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Graphene Oxide/ TiO_2 Composites in Real Time
by *In Situ* Synchrotron X-ray Powder Diffraction
and Pair Distribution Function Analysis**

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Unraveling the Hydrogenation of TiO₂ and Graphene
Oxide/TiO₂ Composites in Real Time by *In Situ*
Synchrotron X-ray Powder Diffraction and Pair
Distribution Function Analysis

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ABSTRACT

The functionalization of graphene oxide (GO) and graphene (GR) by TiO_2 and other metal oxides has attracted considerable attention due to numerous promising applications in catalysis, energy conversion and storage. Hydrogenation of this class of materials has been proposed as a promising way to tune catalytic properties by altering the structural and chemical transformations that occur upon H incorporation. Herein, we investigate the structural changes that occur during the hydrogenation process using *in situ* powder X-ray diffraction (XRD) and pair distribution function (PDF) analysis of GO-TiO_2 and TiO_2 under H_2 reduction. Sequential Rietveld refinement was employed to gain insight into the evolution of crystal growth of TiO_2 nanoparticles in the presence of two-dimensional (2D) GO nanosheets. GO sheets not only significantly retarded the nucleation and growth of rutile impurities, stabilizing the anatase structure, but was also partially reduced to hydrogenated graphene (HG) by the introduction of atomic hydrogen into the honeycomb lattice. We discuss the hydrogenation processes and the resulting composite structure that occurs during the incorporation of atomic H and the dynamic structural transformations that leads to a highly active photocatalyst.

INTRODUCTION

Hydrogen treatment of catalysts by either hydrogenation or hydrogen cracking has been commonly used as a pre-treatment or primary reactant to activate and/or to reduce both metals and oxides or co-reactants either prior or during a catalytic reaction.¹⁻³ This process requires initially the adsorption of molecular H₂, a homolytic scission of the H-H bonds, the diffusion of H into the bulk and subsequent bonding with either M cations or O anions.

In certain cases this process of driving subsurface H into the bulk of the material can form stable hydrides or hydroxides those themselves can be highly active species.¹⁻³ The crystallization of pure hydrogenated materials is not easy to discern, while identification of stored molecularly bound hydrogen/hydrides/hydroxides is equally challenging. However, hydrogenation was used in numerous studies as a way to alter the chemical and structural properties of applied materials to achieve careful tailored functionality. This is especially evident in the case of TiO₂, a well-known photocatalyst. Hydrogenation of TiO₂ leads to the formation of surface-disordered layers and defect-rich TiO_{2-x} termed ‘reduced titania’ or ‘black TiO₂’. The presence of oxygen vacancies and Ti³⁺ species in TiO_{2-x} facilitates the electrical conductivity and charge transport, efficiently suppressing the recombination of photoinduced electrons and holes, which is beneficial for photocatalytic activity and stability.⁴⁻¹¹ In addition, the introduction of abundant lattice disorder and defects extends the photoresponse toward the visible light region

stemming from the band gap narrowing and the emergence of defect energy level below the conduction band of TiO_2 , therefore, increasing the quantum efficiency.⁴⁻¹¹ However, it is also mentioned that the hydrogenation temperature and duration strongly affect the color of TiO_{2-x} , the defect type and concentration of defects in the material because the excess defects can become the recombination centers and diminish the activity.

