

Bimetallic Ions Co-Doped Nanocrystals: Doping Mechanism, Defect Formation and Associated Structural Transition

Qingbo Sun,[†] Changlin Zheng,[‡] Larissa Q. Huston,[§] Terry J. Frankcombe,^{†,*,**} Hua Chen,[‡] Chao Zhou,[†] Zhenxiao Fu,[†] Ray L. Withers,[†] Lasse Norén,[†] Jodie E. Bradby,[§] Joanne Etheridge,^{‡,*} and Yun Liu^{†,*}

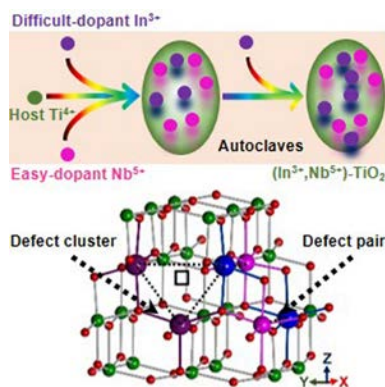
[†]Research School of Chemistry, [§]Research School of Physics and Engineering, [‡]Centre for Advanced Microscopy, the Australian National University, Canberra, Australian Capital Territory, 2601, Australia

^{**}Monash Centre for Electron Microscopy, ^{*}Department of Materials Science and Engineering, Monash University, Victoria, 3800, Australia

[†]School of Physical, Environmental and Mathematical Sciences, University of New South Wales, Australian Capital Territory, 2601, Australia

[†]Fenghua Advanced Technology Holding Co., Ltd., Zhaoqing, Guangdong, 526020, China

ABSTRACT: Ionic co-doping offers a powerful approach for modifying material properties by extending the choice of potential dopant ions. However, it has been a major challenge to introduce certain ions that have hitherto proved difficult to use as dopants (called “difficult-dopants”) into crystal structures at high concentrations, especially through wet chemical synthesis. Furthermore, the lack of a fundamental understanding of how co-dopants are incorporated into host materials; which types of defect structures they form in the equilibrium state; and what roles they play in material performance, has seriously hindered the rational design and development of promising co-doped materials. Here, we take In^{3+} (difficult-dopants) and Nb^{5+} (easy-dopants) co-doped anatase TiO_2 nanocrystals as an example and investigate the doping mechanism of these two different types of metal ions, the defect formation, and their associated impacts on high-pressure induced structural transition behaviours. It is experimentally demonstrated that the dual mechanisms of nucleation and diffusion doping are responsible for the synergic incorporation of these two dopants, and theoretically evidenced that the defect structures created by the introduced In^{3+} , Nb^{5+} co-dopants, their resultant Ti^{3+} and oxygen vacancies are locally composed of both defect clusters and equivalent defect pairs. These formed local defect structures then act as nucleation centres of baddeleyite- and $\alpha\text{-PbO}_2$ -like metastable polymorphic phases and induce the abnormal trans-regime structural transition of co-doped anatase TiO_2 nanocrystals under high pressure. This work thus suggests an effective strategy to design and synthesize co-doped nanocrystals with highly concentrated difficult-dopants. It also unveils the significance of local defect structures on material properties.



Ionic co-doping is a general and effective strategy to significantly improve the macroscopic performances of host materials by tuning their local and average structures. By simultaneously incorporating two or more types of extrinsic ions into the substitutional or interstitial sites of crystal structures, the physicochemical properties of the host materials, such as their dielectric response, optical absorption or magnetic spin, can be modified significantly. Typical cases can be found in titanium dioxide (TiO_2) due to its multifunctional nature and diverse applications. For instance, our previous work¹ suggested that co-doping In^{3+} and Nb^{5+} ions into rutile TiO_2 ceramics enabled the achievement of both colossal permittivity (over 10^5) and low dielectric loss (less than 5%) as a consequence of the formation of electron pinned defect dipoles. Likewise, the simultaneous incorporation of both B^{3+} and N^{3-} ions into anatase TiO_2 microspheres narrowed the host bandgap and thereby enhanced the visible light photocatalytic activity.² Theoretically, Cr and Mn

ion co-doping was predicted to greatly increase magnetic moments and thus induced abnormal ferromagnetism in paramagnetic TiO_2 .³ In other material systems including graphene, carbon nanotubes, tetrahedrites and zinc sulfide, the ionic co-doping strategy has also been broadly utilized to improve their electro-catalytic, thermoelectric or fluorescent properties.⁴⁻⁷

The ionic co-doping strategy also presents many advantages on the resultant chemical compositions of co-doped materials. Ions, which on their own might be difficult to introduce into host materials, can be co-doped at significantly higher concentrations due to the generation of synergistic effects with another dopant ion. For instance, less than 1 at.% In^{3+} ions can be dissolved into TiO_2 without phase segregation,⁸ whereas the dissolution limit can approach ~5 at.% if co-doped with Nb^{5+} ions.¹ Under some scenarios, unwanted species such as oxygen vacancies in the case of N^{3-} single-doped TiO_2 ⁹ or Ti^{3+} ions in the case

of Nb⁵⁺ mono-doped TiO₂,¹⁰ which lead to a deterioration of photocatalytic properties by forming “trapping or recombination centers” of photo-generated electron-hole pairs, can also be efficiently avoided if another appropriate ion is introduced to couple with each other as well as to balance the overall charge of the whole co-doped system (e.g. Nb⁵⁺-N³⁻ co-doping).¹¹

