Enhanced photocatalytic activity of TiO₂-C hybrid aerogels for methylene blue degradation

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Carbon-based TiO₂ composites have many advantages as photocatalysts. However, they suffer from low light efficiency due to the low contrast of TiO₂ with carbon. We synthesized a novel type of anatase-type TiO₂-C hybrid aerogel by a one-pot sol-gel method, which shows a photocatalytic activity for methylene degradation up to 4.23 times that of P25, a commercial photocatalyst from Degussa Inc. The hybrid aerogels are prepared from TiCl₄ and resorcinol–furfural, and have a tunable macropore size from 167 to 996 nm. They are formed of submicrometer particles that consist of interwoven anatase and carbon nanoparticles. The anatase nanoparticles have a size of 8–9 nm and a tunable oxygen vacancy from 7.2 to 18.0%. The extremely high activity is ascribed to the large light absorption caused by macropore scattering and oxygen vacancies in the anatase. These findings may open up a new avenue and stimulate further research to improve photocatalytic performance.

Titanium dioxide (TiO₂) has attracted much attention as a semiconducting photocatalyst for pollution abatement in water or air, owing to its strong oxidizing power, abundance, low cost, high chemical inertness and photostability. Its structure-property relationships have been extensively investigated, and these reveal that phase type¹, particle size², surface hydrophilicity³, crystallinity⁴, morphology⁵ and oxygen vacancy concentration⁶⁷ have a great influence in its photocatalytic activity. But it still suffers from low efficiency and a narrow light response range if it is used alone. Many efforts have been made by forming composites or hybridizing TiO₂ with other materials to overcome these drawbacks, such as combining the photocatalytic activity of TiO₂ with the adsorptivity of porous carbons⁸–¹⁰, reducing electron–hole recombination rate¹¹ and doping to achieve a narrow band gap¹²–¹⁶. TiO₂-carbon (TiO₂-C) hybrids are some of the most extensively investigated and most promising materials to improve the photocatalytic performance of TiO₂ because a variety of carbon materials can be tailor-made to meet the demands of TiO₂ as a photocatalyst. In addition, the lightweight, nonpolar, nonreactive and nontoxic nature of carbon materials and the easy separation of the materials from water are attractive in waste water treatment. There are three types of TiO₂-C hybrids, carbon-supported, carbon doped and carbon coated TiO₂¹⁷, from which many beneficial features have been obtained.

The detailed mechanism of the photocatalytic process on the TiO₂ surface is still not completely clear, particularly that concerning the initial steps involved in the reaction of reactive oxygen species and organic molecules¹⁸. A reasonable assumption is that both photocatalytic oxidative and reductive reactions occur simultaneously on the TiO₂ particle. When the electrons in TiO₂ (anatase phase) are irradiated by UV rays they can be excited from the valence band to the conduction band to generate electron–hole pairs. The holes created in the valence band can react with water molecules to give hydroxide radicals OH and the photogenerated electrons are sufficiently reduced to produce superoxide (O₂⁻). The redox potential of the electron–hole pair permits H₂O₂ formation. Depending on the reaction conditions, the holes, OH radicals, O₂⁻, H₂O₂ and O₂ can play important roles in the photocatalytic reaction mechanism. There are several issues that are important in this process. First, exposing the external surface of TiO₂ particles to light is a prerequisite to make such an excitement happen. Second, the light energy (E = hν) must exceed the band gap (3.20 eV) of the anatase-type TiO₂, therefore lowering the band gap of TiO₂ or using low wave length light is needed to increase the light utilization efficiency. Third, the oxidizing species cannot migrate for a long distance and stay near the active centers in the TiO₂ particles. Therefore, polluting molecules have to diffuse to the photo-excited active centers. Fourth, the recombination of positive holes with excited electrons before they react to create active species and centers has to be avoided. Moreover, the TiO₂ loaded in the composites should not decrease under repeated cycles and must be easy to separate from water from a commercial application point of view.
Most of these issues can be circumvented by hybridizing TiO$_2$ with carbon materials. Loading TiO$_2$ nanoparticles on the surface of activated carbons/activated carbon fibers or mixing the two can significantly increase the photocatalytic activity for methylene blue (MB) degradation in aqueous solutions$^{19-21}$, which can be ascribed to a decreased diffusion path of MB to the active centers by adsorption of MB from the bulk solution by the activated carbon. The interaction of carbon with TiO$_2$ can effectively inhibit TiO$_2$ particle growth and simultaneously increase crystallinity during heat treatment by suppressing the phase transformation from photoactive anatase to less active rutile$^{22}$. Cationic$^{23}$ and anionic$^{16,24,25}$ doping of TiO$_2$ by carbon have been reported to narrow its band gap and significantly enhance catalytic activity in the visible light region. The presence of graphene$^{13}$ or carbon nanotubes$^{26}$ in TiO$_2$-based nanocomposites can effectively inhibit the electron-hole pair recombination, lower the band gap of TiO$_2$, increase the adsorptivity of pollutants, and decrease light weakening due to a small number of graphene layers and therefore a decreased light absorption by carbon as compared with other forms of carbons.