Since the discovery in 2004, graphene (GR) and its derivatives (graphene oxide - GO, reduced graphene oxide - RGO) have become a very appealing material due to its unique structure, extraordinary properties and proposed potential for applications in electronic, photovoltaics, photonic devices, catalysis, biomedicines, energy storage and energy conversion.¹²⁻¹⁴ Unlike GR, fully hydrogenated graphene (known as “*graphane*”), partially/half-hydrogenated graphene (as “*graphone*”) or hydrogenated graphene (HG) in general have not been widely considered in spite of their fascinating properties. By saturation of the aromatic bonds with hydrogen atoms that induces large amount of sp^3 hybridized bonds by high pressure hydrogenation, low pressure hydrogen plasma and wet chemistry (Birch reduction), HG materials have been considered as a promising semiconductor and as an efficient stable support for anchoring metal/metal oxide catalysts.¹⁵⁻²⁶ Due to the attachment of the atomic hydrogen to each site of the atomic scaffold of the lattice, the hybridization of carbon atoms alters the matrix from sp^2 into sp^3 , hence removing the conducting π -bands and opening an energy gap.^{15,16} Accordingly, three conformations of HG can be generated and each conformer is characterized by a specific hydrogen sublattice and by different buckling of the carbon sublattice.¹⁸ Particularly, the hydrogen atoms alternate on both sides of the carbon sheet in the chair conformation (C-graphane); whereas in the boat conformation (B-graphane), pairs of H-atoms alternate along the armchair direction of the carbon sheet. Especially, the washboard W-graphane induces double rows of hydrogen atoms aligned

along the zigzag direction of the carbon sublattice, alternating on both sides of the carbon sheet. According to Cadelano's calculation,¹⁸ C-C bond length in C- and W-graphane is about 1.54 Å, similar to sp³ bond length in diamond and much larger than in graphene (1.42 Å). Two types of C-C bonds are observed in the B conformer, connecting two carbon atoms bonded to hydrogen atoms either lying on opposite sides (bond length 1.57 Å) or lying on the same side of the honeycomb scaffold (bond length 1.54 Å). Otherwise, the C atoms in the graphane sheet became more planar-like as compared to graphane with the C-C bond length of 1.495 Å, lying between those in the GR and graphane structure.^{15,17,20} Such HG materials exhibit ferromagnetism and more importantly, its band gap can be readily tunable, depending on the extent of hydrogen bonding due to reversible hydrogenation. When half of the hydrogen in the graphane sheet is removed, the resulting semi-hydrogenated graphene or graphone becomes a ferromagnetic semiconductor with a small indirect gap arising from the formation of strong σ -bonds and the breakage of the delocalized π -bonding network of GR, leaving the electrons in the unhydrogenated carbon atoms localized and unpaired.¹⁷ Notably, it is very different from graphane, with a large direct band gap and also in comparison to GR, with a zero band gap. Up to now, there are few experimental studies devoted to graphane and graphone.^{16,19,23}

There has been tremendous progress during last decade in the utilization of *in situ* studies to gain deep insight into the structural evolution, chemical reactions, formation and crystal growth of nanomaterials taking place under experimental and reaction conditions.²⁷⁻³² The utilization of numerous *in situ* techniques, *i.e.* X-ray diffraction, pair distribution function analysis, X-ray absorption fine structure, X-ray photoelectron spectroscopy, infrared spectroscopy, transmission electron microscopy, have been strongly developed. However, to the best of our knowledge, to

date no studies have focused on the crystallographic evolution of TiO_2 in the presence of 2D carbonaceous sheets and the subsequent effects of hydrogenation.

Recently, we have reported the hydrogenated graphene- TiO_{2-x} composite prepared by the hydrogenation of graphene oxide- TiO_2 under different environments and the composites exhibited much greater photocatalytic activity toward H_2 production than those obtained over reduced TiO_2 and pristine TiO_2 without noble metal cocatalyst.³³ Such an enhancement could be ascribed to the significant alteration in geometry, structure and electronic properties upon the reduction in H_2 -rich atmosphere. Motivated by this, in this work, we provide a fundamental study of the dynamic structural and atomic changes of GO- TiO_2 during H_2 reduction by means of *in situ* synchrotron radiation powder X-ray diffraction and pair distribution function analysis. We strived to investigate the influence of GO component on the growth and phase transformation of TiO_2 during the hydrogenation process by making direct comparisons to the hydrogenation of plain TiO_2 . The reduction extent of GO to HG during the *in situ* observation was also discussed.