From a structural perspective, ionic co-doping also changes the local structures of the host materials. The selected co-doped ions can exist as isolated point defects, bind together to form defect pairs or form larger local defect clusters^{1,5,12-14} depending upon the chemical compositions or synthesis route. We previously pointed out that co-doping “too big” trivalent In³⁺ ions with Nb⁵⁺ ions was favorable to generate triangular- and diamond-shaped defect clusters in rutile TiO₂¹ while co-doping smaller Al³⁺ ions with Nb⁵⁺ ions locally produced an intergrown, intermediate and metal ion rich structure.¹⁵ In (B, N) co-doped carbon nanotubes,⁵ the B³⁺ and N³⁻ ions could either exist as isolated point defects or chemically bind together depending on their synthesis conditions. The resultant electrocatalytic properties of prepared (B, N) co-doped carbon nanotubes, however, could only be enhanced by the former.

Though ionic co-doping has been successfully used to tune the physicochemical properties of a wide range of host materials by slightly modifying the chemical composition or locally creating different defect states, their reliable wet chemical synthesis remains complicated and rather difficult to control. This is especially the case when the ions that are difficult to dope with (called “difficult-dopants”) are involved since (1) the solubility of the initial reactants should be considered to guarantee enough ions to homogeneously distribute in the reaction solvent; (2) the precipitation of co-dopant ions should be coordinated to inhibit the generation of possible impurities during the reaction process; and (3) the ligands of the metal ions should be modified to achieve the expected doping concentrations in the resultant products. Furthermore, fundamental concerns regarding the synthesis and the resultant co-doped materials themselves still remain unclear, e.g. how are co-dopants introduced into the crystal structures of host materials during the chemical reaction process (i.e. doping mechanism); whether the same types of co-dopants create the same defect states in different polymorph of the same material (i.e. defect formation); and what roles these introduced local defect structures play on the macroscopic properties of the co-doped host materials. Studies on the doping mechanism, the defect formation and their associated impacts are rather important to both design and synthesize novel types of co-doped materials as well as further understand the intrinsic structure-performance relationship.

We herein combine the easy- and difficult-dopant ions together in an attempt to effectively increase the doping levels of the latter. In³⁺ and Nb⁵⁺ co-doped anatase nanocrystals are then synthesized to further demonstrate the effectiveness of the designed co-doping strategies. The potential doping mechanisms of the two different types of metal ions (the In³⁺ difficult-dopant ions and the Nb⁵⁺ easy-dopant ions) are investigated under solvothermal reaction conditions. Through density functional theory (DFT) calculations, we present the local defect structures generated by the In³⁺, Nb⁵⁺ co-dopants, the resultant Ti³⁺ ions and oxygen vacancies. Furthermore, the influence of these intentionally introduced local defect structures on high pressure reaction behaviours of synthesized co-doped nanocrystals are analyzed.

In³⁺ and Nb⁵⁺ co-doped anatase nanocrystals with a chemical formula of (Ti_{1-x-y-z}⁴⁺Ti_x³⁺In_y³⁺Nb_z⁵⁺)(O_{2-(x+y-z)/2}□_{y/2}) are synthesized by a solvothermal method (□ here represents oxygen vacancies and also labelled as V_O^{••}). The x, y and z values in the above chemical formula are experimentally determined to range from 0 up to 0.046 and are controlled by adjusting the concentrations of niobium pentachloride and indium acetate in ethanol solvent while fixing the added volume of titanium chloride. Detailed descriptions about the synthesis and characterization of these nanocrystals are given in the supporting information (SI-1 and SI-2). In³⁺ and Nb⁵⁺ ions are chosen as appropriate co-dopant ions since they enable charge compensating as well as produce a significant local structural change due to the bigger ionic radii of both co-dopants (94 pm for In³⁺ and 78 pm for Nb⁵⁺) as compared to that of Ti⁴⁺ (74.5 pm). Such local structural variation induced the formation of defect clusters in the case of the analogous (In³⁺+Nb⁵⁺) co-doped rutile TiO₂ ceramics¹ to “pin” electrons and thus resulted in an excellent dielectric performance.

In the current anatase case, the ionic radii of the In³⁺ ions are again significantly too large. The calculated apparent valence (AV) or bond valence sum (BVS), of an In³⁺ ion in anatase TiO₂ is 5.33 valence units (v.u.) instead of the ideal 3.00 v.u. estimated using the softBV program (SI-3, supporting information),¹⁶⁻¹⁸ i.e. about 78% over-bonded! Without the removal of at least one of the surrounding oxygen ions and the addition of a further neighboring In³⁺ ion for charge balance, it is rather difficult to introduce In³⁺ ions into TiO₂ to achieve high doping levels by normal wet chemical reaction routes such as sol-gel or co-precipitation. A solvothermal method is thus attempted to combine the higher spontaneous pressure of ethanol with the comparatively higher heating temperature of sealed autoclaves. In contrast to the difficulty in In³⁺ doping, the ionic radii of Nb⁵⁺ ions are almost similar to that of Ti⁴⁺ with an AV of 5.37 v.u., only slightly over-bonded by ~7.4% (SI-3, supporting information). The chemical doping of Nb⁵⁺ ions into anatase TiO₂ is thus relatively easy and can reach up to a concentration of about 14 at.%¹⁹ or more (called “easy-dopants”). Note, however, that charge balance associated with single doping of Nb⁵⁺ ions can only be achieved through generating an equal concentration of reduced Ti³⁺ ions.

