Band Gap Narrowing of Titanium Oxide Semiconductors by Noncompensated Anion-Cation Codoping for Enhanced Visible-Light Photoactivity

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"Noncompensated *n*-*p* codoping" is established as an enabling concept for enhancing the visible-light photoactivity of TiO_2 by narrowing its band gap. The concept embodies two crucial ingredients: The electrostatic attraction within the *n*-*p* dopant pair enhances both the thermodynamic and kinetic solubilities, and the noncompensated nature ensures the creation of tunable intermediate bands that effectively narrow the band gap. The concept is demonstrated using first-principles calculations, and is validated by direct measurements of band gap narrowing using scanning tunneling spectroscopy, dramatically redshifted optical absorbance, and enhanced photoactivity manifested by efficient electron-hole separation in the visible-light region. This concept is broadly applicable to the synthesis of other advanced functional materials that demand optimal dopant control.

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The development of advanced materials for alternative and sustainable energy applications is an extremely active research area of great visibility and importance. In particular, much effort has been devoted to searching for new types of catalytic materials that can readily split water to generate hydrogen as an environmentally friendly fuel via photolysis using the abundant energy from sunlight. In such efforts of property optimization, one often encounters the challenging need to control precisely the concentration and the location of foreign dopants in a host system. Similar issues are also frequently encountered in other areas, such as control of magnetic dopants in diluted magnetic semiconductors for spintronic applications.

TiO_2 is one of the most promising photocatalysts for solar energy utilization and environmental cleanup [1–8]. However, the photoreaction efficiency of TiO_2 is severely limited by its large intrinsic band gap (>3 eV) capable of absorbing only the ultraviolet portion of the solar spectrum [3,5]. A crucial prerequisite for enhancing the solar energy conversion efficiency is to enable TiO_2 to absorb the more abundant visible light by reducing its band gap below 2 eV [5,9]. Since the seminal discovery of Fujishima and Honda [1], numerous attempts have been made to optimize the band gap of TiO_2 by different doping schemes [5,6,10–12]. However, an overwhelming body of the literature reported efforts of trial-and-error nature, lacking a major conceptual breakthrough as the guiding principle. This standing obstacle is inherently tied to the fundamental limitations that the thermodynamic solubility in substitutional doping of TiO_2 is extremely low for most dopants, especially for *p*-type doping [4,6]. As a result, most of the dopants reside at undesirable interstitial sites, which not only compromise the effectiveness of band gap narrowing but also provide numerous recombination centers that are responsible for the loss of photogenerated electron-hole pairs [13,14].

In this Letter, we report a noncompensated *n*-*p* codoping concept to overcome these fundamental limitations. First, the Columbic attraction between the *n*- and *p*-type dopants with opposite charge state substantially enhances both the thermodynamic and, in particular, the kinetic solubilities of the dopant pairs in concerted substitutional doping. More profoundly, the noncompensated nature of the *n*-*p* pairs consisting, for example, of a single acceptor and a double donor ensures the creation of intermediate electronic bands in the gap region, effectively narrowing the band gap. Controlled creation of such intermediate bands is also highly desirable for solar cell applications [15]. We further show that the position and magnitude of the intermediate bands can be tuned by choosing different combinations and concentrations of the noncompensated *n*-*p* pairs. These findings establish the noncompensated *n*-*p* codoping concept as a powerful guiding principle in future design of photocatalysts and other functional materials.

The concept is first demonstrated quantitatively using first-principles calculations, focusing on the band gap narrowing and the enhanced thermodynamic and kinetic solubilities. These studies predict Cr-N as the preferred

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codopant pair. We then use a wet chemistry method to synthesize Cr-N codoped TiO_2 nanocrystals, which exhibit substantially narrowed band gaps, as well as dramatically enhanced photoabsorption and photoactivity in the visible spectral region.

The calculations were performed using the VASP code [16], based on density functional theory (DFT) using the projector augmented wave (PAW) method [17,18] and the generalized gradient approximation (PBE-GGA) [19] for exchange correlation. We used a $3 \times 3 \times 1$ supercell containing 36 Ti atoms and 72 O atoms to model bulk anatase TiO_2. To overcome the well-known band gap problem, we used the GGA + U method to treat the $3d$ electrons of the transition metals [20], producing an intrinsic band gap of 3.2 eV. The "climbing image nudged elastic band" method [21] is used for the calculation of kinetic barriers.