EXPERIMENTAL

Materials synthesis

GO precursor was synthesized from expanded graphite by a modified Hummers method.³⁴ A desirable amount of expandable graphite (grade 1721, Asbury Carbon) was heated for 10 s in a microwave oven, gaining 150 times the volume of its original mass. The three-necked flask containing 500 mL of concentrated H_2SO_4 was chilled in the ice bath to 273 K and 5 g of expanded graphite was gradually added under mechanical stirring. 30 g of KMnO_4 was slowly added so that the temperature did not exceed 293 K. The temperature was then elevated to 308 K and the suspension was stirred for 2 h. The flask was subsequently chilled again on the ice bath and 1 L of deionized water was slowly added to maintain the temperature below 343 K. The

mixture was stirred for 1 h, diluted with 1 L of deionized water and 50 mL of H₂O₂ (30 wt%) was subsequently added. Vigorous bubbles appeared as the color of suspension changed from dark brown to yellow. The suspension was centrifuged and washed with aqueous HCl solution (10%), followed by centrifugation and washing with deionized water to entirely remove the acid until the pH of GO dispersion reached 6. The as-synthesized GO dispersion was in the paste form and the concentration of GO was 3.5 mg mL⁻¹, which was determined by vacuum-drying at 353 K for 24 h.

On the other hand, a mixture of titanium *n*-butoxide and hydrochloric acid (35 wt%) with volume ratio of 7:1 was hydrothermally treated in a Teflon-lined stainless steel autoclave at 150 °C for 6 h. After coagulation by ammonia solution (0.1 M), the white precipitate was washed by ethanol and centrifuged at 15000 rpm and re-dispersed into ethanol. Nominal 1 wt% of GO dispersion (3.5 mg mL⁻¹) was added into this dispersion under vigorous stirring at room temperature and subsequent sonication. The mixture was loaded into the autoclave and statically heated to 80 °C for 4 h. After washing with deionized water and collection by centrifugation, the final powder was obtained by lyophilization using a freeze dry system and named GO-TiO₂. TiO₂ nanoparticles were also obtained without the addition of GO precursor.

***In situ* time-resolved X-ray diffraction and atomic pair distribution function analysis**

In situ time-resolved X-ray diffraction (TR-XRD) patterns were collected at beamline X7B (λ = 0.3196 Å) of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) using a Perkin Elmer amorphous silicon detector. 5 mg of powder were loaded into a 0.9-mm-ID quartz capillary mounted on a flow cell system (**Fig. 1**). A small resistance heater was underneath the capillary and the temperature was monitored with a thermocouple that was placed straight into the capillary near the sample. The reactor was purged

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3 with 5% H₂/He flow for 15 min, followed by subsequent high-purity H₂ flow for 15 min at room
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5 temperature and then heated from 25 to 600 °C under 10 sccm (standard cubic centimeters per
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7 minute) of H₂. The weight hourly space velocity defined as the ratio between the mass flow rate
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9 of H₂ inlet gas and the mass of catalyst loading into the capillary was 10.7 h⁻¹. The heating rate
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11 was 10 °C min⁻¹, the temperature was incrementally kept at 400, 500 and 600 °C for 30 min, and
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13 the fast cooling was proceeded afterwards within 10 min. Two-dimensional diffraction patterns
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15 were collected at sample-detector distances of 400 mm. The raw data was integrated by Fit2D
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17 code (calibrated by LaB₆ standard) while the crystalline phase identification, composition and
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19 lattice parameters were subsequently analyzed by Rietveld refinement with the aid of General
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21 Structure Analysis System (GSAS) program.
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27 *In situ* time-resolved pair distribution function (TR-PDF) profiles were also obtained at the
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29 same beamline used for XRD with the detector distance of 121 mm. Data processing (with Q_{max}
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31 = 20 Å⁻¹) was subsequently performed with Python/PDFgetX3 to describe the distribution of all
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33 pairs of atoms within a sample as a function of interatomic distance.
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Figure 1. (A) Flow cell apparatus for *in situ* time-resolved XRD/PDF studies; (B, C) micrographs of GO-TiO₂ before and after *in situ* hydrogenation, respectively.