Experimentally, we find that nearly all of the Nb⁵⁺ ions in the initial reaction solution can be doped into anatase TiO₂ nanocrystals (Figure 1a). Their doping concentrations are thus easily controlled through just tuning the added weight of starting materials like niobium pentachloride. By contrast, only a small proportion of In³⁺ ions in the reaction solution can be finally incorporated into TiO₂ to achieve a closely equivalent doping level as that of the Nb⁵⁺ ions (Figure 1b). For example, if ~5.0 at.% In³⁺ ions (compared to total titanium ions, i.e. y≈0.046 in the above chemical formula) are designed in co-doped TiO₂ nanocrystals, their actual concentration in the initial reaction solution should be up to ~90 at.%. Most of the In³⁺ ions are left in the reaction solution and should be further separated from the synthesized nanoparticles through post-treatment process for reuse.

In addition, we further found that the doping level of Nb⁵⁺ ions in the co-doped TiO₂ nanocrystals remained virtually unchanged for reaction times between 4 h and 14 h while that of the In³⁺ ions increases almost linearly over the same reaction period (Figure 1c). For reaction times shorter than 4 h, it is dif-

difficult to collect any nanoparticles from the viscous and transparent reaction solution. In such short reaction times, nanoparticles perhaps are not formed or their particle size is too small to be separated for collection. After 14 h, the ratio of In/Ti and Nb/Ti in the nanocrystals does not obviously change. Clearly, the incorporation of Nb⁵⁺ ions is related to a typical nucleation doping. Though the major proportion of the doped In³⁺ ions (~4.1 at.%, compared to total titanium ions) is also introduced together with Nb⁵⁺ ions through nucleation doping, the remaining proportion of them (~0.9 at.%) is actually incorporated into TiO₂ through diffusion doping with a diffusion rate of ~9.52×10⁻⁴ molar per hour. Dual mechanisms (nucleation and diffusion doping) are thus proposed for the introduction of the In³⁺ ions and nucleation-only doping is suggested for that of the Nb⁵⁺ ions. This understanding of doping mechanisms is critical for the controllable synthesis of other metal ion co-doped nanomaterials and the desirable design of material properties.²⁰⁻²²

A schematic, which visually illustrates the two mechanisms of introducing In³⁺ and Nb⁵⁺ ions into TiO₂ nanocrystals, is shown in Figure 1d. Three critical steps are involved during synthesis, *i.e.* (1) homogeneous distribution of all cations (Ti⁴⁺, Nb⁵⁺ and In³⁺) in the ethanol solvent to form one transparent solution; (2) the non-equivalent nucleation co-doping of almost all of the Nb⁵⁺ ions but only a proportion of the In³⁺ ions, which results in the lower doping concentrations of the In³⁺ ions relative to that of the Nb⁵⁺ ions; and (3) the diffusion doping of an additional proportion of In³⁺ ions to achieve equivalent doping levels of the In³⁺ and Nb⁵⁺ ions. It seems that the easy Nb⁵⁺ dopant ions create a synergistic environment for accommodating the more difficult In³⁺ dopant ions. The coupling of these two different types of doped ions is thus demonstrated to be an efficient method to significantly increase the doping concentration of difficult-dopants.

The synthesized (In³⁺+Nb⁵⁺) co-doped TiO₂ nanocrystals were then investigated by X-ray powder diffraction (XRD). All diffraction peaks could be assigned to an average tetragonal anatase-type phase with space group symmetry *I*4₁/*amd* (SI-4, supporting information). This phase analysis was carefully done to be sure that all other analyses were conducted on the single phase sample. The chemical compositions of the optimized, co-doped anatase nanocrystals were then carefully analyzed via energy dispersive X-ray spectroscopy (EDS) in a scanning electron microscope (SEM) and an inductively coupled plasma optical emission spectrometer (ICP-OES). The atomic ratio of indium to niobium is found to be about 1:1 and their respective doping concentrations nearly approach 0, 1.0, 3.0 and 4.6 at.%, *i.e.* $y \approx z \approx 0$, 0.010, 0.030 and 0.046 (SI-5, supporting information). With the gradual increase in the *y* and *z* values, there is a gradual shift of the (101) XRD peak, a linear expansion of the lattice parameters (*a*, *b* and *c*) and of the unit cell volume (*V*, SI-4, supporting information) due to the partial substitution of the smaller Ti⁴⁺ ions with the bigger In³⁺ and Nb⁵⁺ ions. These XRD results and the various microscopic characterization (to be discussed below) suggest the effective co-doping of In³⁺ and Nb⁵⁺ ions into anatase TiO₂ nanoparticles. This is also confirmed by Raman spectra which exhibit similar Raman peaks to the un-doped anatase TiO₂ nanoparticles (SI-6, supporting information).²³ Furthermore, we do not detect any other Raman signals or additional XRD peaks even in the samples with $y \approx z \approx 0.046$ (*i.e.* a total doping concentration of ~9.2 at.%) and thus believe that these (In³⁺+Nb⁵⁺) co-doped TiO₂ nanocrystals represent a single phase solid solution.