In a comparative study, we first consider bulk anatase TiO_2 codoped with four different n-p pairs: Cr-N (net n-type), V-C (net p-type), Cr-C (compensated), and V-N (compensated). The dopants are incorporated substitutionally into anatase TiO_2 by replacing a host Ti atom with an n-type dopant, V or Cr, and a neighboring O atom with a p-type dopant, C or N. For each case, total energy calculations reveal that the n-type and p-type dopants exhibit a strong tendency to form a pair occupying neighboring lattice sites. The energy lowering from the pairing is 1.85 eV, 1.52 eV, 1.89 eV, and 2.44 eV for the Cr-N, V-C, V-N, and Cr-C pair, respectively. Figure 1 illustrates the effect of different codoping combinations on the density of states, as compared with that of intrinsic anatase TiO_2. The appearance of new electronic levels in the intrinsic band gap is tied to the noncompensated nature of the codopants. In particular, due to strong hybridization, the new levels are substantially broader than the localized impurity levels contributed by either Cr or N as a dopant alone, forming intermediate bands. As a consequence, the intrinsic band gap is narrowed to 1.6 eV and 0.9 eV for Cr-N [Fig. 1(a)] and V-C [Fig. 1(b)] codoped TiO_2, respectively. Compensated n-p codoping using V-N as the codopants does not change the basic electronic structure, but generates levels at the band edges [Fig. 1(c)]. Impurity bands with lower spectral weights could also be generated in the gap for the compensated Cr-C codoped system [Fig. 1(d)], where the extra charge associated with the two dopants cannot be completely compensated with each other because the Cr d levels are strongly localized [22]. The distinctive merit of noncompensated n-p codoping is that it ensures the formation of intermediate bands in the gap, while compensated n-p codoping does not [23].

In search for optimal growth conditions, we next compare the formation energies of the n-p codoped systems with different configurations of the dopants occupying interstitial or substitutional sites. The relative formation energies vary as a function of the chemical potentials of the two host elements [4]. Figures 2(a) and 2(b) show the results for the noncompensated Cr-N and V-C codoped anatase TiO_2, respectively. These results indicate that it is energetically unfavorable to dope both V and C into substitutional sites, but simultaneous substitutional doping of Cr and N are favored at O-rich conditions, making Cr-N the preferred noncompensated n-p codoping pair.

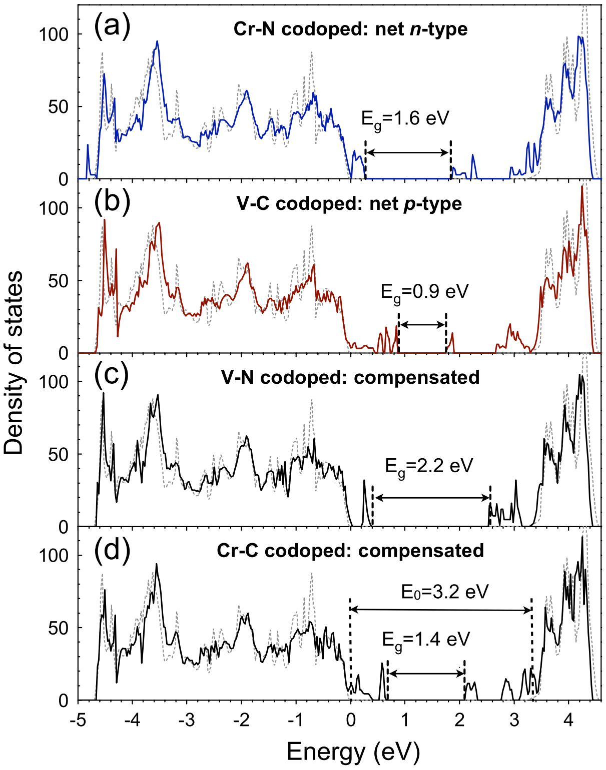

FIG. 1 (color online). Density of states (DOS) of anatase TiO_2 for different n-p codoping pairs: (a) Cr-N resulting in net n-type doping; (b) V-C resulting in net p-type doping; (c) V-N resulting in compensated codoping; and (d) Cr-C resulting in compensated codoping. The dashed lines designate pure anatase TiO_2.