***Ex situ* characterization**

All *ex situ* characterizations of prepared materials were performed using several techniques available at Center for Functional Nanomaterials (CFN) at BNL. The structure and morphology were observed by scanning electron microscopy (SEM) on a Hitachi S-4800 microscope and transmission electron microscopy (TEM) on a FEI Titan 80-300 with an objective-lens aberration corrector and a field-emission gun operated at 300 kV. Raman spectroscopy was performed on WiTec Alpha combination microscope with 532 nm laser as the excitation source.

RESULTS AND DISCUSSION

The structure of GO-TiO₂ was determined *ex situ* by microscopic and spectroscopic techniques. The precise chemical structure of GO has been the subject of considerable debate

over the years, and even to this day no unambiguous model exists due to the complexity of the material and the lack of precise analytical/characterization techniques.³⁵ It has been reported that GO is an electrically insulating material due to disrupted sp^2 bonding network and abundant oxygen-containing functional groups (as seen in **Fig. 2A**), including epoxide, hydroxyl, keto, carboxyl and carbonyl groups, located on the basal plane and at the edge of GO.^{35,36} GO is well exfoliated into monolayers or few-layered stacks through a variety of thermal and mechanical methods and consequently, metal or metal oxide particles are easily incorporated into negatively charged GO sheets by either covalent or non-covalent interactions,³⁵ *i.e.* Van der Waals interaction, hydrogen bonding, electrostatic bonding and π - π stacking. **Fig. 2B** shows representative TEM image of TiO₂ nanoparticles, revealing that the nanoparticles are between the size of 5-7 nm, are composed of highly crystalline structures with well-resolved lattice fringes of 0.35 nm, which can be assigned to the (101) plane of anatase TiO₂. The structure of GO-TiO₂ was observed by SEM as shown in **Fig. 2C**, demonstrating the uniform distribution of TiO₂ nanoparticles onto GO sheets. The structure of these materials are further confirmed by Raman spectra in which numerous distinctive bands at 155 (E_g), 203 (E_g), 407 (B_{1g}), 518 (A_{1g}+B_{1g}) and 638 cm⁻¹ (E_g) associated with tetragonal anatase were detected (**Fig. 2D**). Two representative D and G bands at 1355 and 1616 cm⁻¹ are additionally observed in the GO-TiO₂ sample, corresponding to the breakage of symmetry by edges or a high density of defects and the first-order scattering of the E_{2g} vibration mode observed for the sp^2 domain, respectively.³⁷

Table 1. Rietveld refinement from PXRD patterns of blank TiO₂ and GO-TiO₂ prior to H₂ reduction.

Samples	Anatase cell parameters / Å		Unit cell volume / Å ³	Crystallite size / nm
	$a = b$	c		

TiO ₂	3.7922(7)	9.5009(2)	136.64	5.9(2)
GO-TiO ₂	3.7921(1)	9.4987(2)	136.59	6.0(8)

Figure 2. (A) Structural model of GO/TiO₂, (B) TEM image of TiO₂ nanoparticles, (C) SEM image of GO-TiO₂, and (D) Raman spectra of TiO₂ and GO-TiO₂. Inset of B is corresponding Fast Fourier transforms (FFT) of ordered regions in the TEM images.

The thermal evolution of GO-TiO₂ under high purity H₂ atmosphere was studied by *in situ* TR-XRD as shown in **Fig. 3A**. Prior to hydrogenation, numerous well-defined (101), (004), (200),

(105) and (204) diffraction peaks at $2\theta = 5.2, 7.7, 9.6, 10.8$ and 12.3° (space group $I4_1/amd$) were detected. The Rietveld refined cell parameters of tetragonal anatase TiO_2 are $a = b = 3.7921$ Å and $c = 9.4987$ Å (displayed in **Fig. 3B**) and the average crystallite size was 6.08 nm (**Table 1**). No diffraction associated with the carbonaceous component was detected, possibly due to low nominal concentration of GO, well-exfoliated GO nanosheets during preparation or the shielding of the characteristic (002) peak by the main (101) diffraction of anatase TiO_2 that has been described previously.^{38,39} The well-ordered anatase structure gradually develops with thermal treatment both in terms of the incremental intensity and peak width narrowing. The nucleation of the rutile grain, with a body-centered tetragonal unit cell appears at $585^\circ C$ via the appearance of (110), (111), (211) and (220) reflections at $2\theta = 5.6, 8.3, 10.7$ and 11.2° (space group $P4_2/mnm$).