The chemical valence states of the cations in the co-doped nanocrystals with $y \approx z \approx 0.046$ were subsequently analyzed by X-ray photoelectron spectroscopy (XPS, Figure 2a, 2b and 2c). As seen, the indium and niobium ions have the chemical valence of +3 and +5, respectively, *i.e.* their chemical valences are the same as those of their starting materials. For the titanium ions, the XPS data show two separate peaks with individual binding energies of ~459.3 and 457.6 eV. These two XPS peaks correspond to Ti⁴⁺ and Ti³⁺, respectively. The generation of Ti³⁺ ions can be ascribed to the reduction of a proportion of the Ti⁴⁺ ions induced by the Nb⁵⁺ ions. Their concentration is calculated to be ~3.5 at.% by fitting to the XPS data (Figure 2c). The slight difference between the doping level of Ti³⁺ (3.5 at.%) and that of the Nb⁵⁺ ions (4.6 at.%) is attributed to the oxidization of partial surficial Ti³⁺ ions due to the high surface energy and high reaction activity of the nanoparticles. The presence of Ti³⁺ ions is also confirmed by the electron paramagnetic resonance (EPR) spectrum (Figure 2d). Two EPR signals at $g_1=1.97$ and $g_2=1.94$ should come from the paramagnetic resonances of Ti³⁺ with 3d¹ electrons trapped on the lattices.²⁴ There is no Nb⁴⁺ observed in both XPS and EPR characterization. The prepared (In³⁺+Nb⁵⁺) co-doped TiO₂ nanocrystals thus not only contain In³⁺ and Nb⁵⁺ co-dopants but also include induced Ti³⁺ ions and oxygen vacancies (to balance the charge of the overall co-doped TiO₂ material). The In³⁺, Nb⁵⁺, Ti³⁺ and oxygen vacancies are labelled In_{Ti}[•], Nb_{Ti}[•], Ti_{Ti}[•] and V_O^{••} using Kröger-Vink notation, respectively.

To further investigate In³⁺ and Nb⁵⁺ co-doped TiO₂ nanocrystals, aberration-corrected HAADF-STEM (high-angle annular dark-field scanning transmission electron microscopy) images of the synthesized (Ti_{0.862}⁴⁺Ti_{0.046}³⁺In_{0.046}³⁺Nb_{0.046}⁵⁺)(O_{1.977}□_{0.023}) nanocrystals (*i.e.* $x \approx y \approx z \approx 0.046$) were taken (Figure 3). It is observed that most of the nanocrystals have quasi-spherical shapes (in projection) with small average particle diameters of less than 10 nm. In atomic resolution HAADF-STEM mode, an atomic column containing any indium (atomic number, *Z*=49) and/or niobium atoms (*Z*=41) substituting for the lighter Ti atoms (*Z*=22) should lead to a noticeable local increase in the corresponding image intensity relative to a pure, unsubstituted Ti column (of the same thickness). The inset in Figure 3 shows a HAADF-STEM image of a nanoparticle exhibiting (011) lattice fringes (running vertically). The alternating bright and dark stripes correspond to double rows of metal ions (separated in the horizontal direction by 0.88 Å, and clearly unresolved) and the complete absence of metal ions, respectively. Note that the arrowed bright dots in the inset always fall within the bright metal ion striped regions, suggesting that they represent local atomic columns with an increased density of substituted In and Nb atoms. Indeed, they may well represent individual In or Nb atoms. This directly demonstrates that In³⁺ and Nb⁵⁺ ions are indeed co-doped into the crystal structures of anatase nanocrystals. In addition, the results of element mapping also indicate that In³⁺ and Nb⁵⁺ ions are really co-doped into anatase TiO₂ nanocrystals and homogeneously distributed (SI-7, supporting information).

It also appears that most of the quasi-spherical nanocrystals achieved at the higher doping levels gradually evolve to nanocubes or nanocuboids with a decrease in the co-dopant concentration (SI-7, supporting information), consistent with results reported for Nb mono-doped TiO₂¹⁹ and Mg mono-doped ZnO²⁵ nanoparticles and can be attributed to their changed local crystal structure after co-doping (SI-4, supporting information).

Additionally, the change of co-doping concentration slightly modified the average particle size and higher doping levels lead to smaller particle diameters, but they all remain less than 10 nm both in terms of the size calculated by the Scherrer equation^{26,27} and that estimated via low magnification TEM lattice imaging (SI-8, supporting information). These small nanoparticles potentially provide many practical applications, *e.g.* to prepare thin films by directly depositing them onto substrates, use as building blocks in constructing functional nanodevices or to lower the sintering temperatures of related ceramics as raw materials/additives.