However, in most cases, not all of these issues can be resolved simultaneously, and a compromise must be made because solving some of the problems could make others worse. For example, the coating layer in carbon-coated TiO$_2$ increases adsorptivity, but decreases the light intensity irradiated on TiO$_2$. The former favors catalytic activity while the latter is detrimental. As a compromise, maximum photocatalytic activity is obtained by increasing the thickness of the coating-layer. The carbon layer has a high light absorption that weakens the light intensity arriving at catalyst surface, and this limits the increase in the efficiency of the present TiO$_2$-C hybrids. Therefore, a state-of-the-art design of TiO$_2$-based hybrids is important for their further improvement.

There are several methods to prepare carbon-based TiO$_2$ hybrids, including chemical vapor deposition of alkoxide precursors$^{28}$, impregnation of a sol prepared by alkoxide hydrolysis into activated carbon$^{29}$, loading of a powder prepared in advance directly onto activated carbon$^{30}$, a sol-gel approach$^{23,31}$, hybridizing with nanocarbons such as carbon nanotubes$^{26}$ or graphene$^{13}$, etc. The first three methods normally produce TiO$_2$ particles coated on the external surface or at pore entrances of the activated carbon particles. Adsorbed molecules have to diffuse to the external surface of the composite particles in order to achieve contact with the active sites on the TiO$_2$ particles. Therefore, for these hybrid materials the diffusion paths for the targeted molecules are longer than for carbon nanotube or graphene-based composite materials that are homogeneous at the nanometer scale. The sol-gel approach allows for a nanometer scale mixing of TiO$_2$ nanoparticles with carbon nanoparticles, which is advantageous in this regard. In addition, the microstructure of the sol-gel derived composite materials can be tailored with a wide range of length scale from nanometer to micrometer, which makes it possible for a targeted textural control. Moreover, the nanometer scale mixing of TiO$_2$ with carbon can prevent TiO$_2$ particles from falling off the carbon, which is advantageous in industrial applications.

In this paper, a novel type of TiO$_2$-C hybrid aerogels was synthesized by one-pot sol-gel approach. The hybrid aerogels have dominant macropores and a small fraction of micro and mesopores, but show much higher photocatalytic activities for MB degradation under UV irradiation than P25, a commercial TiO$_2$ (Degussa Co., Ltd., Germany). The reasons for the enhanced performance and the factors affecting the photocatalytic activity of this kind of hybrid material are analyzed.

**Results**

**Crystalline structure.** Fig. 1a shows powder X-ray diffraction (XRD) patterns of the TiO$_2$-C hybrid aerogels. The peaks at 25.5°, 37.8°, 48.3°, 54.1° and 62.8° can be ascribed to the (101), (004), (200), (105) and (204) plane of anatase, respectively. There are no peaks found that belong to the rutile phase or graphite. The absence of graphite peaks indicates that the carbon is in an amorphous state. The absence of rutile is reasonable because carbon suppresses the phase transition from anatase to rutile as revealed in carbon-supported$^{29}$ and carbon-coated TiO$_2$ even if the samples are carbonized at 800°C. It should be noted that the half-width at half maximum (FWHM) of (101) peaks and the crystallite size of anatase obtained from the peaks by the Scherrer equation are the same within experimental error (8.0–8.6 nm) for all samples investigated (Table 1). This may be due to the same procedure and processing conditions being used for all these samples. The TiO$_2$ contents in the TiO$_2$-C hybrid aerogels increase with the mass ratio of TiCl$_4$ to resorcinol (R) and furfural (F), TiCl$_4$/ (R + F) as expected. The FWHMs of the (101) peaks are around

![Figure 1](https://example.com/figure1.png)

**Figure 1** | a) XRD patterns, b) Raman spectra and c) XPS spectra of the TiO$_2$-C hybrid aerogels.
located at 459.0 and 464.7 eV, which can be ascribed to Ti 2p 3/2 and 2p, O 1s, C 1s and N 1s spectra are shown in Fig. S1 and Tables S1, S2.

The peaks at 1338 and 1587 cm⁻² are attributed to the TiN(oxide) ₃⁹ with its Ti 2p 3/2 and Ti 2p 1/2 peaks. The six allowed bands in the first-order Raman spectrum are located at 144 (Eg), 197 (Eg), 399 (B1g), 513 (A1g), 519 (B1g) and 639 (Eg) cm⁻². All the Raman features observed in the spectra are close to those of the single crystal anatase phase as shown in Table 2. It is evident that the TiO₂-C hybrid aerogels possess a certain degree of long-range order of the anatase phase and that no observable rutile features are found. It is found that the Eg peaks at 144 and 639 cm⁻² are blue-shifted and red-shifted to around 153 cm⁻², respectively as compared with single crystal anatase. The Eg peak at 197 cm⁻² is blue shifted to around 203 cm⁻². The red shifts of the B1g and A1g peaks at 399 and 519 cm⁻² all exhibit a maximum at TiCl₄/(R + F) of 0.902, i.e. sample TiO₂-C-3. The apparent blue and red shifts are related to the lower crystal size ₃⁵, number of oxygen vacancies ₃⁶ and pressure ₃⁷ in the anatase phase.

