

# One-Step Solvothermal Synthesis of a Carbon@TiO<sub>2</sub> Dyade Structure Effectively Promoting Visible-Light Photocatalysis

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The development of sunlight harvesting chemical systems to catalyze relevant reactions, i.e., water splitting, CO<sub>2</sub> fixation, and organic mineralization, is the key target in artificial photosynthesis but remains a difficult challenge. Titanium dioxide (TiO<sub>2</sub>) has been widely used as a photocatalyst for solar energy conversion and environmental applications because of its low toxicity, abundance, high photostability, and high efficiency.<sup>[1–4]</sup>

However, the application of pure TiO<sub>2</sub> is limited, because it requires ultraviolet (UV) light, which makes up only a small fraction (<4%) of the total solar spectrum reaching the surface of the earth.

Therefore, over the past few years, considerable efforts have been directed towards the improvement of the photocatalytic efficiency of TiO<sub>2</sub> in the visible (vis)-light region.<sup>[5–7]</sup> This has been mainly achieved by introducing various dopants into the TiO<sub>2</sub> structure which can narrow the bandgap. The initial approach to dope TiO<sub>2</sub> materials was achieved using transition metals ions such as V, Cr, or Fe.<sup>[6,8–10]</sup> However, such metal doped materials lack the necessary thermal stability, exhibit atom diffusion and a remarkably increased electron/hole recombination of defect sites, which results in a low photocatalytic efficiency.<sup>[11]</sup> Non-metal doping has since proved to be far more successful and has been extensively investigated. Thus, numerous reports on TiO<sub>2</sub> doped with B, F, N, C, S, or I have demonstrated a significant improvement of the visible-light photocatalytic efficiency.<sup>[4,12–16]</sup>

Among these, carbon doping received particular attention. For example, carbon-doped TiO<sub>2</sub> for water splitting has been reported by Khan et al.,<sup>[4]</sup> as easily accomplished via the controlled combustion of metallic Ti in a natural gas flame at 850 °C. Hashimoto et al. synthesized C-doped anatase TiO<sub>2</sub> powders by

a two-step oxidative annealing of commercial TiC at 300 °C and 600 °C.<sup>[17]</sup> Sakthivel and Kisch synthesized carbon-modified TiO<sub>2</sub> by hydrolysis of titanium tetrachloride with tetrabutylammonium hydroxide, followed by further heat treatment at 500 °C.<sup>[18]</sup> Morawski et al. reported a new preparation method of carbon-TiO<sub>2</sub> by the carbonization of *n*-hexane deposited on TiO<sub>2</sub> at high temperatures.<sup>[19]</sup> Here, the visible response strongly depends on the form of C in the TiO<sub>2</sub> lattice.<sup>[20,21]</sup>

An active debate regarding the fundamental nature of the non-metal species causing the visible-light absorption in such modified-TiO<sub>2</sub> materials has continued in the community, and two theses have coexisted for several years: i) the non-metal substitutes a lattice atom (i.e., doping), and ii) the non-metal forms chromophoric complexes at the surface (i.e., sensitization). For nitrogen-modified TiO<sub>2</sub> catalysts, substitution doping of lattice O by N, and O vacancies and F-type color centers induced by nitrogen sources during synthesis were proposed by Asahi,<sup>[1]</sup> Serpone<sup>[22]</sup> and others, whereas species such as NO<sub>x</sub> and various other nitrogen oxide complexes were also proposed to sensitize TiO<sub>2</sub> when subjected to visible light irradiation.<sup>[23–25]</sup> Very recently, Kisch and co-workers have suggested that the activity of urea-derived TiO<sub>2</sub>-N in visible light was ascribed to the sensitization of TiO<sub>2</sub> by melon.<sup>[26]</sup> Indeed, this is circumstantially supported by our recent studies on polymeric melon as a water-splitting photocatalyst, being a solid-state “dye” semiconductor with a HOMO–LUMO gap of 2.7 eV and a suitable LUMO level to allow charge transfer from the polymer to TiO<sub>2</sub>.<sup>[27]</sup>