In order to gain further insight into possible local defect clusters created by the co-doping of In³⁺ and Nb⁵⁺ ions, DFT calculations were carried out on our synthesized anatase compounds with the chemical formula of (Ti_{0.862}⁴⁺Ti_{0.046}³⁺In_{0.046}³⁺Nb_{0.046}⁵⁺)(O_{1.977}□_{0.023}). The calculations were performed using the VASP code²⁸⁻³¹ and a 3×3×1 supercell of the anatase TiO₂ structure. Four Ti⁴⁺ ions were substituted by two In³⁺ and two Nb⁵⁺ ions in various configurations. This yielded a respective doping level of 5.56 at.%, which is very close to the experimental value (4.6 at.% In³⁺+4.6 at.% Nb⁵⁺) of this work. More details about the calculation setup are given in SI-9 (supporting information).

The total energy of the co-doped compounds is found to depend strongly on the configuration of the substituted ions. The lowest energy defect structure is provided by the configuration shown in **Figure 4**. The 2In_{Ti}[•]+V_O^{••}+Ti_{Ti}[•] “triangle” motif, which was previously identified in the (In³⁺+Nb⁵⁺) co-doped rutile TiO₂,¹ was also observed here. This configuration was characterized by In³⁺ ions located in adjacent octahedra, with one of the shared oxygen ions removed for local charge balance considerations. A Nb⁵⁺ ion would be in a nearby octahedron such that a Ti ion across the oxygen vacancy from the indium ions was reduced to Ti³⁺. In the low energy configurations, one Nb⁵⁺ ion is connected to the triangular-shaped defect cluster to form a more complicated 2In_{Ti}[•]+V_O^{••}+Ti_{Ti}[•]+Nb_{Ti}[•] defect complex. The other Nb⁵⁺ ion links with the second Ti³⁺ ion to form a Ti_{Ti}[•]+Nb_{Ti}[•] defect pair. This defect pair would be located nearby within the supercell, with the lowest energies found when it was adjacent to the 2In_{Ti}[•]+V_O^{••}+Ti_{Ti}[•]+Nb_{Ti}[•] defect clusters. Although these defect models also contain triangle-shaped defect complexes and are thus similar to that of (In³⁺+Nb⁵⁺) co-doped rutile TiO₂,¹ they also exhibit their own special features with (1) the newly introduced Ti_{Ti}[•]+Nb_{Ti}[•] defect pairs which may be nearby but not adjacent to the triangular In-containing defect clusters; and (2) the triangle-shaped defect complexes is modified by one Nb⁵⁺ ion to form a more complicated 2In_{Ti}[•]+V_O^{••}+Ti_{Ti}[•]+Nb_{Ti}[•] defect cluster. Two polymorphs of a single material can thus locally produce different defect models though the selected co-dopants are the same.

Figure 5 presents the high-pressure reaction behaviour of these defect-cluster and defect-pair modified nanocrystals with $x \approx y \approx z \approx 0.010$. *In situ* Raman signals were collected under compression and decompression conditions. Detailed experimental processes are described in SI-10 (supporting information). A gradual phase transition from anatase to a baddeleyite-like structure can be observed under compression (Figure 5a). Subsequently, the newly formed baddeleyite-like structure transforms to an α-PbO₂-like phase under decompression (Figure 5b). During the entire compression and decompression cycle,

the co-doped anatase nanocrystals undergo an anatase → baddeleyite-like phase (~20.2 GPa, compression) → α-PbO₂-like structure (~33.0 GPa, decompression) phase transition sequence. This structural transition sequence is inconsistent with the pressure-induced amorphisation of un-doped anatase TiO₂ nanocrystals having a similar crystal size,³²⁻³⁵ but is closely analogous to the phase transition behavior of those pure TiO₂ nanocrystals with a larger particle size of 11 to 40 nm.³⁶⁻³⁸ The anatase (Ti_{1-x-y-z}⁴⁺Ti_x³⁺In_y³⁺Nb_z⁵⁺)(O_{2-(x+y-z)/2}□_{y/2}) nanocrystals thus possess an abnormal trans-regime structural transition behaviour under high pressure. This abnormal phase evolution should be related to the intentionally introduced 2In_{Ti}[•]+V_O^{••}+Ti_{Ti}[•]+Nb_{Ti}[•] defect clusters and/or Ti_{Ti}[•]+Nb_{Ti}[•] defect pairs since they can act as nucleation centers of baddeleyite- or α-PbO₂-like metastable polymorphic phases and thus induce the crystallization of new crystal structures.

In conclusion, highly concentrated In³⁺ difficult-dopants are successfully introduced into TiO₂ crystal structures through the synergistic effects of the Nb⁵⁺ easy-dopants. It is found that the dual mechanisms of nucleation and diffusion doping are responsible for the incorporation of the difficult-dopant In³⁺ ions while nucleation-only doping is observed for that of the easy-dopant Nb⁵⁺ ions. The local defect structures generated by co-doped In³⁺, Nb⁵⁺ ions, their resultant Ti³⁺ and oxygen vacancies are composed of both 2In_{Ti}[•]+V_O^{••}+Ti_{Ti}[•]+Nb_{Ti}[•] defect clusters and equivalent Ti_{Ti}[•]+Nb_{Ti}[•] defect pairs. These intentionally introduced defects would act as nucleation centers of baddeleyite- and α-PbO₂-like metastable polymorphic phases and thereby induce an abnormal trans-regime structural transition of co-doped anatase TiO₂ nanocrystals under high pressure. We believe that this work provides new insight into the design and synthesis of other novel co-doped materials with high concentrations of difficult-dopant ions, opens a new avenue to develop new co-doping systems for developing new functional materials, and significantly advances local defect structures in solids.