Fig. 1c contains the XPS spectra of the TiO₂-C hybrid aerogels, showing the presence of elemental C, O, Ti for all samples and of N in TiO₂-C-2. The deconvolutions and assignments of the peaks in the Ti 2p, O 1s, C 1s and N 1s spectra are shown in Fig. S1 and Tables S1, S2 and S3. The spin-orbit splitting of the Ti 2p leads to two 2p peaks located at 459.0 and 464.7 eV, which can be ascribed to Ti 2p₃/₂ and Ti 2p₁/₂, respectively. From the peak positions ₃⁶, it can be concluded that the Ti in the hybrid aerogels is predominantly Ti⁴⁺. For the TiO₂-C-2 sample, a shoulder is found near Ti 2p₁/₂, which can be attributed to the TiN(oxide) ₃⁹ with its Ti 2p₃/₂ and Ti 2p₁/₂ peaks located at 457.3 and 463.0 eV respectively. It is not clear why TiO₂-C-2 has small amount of nitrogen while other samples do not. The O 1s spectra can be fitted by three chemical states at 530.2–530.4, 531.3 and 533.2 eV, which can be ascribed to O in the form of O-Ti, C-O-C and O=C, respectively. From the O-Ti percentages from the O 1s spectra and the O and Ti atom ratios from the XPS overview spectra, we can estimate the number of O atoms bonded with Ti⁴⁺, e.g x in TiOₓ (Table 3). It is found that x values of the anatase phase in all samples varies from 1.64 to 1.86, all of which are non-stoichiometric (less than 2), which corresponds to oxygen vacancy concentrations from 18.0 to 7.2%. The C 1s spectra can be deconvoluted into the following bands based on the literature ₄⁰. The main peak at 284.5 eV can be assigned to sp² hybridized C atoms, while the higher energy peaks arise from sp³ hybridized C at 285.7 eV, C-O-C at 287.1 eV, C=O at 288.7 eV, and the shakeup line of carbon in aromatic compounds at 290.5 eV (π–π*). The oxygen functional groups from C 1s spectra agree with those from O 1s spectra. It should be mentioned that the phenol group in resorcinol is not retained in carbon and converted to C=O group, which might be caused by oxidation of phenol group by TiO₂ at high temperature.

There are rough agreements between XPS and Raman results. The sample TiO₂-C-3 has the lowest oxygen vacancy concentration. The Raman blue shift of TiO₂-C-3 at 144 cm⁻¹ exhibits a minimum and its red shifts of the B1g and A1g peaks at 399 and 519 cm⁻¹ all exhibit a maximum. It was reported that the Raman blue shift of Eg at 144 cm⁻¹ increases with oxygen vacancy concentration and levels off above 5% for nanophase anatase ₄⁶. This can explain why there is no noticeable difference between shifts of the Eg peak at 144 cm⁻¹ although our samples have a wide range of oxygen vacancy concentration (7.2–18%). The incomplete agreement between the XPS and Raman results for all samples might be caused by the pressure ₃⁷ that the carbon structure exerts on anatase, resulting from volume shrinkage of the carbon precursors during carbonization, which is impossible to control.

**Structure and porosity.** Fig. 2 shows SEM, TEM and HRTEM images of the TiO₂-C hybrid aerogels. SEM and TEM show that they are formed by large aggregates that form macropores. The average size of the aggregates decreases from 268 to 216 nm with increasing TiCl₄/(R + F) ratio. The aggregates in SEM images can be seen in more detail by TEM that they are formed of TiO₂ and carbon nanoparticles. The black regions in the TEM images are TiO₂ particles because TiO₂ has a higher electron density and therefore a higher contrast than carbon. It is clear that TiO₂ particles of 8–9 nm are distributed discretely within the carbon, which is in agreement with the particle sizes calculated from XRD. However, we have found that the carbon and anatase are biconsecutive and interwoven, each not coated by the other in the hybrid aerogels from the fact that the TiO₂-C hybrid aerogels retain their monolithic shape after burning in air at 600°C to remove the carbon or leaching in HF.

| Table 2 | Raman vibrational modes, their shifts and linewidths |
|----------------|-----------------------------------------------|
| Samples     | Eg, cm⁻¹ | FWHM, cm⁻¹ | Egy, cm⁻¹ | B1g, cm⁻¹ | A1g+B1g, cm⁻¹ | Eg, cm⁻¹ |
| Single crystal anatase | 144     | ...    | 197       | 399       | 513 + 519     | 639       |
| Single crystal rutile   | 447     | ...    | 612       | 143       | 826(B2g)      | ...       |
| TiO₂-C-1       | 155 ± 1 | 27 ± 1 | 203 ± 4   | 398 ± 4   | 518 ± 4       | 625 ± 4   |
| TiO₂-C-2       | 154 ± 1 | 25 ± 1 | 202 ± 4   | 396 ± 4   | 509 ± 4       | 626 ± 4   |
| TiO₂-C-3       | 153 ± 1 | 25 ± 1 | 202 ± 4   | 392 ± 4   | 508 ± 4       | 626 ± 4   |
| TiO₂-C-4       | 155 ± 1 | 29 ± 1 | 203 ± 4   | 400 ± 4   | 514 ± 4       | 627 ± 4   |
| TiO₂-C-5       | 153 ± 1 | 25 ± 1 | 203 ± 4   | 398 ± 4   | 514 ± 4       | 625 ± 4   |
to remove TiO$_2$ as shown in Fig. S2. The size of TiO$_2$ particles increases significantly after the hybrid aerogels are burned in air, which is caused by crystal growth and sintering at high temperature. The carbon structure remains unchanged after the leaching with HF. This disagreement with TEM observations could be caused by the grinding used to prepare a dispersion for TEM examination, which destroys the continuous anatase since carbon is mechanically stronger than anatase. The strong interaction of TiO$_2$ nanoparticles and polymer nanoparticles via hydrophilic groups, contributes to the small sizes of anatase (8–9 nm) and carbon nanoparticles and inhibits the growth of TiO$_2$ nanoparticles.