The third crucial aspect to be examined is the kinetic solubility [24], as reflected by how the noncompensated n-p codoping changes the kinetic barriers of the dopants going from interstitial to substitutional sites [Fig. 2(c)]. An isolated interstitial Cr atom has to overcome an energy barrier ~2 eV to become a substitutional dopant. For an isolated interstitial N atom, the barrier against converting into substitutional is even higher, 2.34 eV, and the reverse process only has an energy barrier of 0.51 eV, indicating that N strongly prefers interstitial sites. These results also explain why it has been exceptionally difficult to dope sufficiently high concentrations of substitutional N into TiO_2 [25]. In contrast, for a Cr-N pair, the interstitial Cr and N atoms can undergo concerted atomic processes to reach simultaneous substitutional sites by pushing out a Ti and an O atom to interstitial sites, and the overall energy barrier along the kinetic pathway is much lower than that for doping with either element alone. Furthermore, the final state for Cr-N codoping is lowered by about 0.71 eV from that of N dopant alone. Therefore, both the kinetic

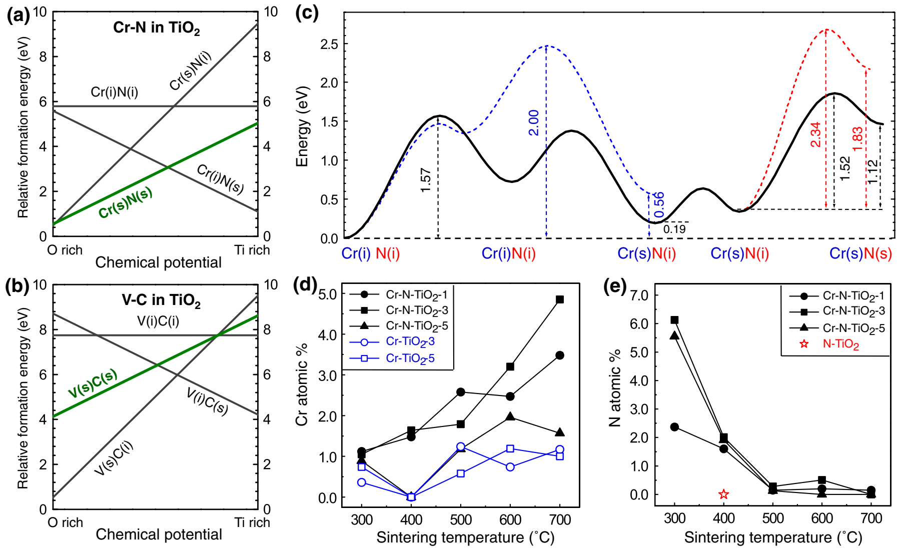

FIG. 2 (color online). (a) and (b) Calculated relative formation energy for all possible combinations of interstitial and substitutional configurations of Cr-N and V-C in anatase TiO_2 as a function of the chemical potential of Ti and O. (c) Calculated kinetic barriers for a single Cr (the blue dashed line), a single N (the red dashed line), and a Cr-N pair (the black solid line) going from interstitial to substitutional sites in anatase TiO_2. (d) and (e) X-ray photoelectron spectroscopy measurements of the Cr and N concentrations in anatase TiO_2 nanocrystals as a function of the annealing temperature. The numbers in the legend designate the nominal at.% of Cr in the precursor.

and thermodynamic solubilities of the dopants in the host semiconductor are substantially enhanced by noncompensated *n-p* codoping.

Next we present compelling experimental evidence that either directly supports or is consistent with the predictions for TiO_2 codoped with Cr and N. A wet chemical technique was used to synthesize TiO_2 and doped TiO_2 nanocrystals by hydrolysis from titanium (IV) tetra-isopropoxide in the absence or presence of ethylenediamine for N and chromium acetylacetonate for Cr [26,27]. X-ray powder diffraction (XRD) shows that the dried precipitate crystallizes into anatase particles of 10 to 20 nm size when annealed in air at 500 °C. The amount of Cr and N dopants remaining in the particles after crystallization was determined by x-ray photoelectron spectroscopy. Compared with single element doping with Cr or N, the signal from the same element is significantly higher in the codoped samples [Figs. 2(d) and 2(e)]. In particular, Cr-N codoping appears effective in retaining N that if doped alone is rapidly lost soon after annealing at 400 °C in air [26].

The unprecedented magnitude of both absorbance and redshift in the visible-light absorption spectra in Fig. 3(a) serves as initial indication that Cr-N doping creates new and accessible electronic states in the band gap of TiO_2. In contrast, Cr doping alone creates only localized electronic states in the band gap of TiO_2 that are known to induce visible-light absorption without affecting the band gap. Similarly, numerous papers report visible-light absorption resulting from N doping alone, but the characteristics of the N electronic states are currently the subject of intense debate [13,14,25,28,29].