ASSOCIATED CONTENT

Supplementary materials about the synthesis and characterization of (Ti_{1-x-y-z}⁴⁺Ti_x³⁺In_y³⁺Nb_z⁵⁺)(O_{2-(x+y-z)/2}□_{y/2}) anatase nanocrystals, the analysis of their chemical compositions, average particle size and other related properties are available in the supporting information (SI).

AUTHOR INFORMATION

Corresponding Author

*yun.liu@anu.edu.au and **t.frankcombe@adfa.edu.au

Author contributions

Q. S., R. L. W., Y. L. and T. J. F. make the main contribution to the preparation of this manuscript. Y. L. initiated this research, planned and coordinated all experimental and theoretical work. T. J. F. did the theoretical work collaborated with Y. L. Q. S. designed the approach for the fabrication of the samples with different compositions and synthetic conditions. Q. S., H. C., L. N. and R. L. W. conducted HRTEM, SEM/EDS, XPS analysis. C. Z. and J. E. conducted the measurement of high-angle annular dark-field scanning transmission electron microscopy. Q. S. and L. Q. H. performed the high-pressure reaction experiments under the supervision of J. E. B. All authors were involved in the data analysis and discussion as well as the manuscript preparation.

Competing financial interests

The authors declare no competing financial interest.

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Figures

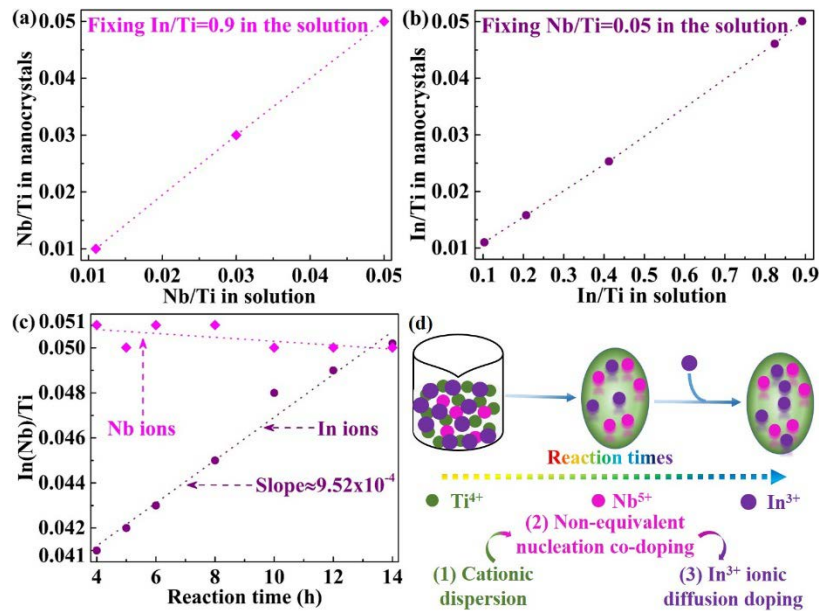


Figure 1. The ratio of Nb/Ti (a) and In/Ti (b) in the initial reaction solution (x axis) and in the resultant co-doped anatase TiO₂ nanocrystals (y axis). These data points were collected at the reaction time of 14 h. It is found that almost all of the Nb ions but only a small proportion of the In ions in the reaction solution can be finally co-doped into TiO₂. (c) is the ratio of Nb/Ti and In/Ti at different reaction times, suggesting that dual mechanisms of nucleation and diffusion doping are responsible for the incorporation of the In³⁺ ions while nucleation-only doping is observed for that of the Nb⁵⁺ ions. (d) is a schematic illustrating the different doping mechanisms for the In³⁺ and Nb⁵⁺ co-dopants. Three critical steps should be involved during the synthesis: (1) cationic homogeneous distribution in the solution; (2) non-equivalent nucleation co-doping of Nb⁵⁺ and In³⁺ ions; and (3) the further diffusion doping of the In³⁺ ions to achieve the equal doping concentrations as that of the Nb⁵⁺ ions.