To gain further insight into the particle growth, GSAS was employed to run sequential Rietveld refinement. The crystalline phase composition as a function of time and temperature is plotted in **Fig. 4A** in which *ca.* 12.6 wt% rutile phase with the average crystallite size of 14 nm was obtained at $600^\circ C$. Table 2 shows the anatase/rutile composition and mean crystallite size of TiO_2 after *in situ* hydrogenation. The gradual thermal lattice expansion occurs through increments in unit cell dimensions as seen in **Fig. 4B** due to the introduction of hydrogen species or defects. **Fig. 4C** presents the stability of axial ratio c/a as prolonging the reduction temperature at 400, 500 and $600^\circ C$ for 25 min. Such aspect ratio becomes stable after heating for 10 min at $500^\circ C$. Subsequently, the appearance of the rutile structure with larger a (4.58-4.59 Å) and smaller c (2.95-2.96 Å) can thus be taken into account. In addition, it is known that the driving force for the phase transformation is the difference between chemical potential of the initial and final phases.⁴⁰ Activation energy is the minimum energy requirement for overcoming the energy barrier for phase transformation between the two phases. The total free energy can be

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determined by volume energy, surface energy, and surface stress induced energy. The higher the anatase surface energy and surface stress energy, the more the contribution to the non-equilibrium transition from anatase to rutile. According to Li et al.,⁴⁰ the higher negative Gibbs free energy ($\Delta G_{A \rightarrow R}$) corresponds to the lower activation energy E_a needed for anatase to rutile transition. It is evident that the addition of GO alters the activation energy for the anatase-to-rutile phase transformation. Herein, assuming the transformation is a first-order reaction,^{40,41} E_a value can be derived from the plot describing the relation between rutile mass fraction and annealing temperature. As shown in Fig. 4D, the activation energy for the phase transition in H₂ atmosphere is 883.4 kJ mol⁻¹ for GO-TiO₂.

Figure 3. (A) *Time-resolved* XRD of GO-TiO₂ under H₂ reduction; and (B) unit cells for both anatase and rutile TiO₂. The blue and red spheres represent titanium and oxygen, respectively.

Figure 4. (A-C) Time evolution of (A) crystal phase transformation, (B) anatase lattice parameters and (C) aspect ratio of GO-TiO₂ during hydrogenation from room temperature to 600 °C and subsequent fast cooling; (D) plot of $\ln(W_R)$ vs. $1/T$ for activation energy determination of GO-TiO₂.

Table 2. Mass fraction and mean crystallite size of TiO₂ and GO-TiO₂ after *in situ* hydrogen reduction at 600 °C obtained from sequential Rietveld refinement.

Samples	Mass fraction / %		Mean crystallite size / nm	
	Anatase	Rutile	Anatase	Rutile
TiO ₂	20.76	79.24	17(1)	25(9)
GO-TiO ₂	87.42	12.58	20(6)	13(9)