Sensitization of TiO<sub>2</sub> and AgCl by the plasmon state of the noble metal (in particular nanostructured Ag and Au) for visible-light photocatalysis has also been documented. In these systems, the collective dipole oscillations of the surface plasmon is believed to create electron–hole pairs by inter-band transition.<sup>[28]</sup>

Here, we show for the first time that the surface of nanometer-sized carbon materials can also show collective polarization modes and therefore, these optical absorption transitions are feasible to sensitize TiO<sub>2</sub> which then acts as a novel “dyade”-type structure,<sup>[29–31]</sup> with an improved TiO<sub>2</sub> hole reactivity, while the electron is taken up by the carbon component. This results in an improved photocatalytic activity over the complete spectral range.

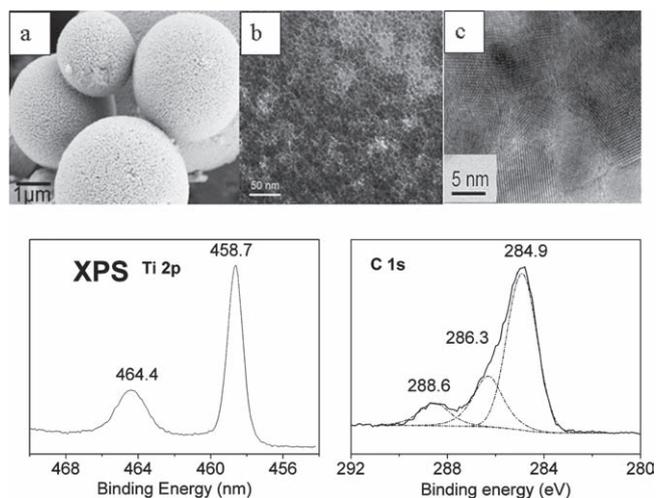
In order to avoid carbon from doping directly into bulk TiO<sub>2</sub> lattice our hybrid TiO<sub>2</sub>/C is synthesized at low temperature under solvothermal conditions by a one-step carbonization of furfural<sup>[32]</sup> in the presence of Ti-isopropoxide, allowing for the formation and co-assembly of carbon and TiO<sub>2</sub> into an interpenetrating C/TiO<sub>2</sub> nanoarchitecture containing 12.6% carbon.

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**Figure 1.** a) SEM, b) TEM, c) HR-TEM and d) XPS of the C@TiO<sub>2</sub> “dyade”-type network.

The morphology and inner structure of such C@TiO<sub>2</sub> interpenetrating arrangement are shown in **Figure 1**. While scanning electron microscopy (SEM) shows porous, spherically shaped colloidal particles with 2–4 μm diameter, the transmission electron microscopy (TEM) image of a microtomed sample, demonstrates a sponge-like, mesoporous architecture. High-resolution (HR)-TEM images of the C@TiO<sub>2</sub> materials show a perfectly crystallized nanomaterial, with the carbon matrix being deposited either on the surface or between particles (**Figure 1c**). This means that the structure can be best understood as a “brick and mortar”-type 3D construction.

