nanoparticle hybrids after HER (Figure 3b) indicates that the 2D Bi2O2CO3 nanoflakes (MeOH ICE) are well adhered to the TiO2 nanoparticles.
Figure 3c shows similar HER photocatalysis data for the large 2D Bi$_2$O$_2$CO$_3$ nanosheets (H$_2$O RT) without/with TiO$_2$. Similar to the small MeOH ICE nanoflakes, we find no HER activity for neat, large H$_2$O RT nanosheets. Again, we find however a significant synergetic effect of 2D Bi$_2$O$_2$CO$_3$ nanosheets (H$_2$O RT)/TiO$_2$ hybridization toward a HER photocatalytic response clearly above the performance of neat TiO$_2$. Post-HER TEM likewise indicates good interfacing of the large 2D Bi$_2$O$_2$CO$_3$ nanosheets with TiO$_2$ nanoparticles (Figure 3d).

We note that we find moderate drops in H$_2$ evolution rate (by 20–25% from maximum rate) over the 60 min UV illumination time from the 2D Bi$_2$O$_2$CO$_3$ nano-sheet and -flake with TiO$_2$ hybrids (Figure 3a,c). Such drops in H$_2$ evolution over these timescales are however not uncommon for HER catalysts, but often observed even for benchmarks systems including archetypical Pt/TiO$_2$. Close inspection of Figure 3c (comparing to Figure 2d) indicates that the 2D Bi$_2$O$_2$CO$_3$ nanosheets have developed small holes (few nm) during the 60 min photocatalytic HER reactions, which may be linked with the observed moderate loss in H$_2$ evolution rate.

Our work introduces 2D Bi$_2$O$_2$CO$_3$ nano-flakes/-sheets as a catalyst component with TiO$_2$ for photocatalytic HER from water splitting. In Figures S23 and S24, Supporting Information, we also provide more experimental data and discuss a tentative mechanism behind the observed H$_2$ evolution in the 2D Bi$_2$O$_2$CO$_3$/TiO$_2$ hybrids, whereby our tentative investigation suggests a type-II heterojunction mechanism in the 2D Bi$_2$O$_2$CO$_3$/TiO$_2$ system. Notably in this context, comparing the obtained H$_2$ evolution rates from our 2D Bi$_2$O$_2$CO$_3$ nano-flakes/-sheets with TiO$_2$ toward photocatalytic HER in our conditions suggests that the 2D Bi$_2$O$_2$CO$_3$ nano-flakes/-sheets facilitate the same order of magnitude of photocatalytic HER optimal rate from UV as recently investigated, promising non-noble co-catalysts such as Ni(O$_x$) or Cu(O$_x$) with TiO$_2$ and are more active than, for example, Mn(O$_x$), Co(O$_x$), and Fe(O$_x$) with TiO$_2$ under similar measurement conditions in the same HER setup.

3. Conclusion

In summary, we present a fabrication route which allows template-free synthesis of 2D Bi$_2$O$_2$CO$_3$ with good control over lateral 2D size, ranging from unusually large µm nanosheets...
to few tens of nm small nanoflakes just based on the suspension medium used. This critically adds to the toolbox for 2D pnictogen compound fabrication with emerging applications in (photo-)catalysis, electronics, and energy. As one application example, we test the newly introduced 2D Bi$_2$O$_2$CO$_3$ nano-sheets/-flakes in photocatalysis for sustainable solar fuel generation. In particular, our work introduces 2D Bi$_2$O$_2$CO$_3$ nano-sheets/-flakes as a prospective catalyst component when hybridized with TiO$_2$ for the important HER in photocatalytic water splitting, which extends Bi$_2$O$_2$CO$_3$’s use beyond the currently well-known utilization of Bi$_2$O$_2$CO$_3$ photocatalysts for organic pollutant degradation. Notably, such an extension of use of a well-known pollutant remediation catalyst to production of H$_2$ suggests future work on 2D Bi$_2$O$_2$CO$_3$/TiO$_2$ hybrids as possible dual-use photocatalysts for coupled pollutant degradation and hydrogen production schemes in, for example, waste water valorization.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
T.G., D.E., and B.C.B. planned the experiments. T.G. and N.R. carried out synthesis. T.G. performed TEM, SAED, SEM, and EDX characterization. N.R. carried out the photocatalysis experiments together with T.G. M.S. and A.F. performed XPS, A.G. and S.M.S. PL, and D.H.A. to solvent characterization with T.G. A.L. and A.C. contributed to photocatalytic measurements. J.R. and S.N. contributed to XRD, D.H.A. to solvent and A.F. performed XPS, A.G. and S.M.S. PL, and M.W. and G.F. AFM characterization. T.G. performed TEM, SAED, SEM, and EDX characterization. T.G., D.E., and B.C.B. planned the experiments. T.G. and N.R. carried out the photocatalysis experiments together with T.G. M.S. acknowledges partial support by the European Commission (ErbeSTA, No. 800942) and the Austrian Academy of Sciences OAW (Quantum Light, No. 1847108). The authors also acknowledge the use of facilities at the University Service Centre for Transmission Electron Microscopy (USTEM), Analytical Instrumentation Centre (AIC), and X-Ray Centre (XRC), TU Wien, Austria for parts of this work. The authors acknowledge TU Wien Bibliothek for financial support through its Open Access Funding Programme.

Data Availability Statement
The data that support the findings of this study are available in the Supporting Information of this article.

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