Noticeably, the crystallization behavior of TiO_2 in the presence of 2D GO sheets is remarkably different from pure TiO_2 as shown in **Fig. 5**. The anatase-to-rutile phase transformation occurs at 530 °C, much earlier than that of GO- TiO_2 and up to 79.2% rutile phase was formed at 600 °C. The time dependent evolution of rutile phase and the unit cell parameters for TiO_2 are shown in **Fig. 6**. Note that the particle size of the anatase structure is ~17 nm whereas that of rutile grain size is *ca.* 25 nm. The activation energy of anatase-to-rutile phase transformation in TiO_2 nanoparticle is 247.4 kJ mol⁻¹, much lower than E_a value obtained in the composite. This further suggests that the re-crystallization of anatase and nucleation of rutile are energetically favored at moderate temperatures at a larger grain size upon hydrogenation. It is well known that the functionalization of GR with metal oxide has been conducted by thermal, chemical, electrochemical and photo-assisted reduction methods that induce unique structural, physical, surface morphologies, mechanical and electronic properties of the materials.^{35,38,39,42} Compared to other approaches, thermally-mediated reduction not only leaves behind vacancies and structural defects due to the release of thermodynamically stable carbon dioxide which strongly affects the mechanical and electrical properties of GR or RGO but also causes the agglomeration of the metal oxide, restacking of carbonaceous layers and crystal growth of impurities, resulting in larger grain sizes that possibly induces diminished performance. It is worth noting that the *in situ* hydrogenation in our study demonstrates that the GO nanosheets significantly retards the nucleation and growth of the rutile phase of TiO_2 as well as the simultaneous hydrogen incorporation into GO. The GO imparts a stabilizing effect on either the anatase structure or crystallite size. Therefore, we have combined the thermal reduction and hydrogenation to fabricate hydrogenated graphene- TiO_2 composites directly from GO- TiO_2 .

Figure 5. Time-resolved XRD of TiO_2 under H_2 reduction.

Figure 6. (A-C) Time evolution of (A) anatase-to-rutile transformation, (B) anatase lattice parameters, and (C) aspect ratio of TiO₂ during hydrogenation; (D) plot of $\ln(W_R)$ vs. $1/T$ for activation energy calculation of TiO₂ nanoparticles.

PDF analysis using Python/PDFgetX3 was also performed (**Fig. 7**), where the local atomic geometry and short/long-range order of the material was determined. The function $G(r)$ defines the probability of finding a pair of atoms at a given interatomic distance r , with an integrated intensity depending on the coherence scattering lengths of the elements involved and their multiplicities. The PDF signal takes into account all components of the XRD pattern and contains all characteristic interatomic distances in the materials, the shortest bond length producing the first peak.²⁷ As plotted in **Fig. 7A**, similar aspects were observed over both TiO₂

and GO-TiO₂ before hydrogenation except the shoulder at 1.64 Å as well as two small features at 2.35 and 2.68 Å. The shoulder at 1.64 Å might be stemming from carbon-oxygen (C-O and/or C=O) bond length of functional groups. The indicative maxima located at 1.96 and 3.05 Å for the TiO₂ sample are ascribed to the mean bond lengths of Ti-O and Ti-Ti pairs for the first neighbor coordination shell for [TiO₆] octahedra (the closet O shell around a Ti atom); meanwhile the peaks at 3.83 Å represents the second asymmetric Ti-Ti/O-O coordination sphere. Each Ti ion in the anatase structure octahedrally coordinates to six O ions with the atypical Ti-O bond length of 1.98 Å and equatorial bond length of 1.93 Å.⁴³ The octahedra from zigzag chains along the *a* and *b* axes with each octahedron sharing four edges (illustrated in **Fig. 7B**). Two small features at 2.35 and 2.68 Å of GO-TiO₂ can be assigned to O-O pairs from TiO₂ and GO, respectively.⁴⁴ Due to the different appearance of short-range neighborhoods of those two materials, the subtraction spectrum was generated to probe the difference in short and long-range order as seen in **Fig. 7C**. According to Petkov et al.,⁴⁵ the first two PDF peaks in all carbon samples centered at 1.41 Å and 2.42 Å are assigned to the two shortest distances between carbon atoms sitting on the vertices of hexagonal rings, confirming the (*sp*²) carbon-(*sp*²) carbon bonding. Because X-rays are sensitive to carbon distances, distinct different behavior in PDF profiles are obtained for mesoporous carbon, single carbon nanotubes, multiwalled carbon nanotubes, graphitic carbon, and graphene in which carbon atoms arrange in different ways at longer interatomic distances.⁴⁴

Figure 7. (A, C) PDF analysis of TiO_2 and GO-TiO_2 before hydrogenation: (A) short-range order and (C) long-range order. (B) Crystal structure of anatase and rutile TiO_2 composed of $[\text{TiO}_6]$ polyhedra.