N$_2$ adsorption–desorption isotherms at $-196^\circ$C are shown in Fig. 3a and the pore size distributions obtained using a DFT model are shown in Fig. 3b. The pore parameters are listed in Table 1. N$_2$ adsorption isotherms of the samples belong to Type II with reference to the IUPAC classification, which is typical of macroporous solids. These isotherms show a steep uptake at high relative pressures with no sign of levelling off due to capillary condensation mainly in the macropores. There is also a small steep uptake of N$_2$ at low relative pressures in the initial part of these isotherms, which can be attributed to micropore filling of N$_2$. The hysteresis loop of these samples is so small that it is hard to make an assignment, but it is approximately close to Type H3 according to the IUPAC classification. Fig. 3b shows that there is small amount of mesopores. The volume of mesopores larger than 30 nm first increases then levels off with increasing TiCl$_4/(R + F)$ ratio. The volume of mesopores between 10 and 30 nm is the largest for TiO$_2$-C-3 and the volume of mesopores between 2 and 10 nm is the largest for TiO$_2$-C-1. There is no regular trend found for micropore sizes. The micropore volume of the hybrid aerogels exhibits a maximum of 0.043 cm$^3$/g at 0.720 with the TiCl$_4/(R + F)$ ratio as shown in Table 1. As macropore size is out of the detection range for nitrogen adsorption, we carried out mercury porosimetry to determine the macroporosity. The hybrid aerogels are not elastic, but stiff materials. There are no apparent compression stages in the uptake curves except for TiO$_2$-C-5 that has a small compression as shown in Fig. 3c. The mercury uptake abruptly increases at intrusion pressures from 50 to 400 psi with increasing TiCl$_4/(R + F)$ ratio. Therefore, the Washburn equation can be used to extract pore size distributions that are displayed in Fig. 3d. It can be seen that the pore sizes of the hybrid aerogels decrease from 966 to 167 nm with increasing TiCl$_4/(R + F)$ ratio from 0.629 to 1.261, which is in accordance with the trend from SEM.

Table 3 | Atom ratios, contents of oxygen bonded with Ti and carbon, and oxygen vacancy from X-ray photoelectron spectroscopy

| Samples     | C  | Ti  | O    | N  | Ti(N)| Ti(O) | O(Ti)| xTiOx | Oxygen vacancy,% | O(C)/C | at% |
|-------------|----|-----|------|----|------|-------|------|------|-----------------|--------|-----|
| TiO$_2$-C-1 | 74.83 | 6.90 | 18.27 | 0  | 0    | 6.90  | 11.89 | 1.72 | 13.8            | 0.085  | 0.075|
| TiO$_2$-C-2 | 74.60 | 7.40 | 16.90 | 1.10 | 1.10 | 6.40  | 10.73 | 1.68 | 16.2            | 0.083  |     |
| TiO$_2$-C-3 | 72.87 | 7.75 | 19.37 | 0  | 0    | 7.75  | 14.39 | 1.86 | 7.2             | 0.068  |     |
| TiO$_2$-C-4 | 72.70 | 8.10 | 19.20 | 0  | 0    | 8.10  | 14.19 | 1.75 | 12.4            | 0.069  |     |
| TiO$_2$-C-5 | 72.61 | 8.30 | 19.08 | 0  | 0    | 8.30  | 13.61 | 1.64 | 18.0            | 0.075  |     |

Figure 2 | SEM (top), TEM (middle) and HRTEM (bottom) images of the samples: a) TiO$_2$-C-1, b) TiO$_2$-C-2, c) TiO$_2$-C-3, d) TiO$_2$-C-4 and e) TiO$_2$-C-5.
observations. From Table 1, we have found that the pore (>3.7 nm) volumes of the hybrid aerogels from mercury porosimetry exhibit a minimum of 1.62 cm$^3$/g at 0.902 (i.e., sample TiO$_2$-C-3) with increasing the TiCl$_4$/(R + F) ratio. The macropore volumes are dominantly larger than the micropore or mesopore volumes, which agree well with the non-level off uptake of nitrogen in the adsorption isotherms (Fig. 3a). Therefore, the hybrid aerogels have dominant macropores with small amounts of micro and mesopores.