Scanning tunneling spectroscopy (STS) demonstrates the central message of this work that noncompensated *n-p* codoping effectively narrows the band gap of TiO_2. The STS spectra were measured by recording the tunneling current while ramping the tunneling bias at specific locations on the nanocrystals as illustrated in the inset of Fig. 3(b). In agreement with recent reports in the literature, the STS spectra show that single element doping fails to reduce substantially the band gap of TiO_2 [30,31]. In contrast, striking band gap narrowing to 1.5 ± 0.2 eV was observed in Cr-N codoped TiO_2 samples. The reproducibility of this finding was confirmed on many nanocrystals from different batches and with different

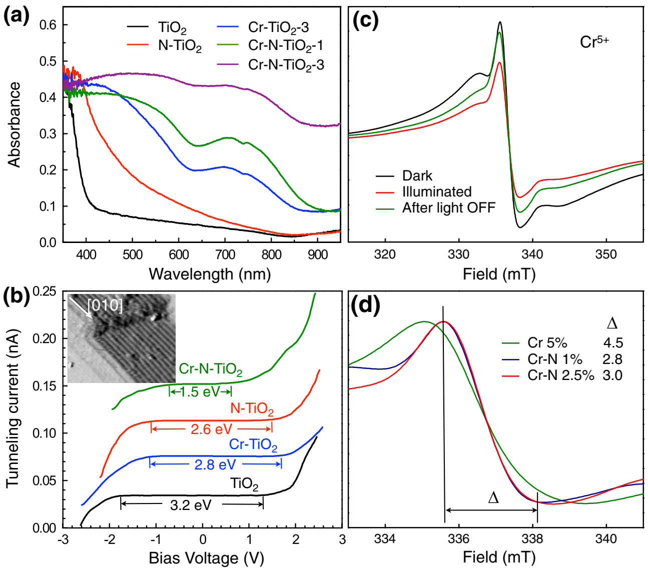

FIG. 3 (color online). (a) UV-vis diffuse reflectance spectra of pure and doped anatase TiO_2 nanocrystals annealed at 500 °C. The numbers in the legend designate the nominal at.% of Cr in the precursor. (b) STS spectra of pure and doped anatase TiO_2. The *I-V* curves are shifted vertically for better visualization. The inset displays a STM image of undoped TiO_2 nanocrystal surface. (c) The red line shows the effect of charge generation on the EPR signal from 1 at.% Cr-N codoped anatase TiO_2 nanocrystals induced by ≤2.5 eV light illumination. The green line shows the recovery of the EPR signal after the light is turned off. (d) The narrower EPR linewidth Δ for 1, and 2.5 at.% Cr-N codoping than for Cr only doping is indication of enhanced photocatalytic efficiency in Cr-N codoping.

STM tips. The STS spectrum of Cr-N codoped TiO_2 is also in excellent agreement with the calculated density of states [Fig. 1(a)]. The DFT results show that when N is doped into TiO_2 with the assistance of codoped Cr, the hybridization of the Cr and N electronic states substantially broadens the impurity levels, thereby enhancing the formation of extended intermediate bands. This broadening, in turn, explains the enhanced optical absorption and the band gap narrowing observed in Cr-N codoped TiO_2.

Band gap narrowing in Cr-N doped TiO_2 was further confirmed by demonstration of visible-light induced electron-hole separation using low temperature electron paramagnetic resonance (EPR) spectroscopy [Figs. 3(c) and 3(d)]. The EPR signal from nonilluminated (black line) samples shows that Cr-N codoping generates paramagnetic species that are absent in undoped TiO_2. The EPR signal consists of an intense surface component at $g = 1.97$, corresponding to Cr^{5+} surface species that is attributed to formation of Cr-O-Ti bridging complexes [Fig. 3(c)], and a broad weak component at $g \sim 4.6$ (not shown), originating from isolated Cr^{3+} ions in substitutional TiO_2 lattice sites [32,33]. The signal from N radicals could not be resolved because it is obscured by the strong Cr signal [25]. Continuous irradiation with photons of subband gap ($<$2.5 eV) energy causes a drop in the EPR signal shown in Fig. 3(c) by the red line because of reduction of Cr ions by photogenerated electrons. The efficient charge separation is followed by recombination of charges and recovery of the EPR signal shown by the green line after the light is turned off. The sharper and more intense Cr signal in Cr-N codoped samples compared to that in the Cr only doped sample in Fig. 3(d) suggests that the presence of N breaks up clustering of Cr ions resulting in a more efficient photocatalyst.

In summary, we describe first-principles calculations and present compelling experimental evidence that validate the concept of noncompensated *n*-*p* codoping for narrowing the band gap of TiO_2 by simultaneously incorporating *n*- and *p*-type dopants with unequal charge states. This concept is particularly important for the development of a new class of TiO_2-based photocatalysts for solar energy conversion, hydrogen generation from water, and a variety of industrial and environmental applications. Because the ideas have a broad significance they are also expected to impact related areas demanding optimal dopant control [34–36].

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