Figure 8. Time-resolved PDF profiles of (A) TiO₂ and (B) GO-TiO₂ upon annealing in a H₂ atmosphere. Black arrows indicate obvious changes in peak position, intensity and width.

The *in situ* time-resolved PDF profiles of TiO₂ and GO-TiO₂ are displayed in **Fig. 8**. It is worth noting that increasing the temperature up to 600 °C remarkably alters both maxima

intensity and width, and the obvious shrinkage in interatomic distances of Ti-Ti, O and Ti-O pairs occurs in >2 coordination sphere (**Fig. 8A**). The shorter distance can be ascribed to a more dense local packing arrangement stemming from rutile nucleation and/or the removal of oxygen atoms creating the defects. Considering the rutile unit cell, the corner-sharing octahedra have one Ti-O bond linking them, whereas edge-sharing octahedra share two Ti-O bonds (**Fig. 7B**). The Ti-O bond distances in the rutile structure are similar to anatase (1.95 and 1.98 Å for the short and long Ti-O bond lengths, respectively). The four equatorial O ions are coplanar occupying a rectangular arrangement with the long edge (2.954 Å) along the c axis and the short edge (2.53 Å) lying diagonally across the plane defined by the a direction.⁴³ Thus the rutile unit cell is more compact than anatase or more compressible in the ab plane where external stress can be taken up by the hinging of the octahedra than in c direction which is supported by relatively inflexible “pillars” of edge-sharing octahedra.⁴⁴ The lowest-energy structure is one which minimizes Ti-Ti and O-O repulsions while maximizing Ti-O attraction.⁴⁴ It should be noticed that a more dense local atomic arrangement may balance the energy loss coming from the long-range electrostatic interactions and indeed, the local distribution of distances can be interpreted by a strong shrinking along anatase a cell parameter direction along with a small elongation along c -axis direction as increasing temperature.²⁷

Due to the fact that the rutile nucleation onset temperature on GO-TiO₂ is higher than that on TiO₂ (demonstrated by TR-XRD) and the rutile crystal growth is strongly inhibited by GO sheets, the alteration in bond length of Ti-O and Ti-Ti pairs, and the merging of two O-O pairs into one peak at 2.39 Å, over composite material during H₂ reduction is much restricted in comparison with those observed in TiO₂ (as depicted in **Fig. 8B**). Annealing in a reducing atmosphere might create abundant defects in the structure, particularly oxygen vacancies, arising

from the interaction between TiO_2 and molecular H_2 , to overcome the activation energy of TiO_2 lattice arrangement and accelerate it.^{27,45,46} The disappearance of carbon-oxygen shoulder at 1.64 Å and O-O pairs from GO at 2.68 Å, correlated with an obvious formation of a peak at 1.36 Å, demonstrates the possible reduction of GO to HG by removing oxygen from GO and partially creating carbon-carbon (C-C and/or C=C) bonds after heating up to 600 °C. It has been reported that the transformation of sp^2 -hybridized carbon in ideal graphene to sp^3 hybridization in hydrogenated graphene, graphone or graphane results in a change of bond lengths and angles.⁴⁷ A typical bond length of sp^2 C=C is 1.42 Å for GR and graphite, and 1.47 Å for other carbon compounds, whereas sp^3 -hybridized C-C bond length in graphane is 1.53-1.54 Å, near that of diamond.^{15-17,47} As mentioned previously, the C atoms in graphone become more planar-like as compared to graphane with C-C bond length of 1.495 Å, lying between that in GR and graphane.¹⁷ A typical value for single C-H bond length is *ca.* 1.1 Å and depending on the number of hydrogen molecules adsorbed and the coordination of hydrogen atom on single or both sides of graphene sheet, the hydrogen-carbon distance fluctuates in range of 1.1- 1.25 Å.^{15,47} Meanwhile, the average Ti-C and Ti-H bond lengths are 1.7-2.1 Å⁴⁸ and 1.6-1.9 Å,⁴⁹ respectively. Therefore, due to the broadening of all maxima at high temperature, the superposition of Ti-O, Ti-Ti and O-O pairs with Ti-C, Ti-H, C-C pair can take place in the present work. Unfortunately, we do not see a clear evidence from PDF to show the time-resolved transformation from sp^2 to sp^3 as hydrogen attaches to carbon atoms. Ideally, it is expected that the peak at 1.36 Å shifts to 1.54 Å upon full hydrogenation. Herein, our results indicate the possible formation of partially hydrogenated graphene. However, such partial hydrogenation of GO was elucidated by the increase of relative intensity ratio between D band and G band (I_D/I_G)