The mesoporosity was also confirmed by N<sub>2</sub> gas sorption which showed a type IV adsorption with a H1 hysteresis loop according to the IUPAC classification,<sup>[33]</sup> typical for mesoporous materials with a surface area of 120 m<sup>2</sup> g<sup>-1</sup>, and a maximum in the DFT pore size distribution at ca. 6 nm (**Figure S1**). The XRD pattern (**Figure S2**) show that the material solvothermally crystallises at 180 °C as anatase. In order to prove that the carbon precursor plays a supporting role in the formation of the crystalline phase but also for further comparison regarding the photocatalytic activity we also synthesized two different pure, undoped TiO<sub>2</sub> materials. One was produced by simply removing the carbon using calcination under air from the C@TiO<sub>2</sub> hybrid and one in exact same solvothermal conditions except the addition of furfural to the solvothermal synthesis. X-ray diffraction (XRD) shows that the C@TiO<sub>2</sub> has smaller primary nanocrystal size (7.7 nm) than the calcined TiO<sub>2</sub> (13.7 nm) and that the pattern of the sample produced in the absence of furfural as carbon precursor indicates much less ordering (**Figure S2**) and smaller primary titania particles (3.4 nm). This demonstrates that indeed the carbon precursor plays a supporting role in the formation of the crystalline phase through crystallite surface stabilization. SEM and TEM microscopy images of the pure TiO<sub>2</sub> materials (provided in **Figure S3**) show also micrometer shaped spheres. The beneficial presence of carbon is again proved since the TiO<sub>2</sub> spheres prepared in its absence are less uniform and smooth. TEM also confirms that indeed that the crystallites size is smaller in the directly

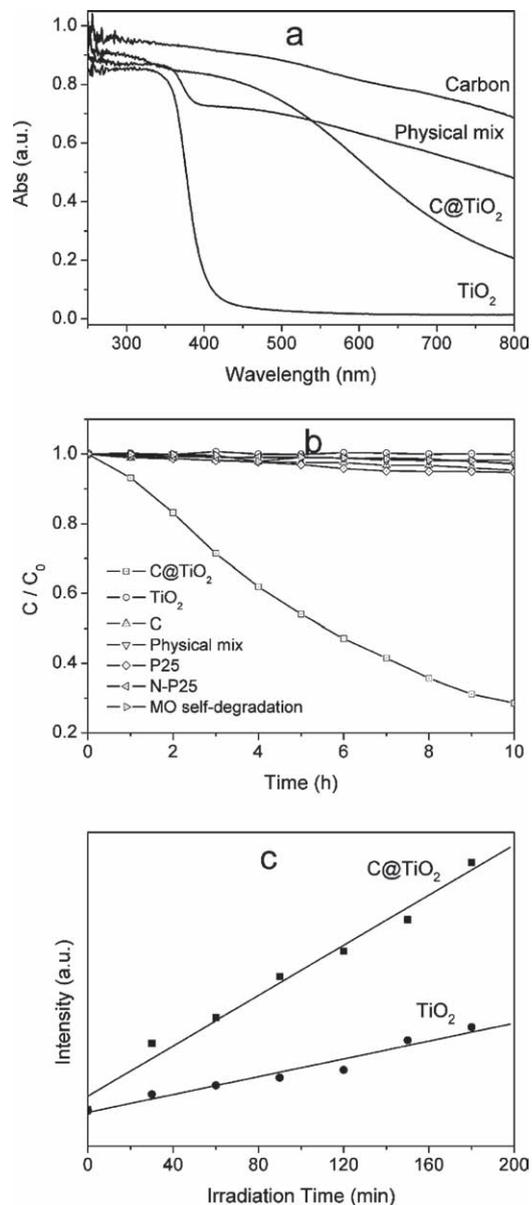
synthesized TiO<sub>2</sub> material and also that the size of the TiO<sub>2</sub> crystallites increases upon removal of the carbon layer presumably due to some aggregation occurring during calcination step.