**Photocatalytic activity.** Photocatalytic degradation of MB in an aqueous suspension of the TiO$_2$-C hybrid aerogels was performed to evaluate their photocatalytic activity. Adsorption in the dark was also carried out in order to investigate the effect of adsorption on their photocatalytic activity. For comparison, adsorption and photodegradation of MB by P25 were also investigated under the same conditions. Fig. 4 shows the adsorption percentage for MB versus time in the dark and photocatalytic degradation percentage of MB versus time under UV light for the TiO$_2$-C hybrid aerogels and P25. Table 4 lists the kinetic parameters for MB adsorption and photocatalytic degradation. The MB adsorption follows a pseudo-second-order kinetics model for the first 180 min. The MB degradation-time curves can be well fitted by a first order kinetics model for 60 min. Above 60 min, a significant deviation from first order kinetics is observed. The adsorption of MB is the quickest and the equilibrium adsorption capacity is the smallest for P25. The adsorption capacity increases with increasing micropore volume except for TiO$_2$-C-1 because the dimensional size of the MB molecule (1.43 × 0.61 × 0.4 nm) is smaller than micropore size and the micropore has a relatively high adsorption potential. The exceptional high MB adsorption capacity of the TiO$_2$-C-1 can be attributed to its high volume of small mesopores (2–5 nm) as revealed by mesopore size distributions in Fig. 3b since the smaller mesopores (2–5 nm) contribute more surface area than the larger mesopores. Therefore, MB tends to be adsorbed preferentially in the micropores and small mesopores. The pseudo-second-order rate constants ($k_2$) are similar among the hybrid aerogels within experimental error. However the $k_2$ for P25 is four times higher than those of the hybrid aerogels, which can be ascribed to the short diffusion path for P25 (around 27 nm) while the particle size of the hybrid aerogels is of submicrometer scale.

The photocatalytic activities of the hybrid aerogels can be quantitatively evaluated by comparing the first order reaction rate constants ($k_1$). Direct comparison of the rate constants between the hybrid aerogels shows that they are markedly improved and vary widely compared with that of P25. This is due to the small particle size of anatase, a high loading level, reduced recombination of electron-hole pairs$^{11}$, and band gap narrowing$^{13}$. The increasing order of the rate constants based on the weight of TiO$_2$ in the samples is TiO$_2$-C-4 < TiO$_2$-C-5 < TiO$_2$-C-2 < TiO$_2$-C-1 < TiO$_2$-C-3. The rate constant exhibit a maximum of 0.060 min$^{-1}$ at 0.902 (TiO$_2$-C-3) with increasing TiCl$_4$/(R + F) ratio, a value that is 4.23 times higher than that of P25 under the same conditions. The maximum rate ratio of TiO$_2$-C-3 to P25 is also much larger than that of TiO$_2$-GR5% and TiO$_2$-CNT5% to P25, which are 2.32 and 2.00 respectively as extracted from the curves in reference$^{13}$.

**Optical properties.** Fig. 4c shows the UV-vis diffuse reflectance spectra of the TiO$_2$-C hybrid aerogels. The presence of carbon induces increased light absorption in the visible region. A red shift to higher wavelengths in the absorption edge of the hybrid aerogels has also been observed, therefore indicating a narrowing of the band gap of TiO$_2$. It is difficult to determine the value of the red shifts because the background absorption ranging from 400 to 800 nm is very high. However, this red shift of our samples is higher than that of graphene-p25 nanocomposites by comparing the wavelengths at which curving of the lines by the superposition of TiO$_2$ and carbon absorption occurs (around 425 nm for our samples and 405 nm for
In addition, the UV-vis diffuse reflectance increases in the following order: TiO_2-C-4 < TiO_2-C-5 < TiO_2-C-2 < TiO_2-C-1 < TiO_2-C-3. This is exactly that of the increasing order of the photocatalytic reaction rate constants normalized to the weights of TiO_2 in the samples. Therefore, light absorption by scattering is an important factor that determines the photocatalytic activity of the TiO_2-C hybrid aerogels.

Discussion

The structural formation mechanism of the hybrid aerogels can be understood as follows. The alcoholysis of TiCl_4 in the presence of the bidentate ligand, ethyl acetoacetate (EA), leads to the formation of Ti(OEt)\_3EA. The condensed Ti(OEt)\_3EA forms inorganic colloid particles, growth of which is greatly inhibited compared with Ti(OEt)\_4. At the same time, the addition and condensation of resorcinol with furfural gives rise to organic nanoparticles under catalysis of in-situ formed HCl. Aggregation of inorganic and organic particles forms large submicrometer particles. Interaction among the submicrometer particles leads to a gelation of the solution and the formation of a macroporous gel. These pore structures are mostly retained after carbonization at 800°C since the polymers generated by the condensation of resorcinol with furfural are thermosetting. The interwoven structure of carbon and TiO_2 nanoparticles in the aggregates is caused by the strong hydrophilic interaction between TiO_2 colloidal particles and organic nanoparticles. The micropores are formed mainly in carbon nanoparticles during carbonization of the polymers by gas evolution. The mesopores are due to inter-nanoparticle voids and interstices between the contacting submicrometer particles. The macropores are formed by the inter-submicrometer particle voids.