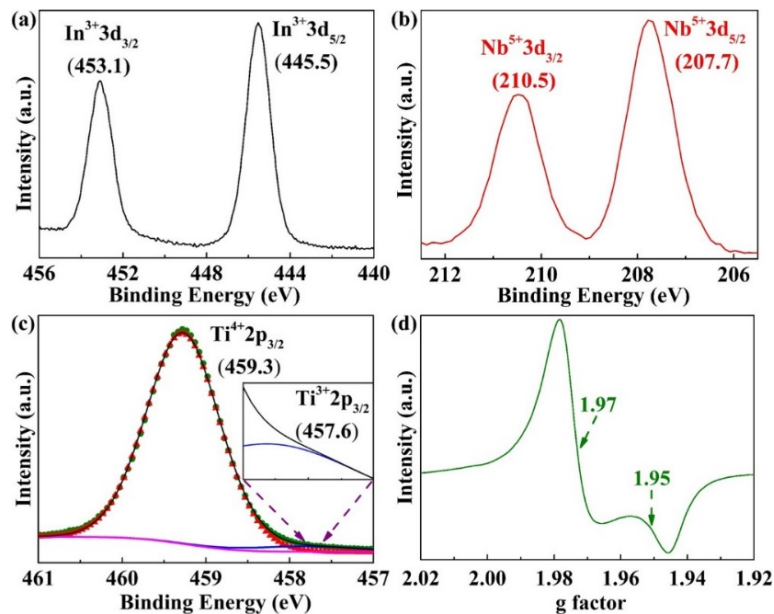


Figure 2. The XPS (a-c) and room temperature EPR (d) spectra of the synthesized $(\text{Ti}_{0.862}^{4+}\text{Ti}_{0.046}^{3+}\text{In}_{0.046}^{3+}\text{Nb}_{0.046}^{5+})(\text{O}_{1.977}^{2-}\square_{0.023})$ anatase nanocrystals with $x=y=z\approx 0.046$, determining the chemical valence states of indium (+3) and niobium (+5) co-dopants as well as the titanium (+4 and +3).

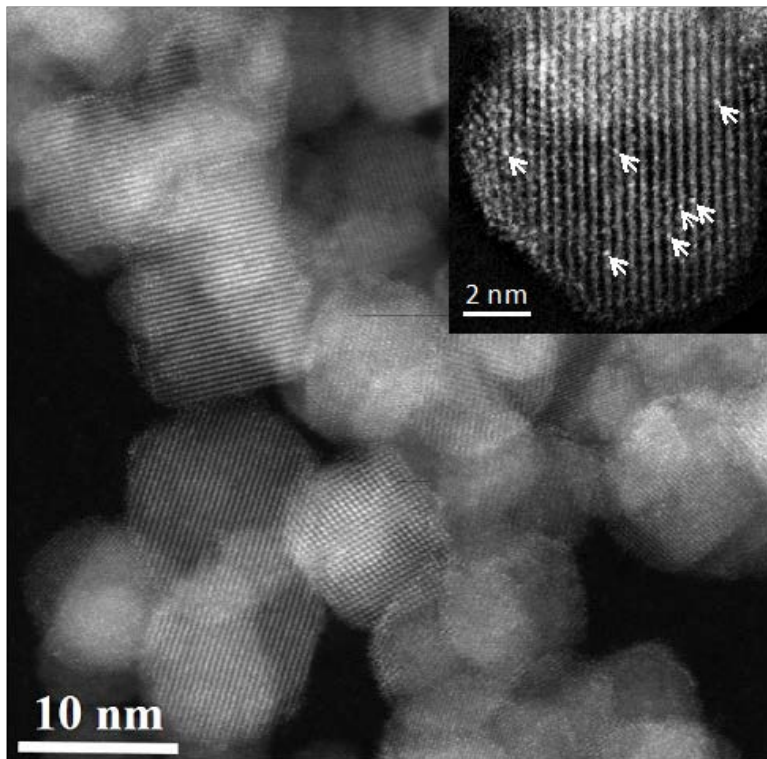


Figure 3. A typical aberration-corrected HAADF-STEM image of the synthesized anatase ($\text{Ti}_{0.862}^{4+}\text{Ti}_{0.046}^{3+}\text{In}_{0.046}^{3+}\text{Nb}_{0.046}^{5+}(\text{O}_{1.977}^{2-}\square_{0.023})$) nano-crystals with $x \approx y \approx z \approx 0.046$. The arrowed brighter dots in the inset show the presence of atomic columns with a greater density of heavier atoms (indium and/or niobium), indicating that the In^{3+} and Nb^{5+} ions are indeed co-doped into TiO_2 host materials.