More detailed information regarding the chemical and bonding environment of the TiO<sub>2</sub> matrix and carbon phase were ascertained using X-ray photoelectron spectroscopy (XPS, **Figure 1d**, the survey spectrum given in **Figure S4**). The binding energies (BE) of Ti 2p<sub>3/2</sub> and O 1s were 458.7 and 530.0 eV, respectively, which is virtually identical to those for standard TiO<sub>2</sub>. The main C 1s peak is dominated by elemental carbon at 284.9 eV, attributed mainly to sp<sup>2</sup> hybridized carbon (BE = 284.6 eV). Two weak peaks at 286.3 and 288.6 eV are assigned to the oxygen bound species C–O and C=O respectively.<sup>[34,35]</sup> No C 1s peak at ~281 eV (Ti–C bond)<sup>[17]</sup> was observed, and the chemical environments for Ti and O were not changed, strongly suggesting that carbon does not enter the TiO<sub>2</sub>-phase. This is not expected as many conventional C-doped TiO<sub>2</sub> is synthesized at temperatures higher than 600 °C.<sup>[4,17,36,37]</sup> Under mild solvothermal conditions used here, it is thought that a polymeric carbonaceous layer is grafted onto the surface of TiO<sub>2</sub> via C–O–Ti bonds, with such structuring favouring the desired charge transfer upon light excitation.<sup>[38]</sup> It is significant to note that C@TiO<sub>2</sub> material prepared via this direct solvothermal synthesis is brown, while a physical mixture of hydrothermal carbon and TiO<sub>2</sub> is gray, suggesting an electronic interaction and different bonding in this intensively interpenetrating material.

Raman spectra of C@TiO<sub>2</sub> material confirmed the formation of a carbon@anatase-nanohybrid only indirectly (**Figure S5**). Opposite to the physical mixture of hydrothermal carbon and pure TiO<sub>2</sub>, all titania relaxations are smeared out, and only a very broad, unstructured spectrum is obtained, presumably due to a significant majority of light being absorbed and partly transformed into separated charges within the hybrid material. This makes the acquisition of Raman spectra impossible. However, such analysis does exclude the presence of unhybridized titania, which would generate a spectrum similar to the physical mixture.

UV–vis diffuse reflectance spectroscopy (DRUVS) demonstrates that C@TiO<sub>2</sub> material can adsorb significantly more light in the 420–800 nm regions as compared with pure TiO<sub>2</sub> (**Figure 2a**). The comparison with the simple mixture of hydrothermal carbon with TiO<sub>2</sub> (13 wt% C) and the pure carbon sample underlines that the anatase phase and the carbon phase are indeed tightly synergistically coupled. The TiO<sub>2</sub> bandgap is clearly smeared out to longer wavelengths, whilst the carbon spectrum has changed, while more absorption in the visible range observed concurrently with less extinction in the IR region. This different behavior defines the C@TiO<sub>2</sub> as a “dyade” structure, where the combination of two parts gives rise in synergistic properties arising from the beneficial interaction of the two. In other words: the two components form a joint electronic system.

Since DRUVS spectra clearly shows that the optical response of C@TiO<sub>2</sub> shifts into the visible-light region, we hoped that the C@TiO<sub>2</sub> material presents photochemical activity in the visible light region. Therefore, the degradation of methyl orange (MO) in aqueous solution under visible light was investigated. **Figure 2b** shows the comparison between C@TiO<sub>2</sub> and some control samples. The C@TiO<sub>2</sub> shows the highest photocatalytic activity of all compared materials in visible light (λ > 420 nm),



**Figure 2.** a) UV-vis diffuse reflectance spectra of modified and pure. b) Photocatalytic degradation of MO in the presence of C@TiO<sub>2</sub> and other samples under visible light irradiation ( $\lambda > 420$  nm). c) Time dependence of the fluorescence intensity of the supernatant liquid for the two different systems, recorded at 426 nm.

thus proving that indeed a special behavior is to be expected, due to the dyadic bonding between the carbon and TiO<sub>2</sub>. Both the commercial P25 and N-doped P25 showed only an activity level comparable with the self-degradation of MO under the same irradiation conditions.