The changing macropore size and volume with TiCl_4/(R+F) ratio can be accounted for by this mechanism. As the RF concentration is fixed at a constant value for all the samples, increasing the TiCl_4/(R+F) ratio leads to an increase of the total amount of TiO_2 and polymer nanoparticles, which favors a more robust gels formed at a higher TiCl_4/(R+F) ratio. Therefore, the gels formed at a higher TiCl_4/(R+F) ratio is more difficult to shrink during supercritical drying and carbonization than that at a lower TiCl_4/(R+F) ratio. This factor leads to an increase of pore volume with TiCl_4/(R+F) ratio. On the other hand, an increase of TiCl_4/(R+F) ratio could cause a decrease in the total pore volume if judged merely by the volume filling effect of the submicrometer particles. Also, the smaller the submicrometer particle, the higher the driving forces for coarsening after gelation and sintering during carbonization and these decrease the pore volume with increasing TiCl_4/(R+F) ratio. Therefore, these opposing actions cause a minimum of total pore volumes with increasing TiCl_4/(R+F) ratio.

Adsorption kinetics is not the main factor that contributes to the difference of the photocatalytic activities as it suggests a similar rate constant, which is ascribed to the hierarchical macro, meso and micropores. Adsorption of MB can decrease the diffusion path of MB to TiO_2 nanoparticles by surface diffusion and increase photocatalytic activities for all samples. As the carbon and TiO_2 nanoparticles are evenly distributed and interwoven with each other at the nanometer scale, the interfacial diffusion rate of MB from carbon pore walls to the hydrophilic external surface of TiO_2 active centers should be high. The macropore sizes and volumes also cannot explain the quite different apparent reaction rate constants. The TiO_2-C-3 has a minimum total pore volume, which seems inconsistent with it having the maximum apparent reaction rate constant. The macropore size decreases with increasing TiCl_4/(R+F) ratio, which should result in a decreased diffusion rate with increasing the TiCl_4/(R+F) ratio and therefore a decreased reaction rate constant. This is apparently not what happens. Neither can mesopore volume rationalize the maximum reaction rate constant because TiO_2-C-5 has a comparable mesopore volume to TiO_2-C-3, but the rate constant of the former is significantly lower than that of the latter.

The crystallinity and crystallite size of the TiO_2 nanoparticles are all similar within experimental error for the hybrid aerogels, and therefore do not account for the different photocatalytic activities. The smaller the submicrometer particle, the higher is percentage of...
TiO\textsubscript{2} exposed to UV light. As the sizes of submicrometer particles decrease and weight percentages of TiO\textsubscript{2} increase with increasing TiCl\textsubscript{4}/(R + F) ratio, the amount of the exposed TiO\textsubscript{2} nanoparticles and photodegradation activity should increase accordingly. This can explain the increasing rate constant with increasing TiCl\textsubscript{4}/(R + F) ratio except for sample TiO\textsubscript{2}-C-3 with the experimentally-observed maximum.

Since oxygen vacancies in anatase are preferably located at the subsurface\textsuperscript{7}, the high percentage of oxygen vacancies (7.2–18%) in our samples can be ascribed to the small size of the TiO\textsubscript{2} because a size decrease of TiO\textsubscript{2} nanoparticles favors an increase in subsurface area. Carbon thermal reduction is another factor that our samples have high oxygen vacancies in TiO\textsubscript{2}. The minimum oxygen vacancy for TiO\textsubscript{2}-C-3 could be caused by coarsening and sintering that increases surface contact between anatase nanoparticles, which decreases subsurface area. This could be accounted for by the following two opposing factors. On the one hand, the interaction between polymer nanoparticles, (precursors of the carbon nanostructure) and the TiO\textsubscript{2} nanoparticles decreases with increasing TiCl\textsubscript{4}/(R + F) ratio, therefore, the interaction between TiO\textsubscript{2} nanoparticles increases, leading to an increase of coarsening and sintering during aging and carbonization. On the other hand, with increasing TiCl\textsubscript{4}/(R + F) ratio, the amount of catalytic HCl generated increases, the addition and polymerization rate of resorcinol with furfural increases, the cross-linking density of the polymer increases, the size of the polymer nanoparticles decreases and the interaction of polymer nanoparticles with TiO\textsubscript{2} nanoparticles increases, leading to a decrease of coarsening and sintering during aging and carbonization.

As a compromise result, the coarsening and sintering during the aging and carbonization of TiO\textsubscript{2} nanoparticles reach a maximum with TiCl\textsubscript{4}/(R + F) ratio, and oxygen vacancy concentration exhibits a minimum because coarsening and sintering of TiO\textsubscript{2} nanoparticles decrease the anatase subsurface area. The minimum O/C ratio in carbon is another indication that interaction between carbon and TiO\textsubscript{2} nanoparticles reaches a minimum at 0.902 (i.e. sample TiO\textsubscript{2}-C-3) with TiCl\textsubscript{4}/(R + F) ratio as carbon nanoparticles can reduce TiO\textsubscript{2} particles and increase oxygen vacancy in TiO\textsubscript{2}.