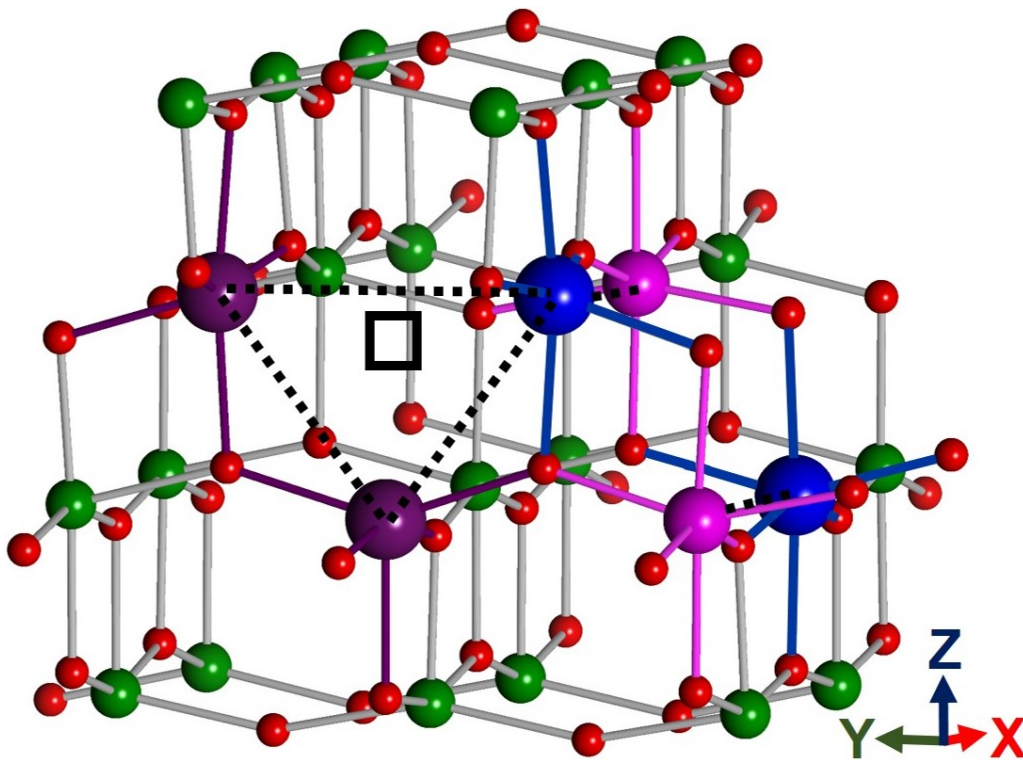


Figure 4. The motif of the lowest energy defect structures. Balls representing ions are colored according to In^{3+} : purple; Nb^{5+} : pink; Ti^{3+} : blue; Ti^{4+} : green; O^{2-} : red. Dashed lines indicate the $2\text{In}_{\text{Ti}}^{3+} + \text{V}_{\text{O}}^{*} + \text{Ti}_{\text{Ti}}^{3+} + \text{Nb}_{\text{Ti}}^{5+}$ defect clusters and adjacent $\text{Ti}_{\text{Ti}}^{3+} + \text{Nb}_{\text{Ti}}^{5+}$ defect pairs.

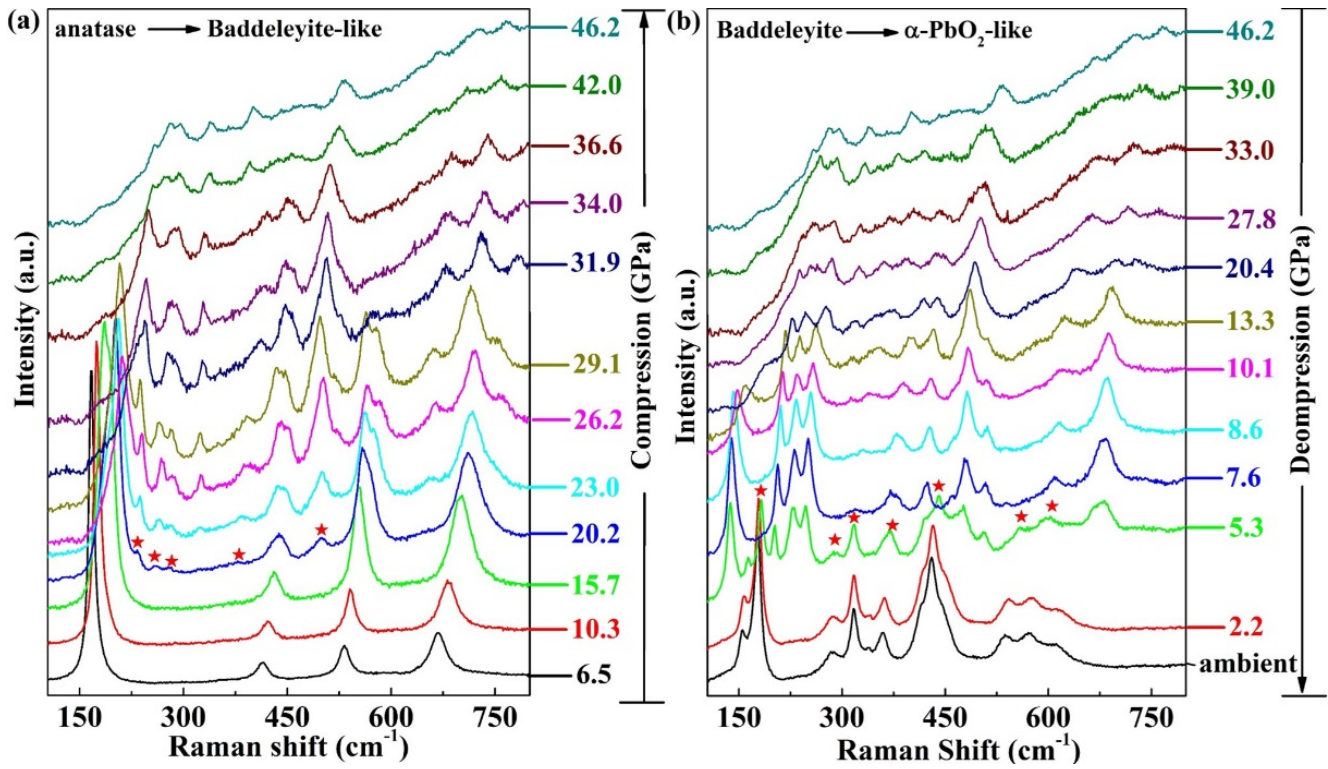


Figure 5. *In situ* Raman spectra of anatase ($\text{Ti}_{0.970}\text{Ti}_{0.010}\text{In}_{0.010}\text{Nb}_{0.010}$)($\text{O}_{1.995}\square_{0.005}$) nanocrystals ($x=y=z=0.010$) collected under compression (a) and decompression (b) conditions. Their crystallographic evolution follows the sequence of anatase → baddeleyite-like phase (compression) → $\alpha\text{-PbO}_2$ -like structure (decompression).