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3 in our previous study,³³ indicating an increment in the number of defects, disorders and sp^3 C-C
4 bonds.
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8 In an attempt to gain more detailed information, the difference profiles for both GO-TiO₂ and
9 TiO₂ after subtracting the plots before reduction from after *in situ* hydrogenation are presented in
10 **Fig. 9** and **Fig. 10**, respectively. The changes in the atomic geometry arising from hydrogenation
11 are clear both in the short range (A) and long range (B) nearest neighbor atomic distances. In the
12 case of GO-TiO₂, there is a little or no shift to the atomic positions, however clear loss of
13 intensity of features corresponding to the Ti-O, Ti-Ti distances occurs as a result of
14 hydrogenation. As we mentioned before, it is challenging to assign the transformation likely to
15 occur for GO to HG from features here but C-C and Ti-C or Ti-H contributions are likely to be
16 evident under the Ti-O transitions. In TiO₂ alone (**Fig. 10**), the differences upon hydrogenation
17 are notably evident with shifts to the second and third nearest Ti-Ti and Ti-O shells. Relative
18 intensity changes are however, notably stable in the first coordination sphere but appear to
19 increase in >2 coordination spheres.
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Figure 9. (A) Short/medium-range order; and (B) long-range order PDF analysis of GO-TiO₂ before and after hydrogenation.

Figure 10. (A) Short-medium-range; and (B) long-range PDF analysis for TiO_2 before and after hydrogenation.

In addition, the alteration in atomic structure of TiO_2 and GO-TiO_2 after hydrogenation is also analyzed in **Fig. 11**. It is clear that the maxima positions representative of first, second and third nearest neighbor distances shift toward larger atomic distances in the presence of GO, implying the lattice expansion of TiO_2 is as a result of the reduction of Ti^{4+} to Ti^{3+} , and/or the formation of

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Ti-C bonding and Ti-O-C linkage *via* the substitution of lattice oxygen atoms by carbon in GO. One can see the appearance of a small peak at 1.36 Å over GO-TiO₂, which is quite close to the value of theoretical C=C and C-C bond length of graphene and graphone. It is interesting to note that the changes in intensity and maxima position are visible also in larger coordination spheres. However, it is not easy to attribute this change to H incorporation into either the GO or TiO₂, which we have established as prevalent. At present, no model of this transformation (M-H, O-H) has been possible and it is important to note that changes observed here in the PDF are very likely a product of hydrogenation. The theoretical modelling of this structure is at present the focus of ongoing research efforts.

Figure 11. (A) Short-medium-range; and (B) long-range PDF analysis and differential PDF for TiO_2 and GO-TiO_2 after hydrogenation.

CONCLUSIONS

We have investigated the hydrogenation of TiO_2 and GO-TiO_2 , a process which gives rise to a very new prototype of photocatalyst: hydrogenated graphene- TiO_2 . We have employed *in situ*

XRD and PDF to unravel in real time the long range and local atomic structure of these catalyst materials during the hydrogenation reaction. It is evident that the hydrogen reduction of TiO_2 and GO-TiO_2 occurs with a strong influence of the GO on TiO_2 to minimize the transformation from anatase to rutile phase, accompanied by the hydrogenation of graphene oxide inducing partially hydrogenated graphene. The local atomic structural changes are complex and show a gradual yet permanent transformation to the atomic distances of the TiO_2 and GO-TiO_2 upon hydrogenation in real time.

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Notes

The authors declare no competing financial interest.

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