It has long been established that TiO\textsubscript{2} surfaces containing O vacancies exhibit a higher catalytic activity than defect-free surfaces to reactions such as the dissociation of water\textsuperscript{44}. However, it is argued\textsuperscript{45} that photocatalytic activity is enhanced by a good mixing between Ti and O states around the Fermi energy. These effects act in opposition, in turn suggesting that there is an optimum defect concentration for activity in photocatalysis, above and below which activity should decrease. As our samples have high oxygen vacancy concentrations, it might be possible that these defect concentrations are all above the optimum value and therefore TiO\textsubscript{2}-C-3 with the lowest oxygen vacancy concentration has the highest photocatalytic activity among our samples.

The maximum reaction rate can be ascribed to the maximum absorption of UV light due to the pore scattering as explained below. According to the Beer-Lambert law, the light intensity percentage passing through a sample can be calculated by equation (1).

\[
\frac{I}{I_0} \times 100\% = (1 - R)^2 \exp(\beta + S)x
\]  

Where \( \frac{I}{I_0} \times 100\% \) is the light intensity percentage passing through the sample, \( R \) the reflectance, \( \beta \) the absorption coefficient caused by the electron excitation, \( x \) the light transmission length and \( S \) the scattering coefficient. The greater the light intensity passing through the sample, the lower the light absorption in the sample. The absorption coefficient is independent of the pore structure of the hybrid aerogels while the scattering coefficient depends on the pore size and size distribution. Since the wavelength (\( \lambda = 365 \text{ nm} \)) of UV light is comparable to the macropore sizes, the samples show different scattering properties. When the pore size increases and is close to the wavelength of UV light, the scattering changes from forward scattering to large angle scattering. On the other hand, large size pores mainly contribute backward scattering. The large angle scattering will enhance the absorption since more light propagates inside the sample. There is an optimum pore size (\( d_{\text{max}} \)) described by the equation (2), at which light scattering and absorption reach a maximum.

\[
d_{\text{max}} = \frac{4.1\lambda}{2\pi(n-1)}
\]  

Where \( \lambda \) is the UV wavelength and \( n \) the relative index of refraction. Therefore, the maximum rate constant may be ascribed to a maximum light absorption from macropore scattering since the macropore size of the TiO\textsubscript{2}-C-3 is close to the optimum pore size. The difference in the UV-vis diffuse reflectance of TiO\textsubscript{2}-C-3 compared to the other samples is not as large as the difference in their reaction rate constants. This might be caused by light absorption by the sample.

The percentage of TiO\textsubscript{2} nanoparticles exposed to UV light in the submicrometer particles can be estimated by their sizes and light penetrating depth. The absorption of light incident on 8–9 nm carbon nanoparticles is estimated to be around 54–61% since single layer graphene has a light absorption of 2.3%\textsuperscript{45}. Therefore, the light penetrating depth of UV light in submicrometer particles is around 15 nm, which means that if 100% of the TiO\textsubscript{2} particles were reached by the UV light, the sizes of the secondary aggregates would have to be less than 30 nm. In light of the fact that the hybrid TiO\textsubscript{2}-C aerogels have secondary aggregated particles from 216 to 268 nm, the utilization ratio of TiO\textsubscript{2} particles in terms of light penetrability is rather low, and photocatalytic activity of the TiO\textsubscript{2} nanoparticles is extremely high. This indicates that a further significant increase of photocatalytic activity is possible by decreasing the aggregate size.

In summary, we have synthesized novel TiO\textsubscript{2}-C hybrid aerogels, in which anatase TiO\textsubscript{2} and carbon nanoparticles are interwoven to form submicrometer aggregates that form macroporous pores with sizes tunable from 966 to 166 nm. The oxygen vacancy concentration in the anatase TiO\textsubscript{2} nanoparticles is between 7.2 to 18.0% and the size of the TiO\textsubscript{2} nanoparticles is around 8–9 nm. Reduced electron-hole recombination, small particle size, high oxygen vacancy concentration, reduced band gap, a short diffusion path for the reactant and pore scattering are responsible for the high photocatalytic activity of the hybrid aerogels. The highest photocatalytic activity of TiO\textsubscript{2}-C-3 is due to an optimum macropore size that can increase light utilization by pore scattering and possibly an appropriate oxygen vacancy concentration.

### Table 4 | Adsorption kinetics and photocatalytic activities of the TiO\textsubscript{2}-C hybrid aerogels

|       | P25     | TiO\textsubscript{2}-C-1 | TiO\textsubscript{2}-C-2 | TiO\textsubscript{2}-C-3 | TiO\textsubscript{2}-C-4 | TiO\textsubscript{2}-C-5 |
|-------|---------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| \( q_r \), mg/g | 3.91 ± 0.03 | 8.83 ± 0.08 | 7.93 ± 0.10 | 7.61 ± 0.11 | 7.08 ± 0.15 | 6.36 ± 0.15 |
| \( k_2 \), \( 10^{-2} \) min\(^{-1}\), g/mg | 4.4 ± 0.8 | 1.0 ± 0.1 | 1.2 ± 0.2 | 0.9 ± 0.1 | 0.7 ± 0.1 | 0.8 ± 0.2 |
| \( r_{on} \) | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 |
| \( k_p \), \( 10^{-2} \) min\(^{-1}\) | 1.4 ± 0.1 | 1.9 ± 0.1 | 2.2 ± 0.2 | 6.0 ± 0.2 | 2.6 ± 0.4 | 3.2 ± 0.4 |
| \( r_{CO} \) | 0.97 | 0.98 | 0.96 | 0.99 | 0.94 | 0.94 |
| Rate ratio to P25 | 1.00 ± 0.00 | 1.34 ± 0.04 | 1.54 ± 0.03 | 4.23 ± 0.22 | 1.87 ± 0.03 | 2.26 ± 0.10 |
Methods