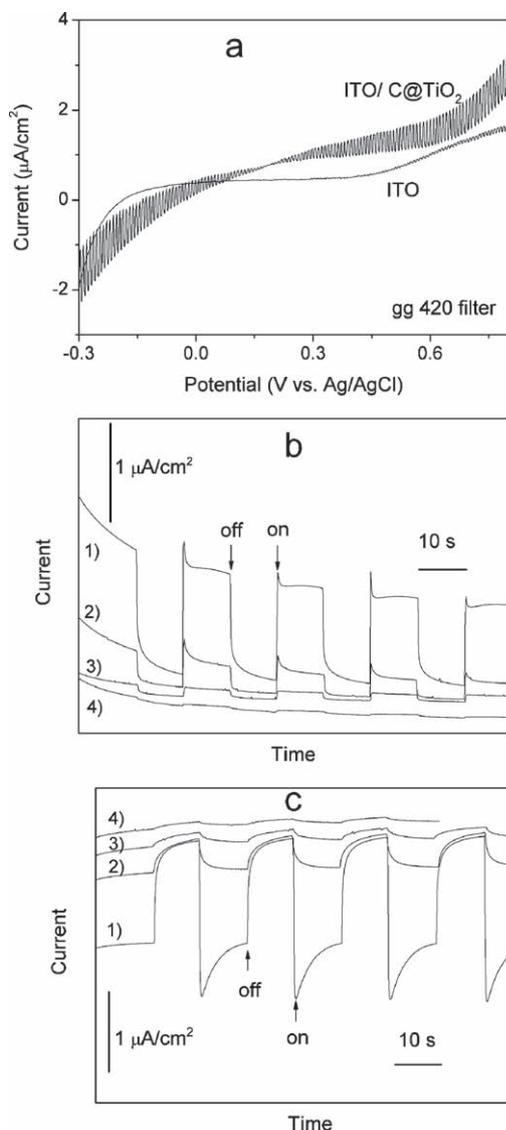
The specific mechanism of this reaction warrants some further discussion. It seems that the C@TiO<sub>2</sub> can induce the formation of hydroxyl radicals under visible-light irradiation ( $\lambda > 420$  nm). However this ability relies on the fact that the hole of the joint system is positioned near the TiO<sub>2</sub> valence band, as it needs  $\sim 2.4$  V versus normal hydrogen electrode (NHE) at pH7 to drive

the hydroxyl radical formation. This would be not possible for the usual “sensitizing” situation, which would fill the much less noble and therefore less reactive carbon sub-gaps. We propose on the base of our data that the synergistic dyade structure of the C@TiO<sub>2</sub> material provides access to optically active charge transfer transitions (Scheme S1), where the electron is transferred to joint charge transfer states more located at the carbon, while the hole stays electronically and structurally near TiO<sub>2</sub>, as only in this situation we can subsequently convert a surface bound water molecule into a hydroxyl radical. The hydroxyl radicals then subsequently photobleach the methyl orange (and all other organic compounds), while the carbon is protected by the previous electron transfer.

Hydroxyl radicals were detected by a terephthalic acid photoluminescence probing assay (TA-PL).<sup>[39]</sup> Figure 2c shows a comparison between C@TiO<sub>2</sub> and the pure TiO<sub>2</sub> fluorescence spectra of the supernatant solutions irradiated with visible light ( $\lambda > 420$  nm). The experiments indicate that a significantly higher amount of hydroxyl radicals is generated by the C@TiO<sub>2</sub> material than for pure TiO<sub>2</sub>. The fluorescence intensity was found to increase steadily with irradiation time (Figure S6). Therefore, it can be concluded that hydroxyl radicals are generated on C@TiO<sub>2</sub> by visible light ( $\lambda > 420$  nm), and the rate of hydroxyl radical generation is in accordance with the improved decoloration performance. This not only suggests that photo-oxidation by hydroxyl radicals is the main reaction path, but also confirms the very low lying photoreactive holes of the dyadic structure.