Preparation. All the reagents were analytical grade and used as received. 10 g of resorcinol (R) and furfural (F) with a molar ratio of 1:3 was mixed and stirred to form a clear solution. Anhydrous ethanol and ethyl acetocetate (EA) was mixed in an ice bath to form a solution, to which TiCl₄ was dropped over slowly under rigorous agitation and thereafter propylene oxide (PO) was added drop-wise to form a solution. B. Finally, solution A was added drop-wise to solution B with rigorous stirring at room temperature. The formulations of the samples were determined as following. The amounts of resorcinol and furfural were kept the same as above. The mass ratios of TiCl₄/(R + F) were 0.62, 0.70, 0.90, 1.17, and 1.26 for the five samples. The amount of PO and EA was calculated by keeping the same molar ratios of PO/Ti and EA/Ti at 6 and 0.6, respectively. The total mass of resorcinol, furfural, anhydrous ethanol, and PO was 100 g and the amount of anhydrous ethanol was calculated from the mass balance. The five samples were named TiO₂-C-1, TiO₂-C-2, TiO₂-C-3, TiO₂-C-4, and TiO₂-C-5 with increasing mass ratio of TiCl₄/(R + F). After completing the above process, the final solution was aged for 10 min, transferred to ampoules (30 ml each) and sealed by a gas torch. The sealed ampoules were placed in a water bath at 70 °C for 5 days to form the TiO₂-RF wet gels, and then were broken and put into a n-hexane-filled autoclave to carry out supercritical drying at 240 °C and 6 MPa for 1 h, afterwards the autoclave was depressurized at a rate of 0.1 MPa/min to atmosphere pressure and cooled to room temperature naturally. The dried TiO₂-RF hybrid aerogels were carbonized in a vertical tube furnace at 800 °C for 3 h to obtain the hybrid TiO₂-C aerogels using a heating rate of 2 °C/min under a nitrogen flow.

Microstructural characterization. TiO₂ content was calculated based on weight loss determined by burning the TiO₂-C hybrid aerogels at 800 °C in air for 3 h. The X-ray diffraction patterns of the samples were collected on a D/MAX-II type X-ray diffractometer (Rigaku, Japan) with Cu Kα radiation. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The crystallite size of TiO₂ was calculated using the Scherrer equation based on the (101) diffraction peak of anatase. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images were collected using a JEM 2100 EX microscope (JEOL, Japan) and a Scanning Electron Microscope Quantax 200 FEG (PEI Co., USA) with accelerating voltages of 30 and 200 keV, respectively. The histograms of aggregate sizes were obtained by measuring the sizes and counting the numbers of the aggregated particles. Nitrogen adsorption and desorption isotherms of samples were obtained on a Tristar volumetric adsorption apparatus (Micromeritics Corp., USA) at 77 K. Surface areas of samples were determined by applying adsorption data of p/p₀ between 0.01 and 0.26 to the Brunauer Emmett Teller (BET) equation. Pore size distributions were obtained by a non-local density functional theory (DFT) model, assuming a slit pore geometry. Micropore and mesopore volumes were estimated by the DFT method for pores with volumes less than 2 nm and between 2 and 50 nm. The external surface areas were obtained by the t-plot method. Mercury intrusion porosimetry of monolithic TiO₂-C hybrid aerogels was carried out in the chamber of an AutoPore IV 9500 porosimeter (Micromeritics Corp., USA). After the chamber was evacuated to 20 Pa, mercury was subsequently introduced to the chamber, the hydrostatic head of which yielded an initial low pressure of 3 kPa. Pressure was subsequently increased to a maximum pressure of 300 MPa/min to atmosphere pressure and cooled to room temperature naturally. The formulations of the samples were determined as following. The MB degradation percentages, (1-qt/qe)×100% are plotted by applying MB photodegradation kinetics data to equation (3). The correlation coefficients rₛ values and standard errors (SE) of the fit were extracted.

\[
\log(q_t - q_e) = -\frac{k_1}{2.303} t
\]

(3)

Where \(q_t\) is the amount of MB degraded at time \(t\) in mg/g, \(q_e\) the amount of MB adsorbed at equilibrium in mg/g, and \(k_1\) the first-order rate constant in min⁻¹. We can obtain \(k_2\) and \(q_e\) by applying MB photodegradation kinetics data to equation (3). The correlation coefficients rₛ values and standard errors (SE) of the fit were also extracted.

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Author contributions
R.Z. and W.C.L. conceived and designed the experiments, R.Z. and X.S. co-wrote the paper, UV-vis diffuse reflectance experiments, R.Z. and X.S. carried out photocatalytic activity including XRD, XPS, Raman, SEM, TEM, nitrogen adsorption, mercury porosimetry and special reference to the determination of surface area and porosity. Pure Appl. Chem. 57, 603–619 (1985).

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