To learn more about the position and potential reactivity of the generated electrons, we also investigated gas-phase heterogeneous photo-oxidation of organic gases with oxygen under C@TiO<sub>2</sub> photocatalysis. This is known to progress via an O<sub>2</sub>/O<sub>2</sub><sup>-</sup> activation cycle, i.e., we learn if some electrons are positioned higher than  $-0.16$  V versus NHE (O<sub>2</sub>/O<sub>2</sub><sup>-</sup> transfer at pH = 7). The results showed that CO<sub>2</sub> was produced from the C@TiO<sub>2</sub> system with visible light, while, however, no measurable degradation of ethylene as a model organic was observed (Figure S7). This can only be explained by the self-sensitized degradation of carbon on C@TiO<sub>2</sub>. In an oxygen-containing atmosphere, adsorbed O<sub>2</sub> can be reduced to superoxide anions, whereas the TiO<sub>2</sub> bound hole is to be compensated in a later stage of reaction. Superoxide radicals can indeed convert carbon into CO<sub>2</sub>. A catalyzed photo-oxidation reaction in the gas phase is therefore only possible for organic substrates more reactive than the thin carbon film, which is obviously not true for ethylene. At least these experiments could prove the existence of such high energy electrons in the dyadic structure. It is important to note that the formation of the C@TiO<sub>2</sub> nanocomposite is necessary also for this type of heterogeneous photoreaction, as the physically mixed C@TiO<sub>2</sub> powder is completely inactive as showed by reference experiments (Figure S7), i.e., the lifetime of the high-energy electrons is presumably in the classical system too short to result in significant O<sub>2</sub> activation.

Complementing the chemical reactivity experiments, we also investigated the photocurrent generation of C@TiO<sub>2</sub> (Figure 3). Promisingly, the C@TiO<sub>2</sub> material is indeed able to generate significant photocurrents under both UV and visible-light irradiation. A typical n-type photocurrent was generated with UV ( $\lambda > 320$  nm), while under visible-light irradiation the material



**Figure 3.** a) Photocurrent of ITO/C@TiO<sub>2</sub> as a function of potential under chopped visible light. b,c) Transient photocurrent responses of ITO/C@TiO<sub>2</sub> biased at 0.5 V (b) and -0.2 V (c) under light with a wavelength larger than 420, 590, 695, and 780 nm, respectively (different filters: 1) GG 420; 2) OG 590; 3) RG 695; and 4) RG 780).

exhibits both n-type and p-type currents. We explain this by the fact that UV-absorption also activates pure TiO<sub>2</sub> bands, while the ambipolar, biphasic nature of C@TiO<sub>2</sub> is activated under visible light. This allows both electrons and holes to contribute to the charge transport, which is crucial for photo-electrochemical applications. As expected, the photocurrent decreases when increasing the incident-light wavelength, but there was still a noticeable photocurrent found at  $\lambda = 780$  nm (Figure 3b and 3c). The photocurrent from ITO as a background was negligible (Figure S8). Previously described C-doped TiO<sub>2</sub> materials only showed optical absorption bands lower than 650 nm.<sup>[4,17,35]</sup> Therefore, the photo-electrochemical activity at even longer wavelengths supports the very usual entanglement of the two materials into a joint dyadic activation state.

In summary, a novel carbon-doped TiO<sub>2</sub> catalyst was successfully synthesized by an easy, low-cost, green and one-step solvothermal method. This C@TiO<sub>2</sub> has a high surface area and anatase structure and is able to absorb a high amount of photoenergy in the visible, driving effectively photochemical degradation reactions. Diverse structural and photochemical characterization results of C@TiO<sub>2</sub> provide strong evidence that the origin of photocatalytic activity under visible light is due to a direct optical charge transfer transition involving both the TiO<sub>2</sub> and carbon phase, keeping the high reactivity of the photogenerated electron and hole. This clearly complements most previous “dye-sensitization” experiments, where in fact only electrons and holes with lowest possible energy can be used. We claim that it is the coupling into a “dyade” structure, which gives rise to the very special properties of the structurally entangled hybrid structure. It was also shown that all extra properties remain non-accessible in the physical mixture of the two components.

We hope that our results for this very simple and sustainable system will stimulate further fundamental work on the chemical interface design in bulk heterojunction materials. This is certainly needed for the better understanding and design of more optimized systems to enable and promote artificial photosynthesis.

### Supporting Information

Supporting Information is available online from Wiley InterScience or from the authors.

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