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## Origin of the Visible-Light Response of Nickel(II) Oxide Cluster <sup>2</sup> Surface Modified Titanium(IV) Dioxide

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S Supporting Information

ABSTRACT: A number of NiO clusters have been formed on TiO<sub>2</sub> (anatase/rutile = 8 4/1 w/w, P-25, Degussa) in a highly dispersed state (NiO/TiO<sub>2</sub>) by the 9 chemisorption-calcination cycle technique. The NiO/TiO2 causes high visible-light 10 activities for the degradations of 2-naphthol and p-cresol exceeding those of  $FeO_{x}$ 11 TiO<sub>2</sub> (Tada et al. Angew. Chem., Int. Ed. **2011**, 50, 3501–3505). The main purpose of 12 this study is to clarify the origin at an electronic level by the density functional 13 simulation for NiO, Ni<sub>2</sub>O<sub>2</sub>, and Ni<sub>4</sub>O<sub>4</sub> clusters supported on TiO<sub>2</sub> rutile (110) and 14 anatase (001) surfaces. The clusters adsorb strongly on both rutile and anatase with 15 adsorption energies ranging from -3.18 to -6.15 eV, creating new interfacial bonds 16 between the clusters and both surfaces. On rutile, intermetallic Ni-Ti bonds facilitate 17 stronger binding compared with anatase. The electronic structure shows that the top 18 19 of the valence bands (VBs) of rutile and anatase arises from electronic states on the 20 NiO cluster. On the other hand, the conduction band of rutile is from the Ti 3d states, whereas NiO cluster levels are generated near the conduction band minimum 21



of anatase. This is in contrast to the SnO<sub>2</sub>/rutile TiO<sub>2</sub> system, where the density of states near the conduction band minimum 22 increases with the VB unmodified. In the NiO/TiO<sub>2</sub> system, the band gaps of both rutile and anatase are narrowed by up to 0.8 23

eV compared with pristine TiO<sub>2</sub>, which pushes the photoactivity into the visible region. In view of the calculated electronic 24 structure, we have attributed the enhanced photocataltyic activity both to the charge separation due to the excitation from the Ni 25

3d surface sub-band to the TiO<sub>2</sub> conduction band and the action of the NiO species as a mediator for the electron transfer from 26

the  $TiO_2$  conduction band to  $O_2$ . 27

### 1. INTRODUCTION

28 One of the biggest challenges for our energy security is to be 29 independent of fossil fuels, and the development of suitable 30 photocatalysts may help in solar energy harvesting. TiO<sub>2</sub> has 31 gathered much attention because it is relatively cheap, readily 32 available, stable, and nontoxic. Since TiO<sub>2</sub> absorbs only in the 33 ultraviolet region, there have been many attempts to modify it 34 in such a way that it will also absorb visible light.<sup>1,2</sup> A popular 35 approach for material modification over many years has been 36 substitutional cation or anion doping at titanium or oxygen 37 sites.<sup>3–19</sup>In 2001, Asahi et al. demonstrated that N-doping of 38 TiO<sub>2</sub> results in visible light absorption,<sup>3</sup> and there has been 39 much work since devoted to examining doping as a means to 40 shifting the band gap of TiO<sub>2</sub> from the UV to the visible. N-41 doped TiO<sub>2</sub> continues to be of great interest and has been 42 studied in depth by Di Valentin, Pacchioni, and Selloni in refs 4 43 and 5, while there have been recent experimental and modeling <sup>44</sup> reports on this prototype of doped TiO<sub>2</sub>.<sup>6,7</sup> Carbon-doped <sup>45</sup> TiO<sub>2</sub> has also been of great interest,<sup>8–11</sup> while Wang and Lewis 46 have used the FIREBALL code to study doping of TiO<sub>2</sub><sup>12,13</sup> 47 and obtained results that were used to explain the band gap 48 changes in doped TiO<sub>2</sub>. Finally, other studies of doped TiO<sub>2</sub> in

refs 14-19 serve to highlight the range of dopants that have 49 been studied.

It has been highlighted that there are practical questions 51 associated with doping of TiO2, including solubility, stability, 52 determining that doping has actually taken place, and charge 53 recombination.<sup>20,21</sup> Herrmann has shown that Cr-doping of 54 TiO<sub>2</sub>, which does reduce the band gap, will in fact have a 55 detrimental effect on the photocatalytic activity.<sup>22</sup> With this in 56 mind, there have been many efforts to find alternative ways to 57 shift the band gap of TiO<sub>2</sub> in order to make it more efficient in 58 terms of visible-light absorption and reducing charge 59 recombination. This includes modification with metal particles, 60 such as gold,<sup>21</sup> modification with quantum dots, for example, 61 CdS<sup>23</sup> (which, although displaying an initially high photo- 62 catalytic efficiency, does subsequently degrade as a result of 63 CdS oxidation), and heterostructures of graphene and  $TiO_2^{24}$  64

Recent studies have demonstrated that oxide-oxide 65 heterostructures composed of nanoscale metal oxide clusters 66 on TiO<sub>2</sub> can drastically improve the photocatalytic properties 67

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 $^{68}$  compared to pure TiO<sub>2</sub>. $^{25-31}$  Modification of TiO<sub>2</sub> with metal  $^{69}$  oxide nanoclusters has been investigated by Libera et al. $^{29}$  and 70 Tada et al.<sup>30,31</sup> Libera et al. used the atomic layer deposition 71 technique to deposit Fe2O3 nanoclusters on TiO2 and found 72 visible-light absorption and efficient photocatalytic degradation 73 of methylene blue.<sup>29</sup> Tada et al. synthesized FeO<sub>x</sub>-modified 74 TiO<sub>2</sub> using the chemisorption-calcination cycle (CCC) that 75 deposits highly dispersed metal oxide nanoclusters on the TiO<sub>2</sub> 76 surface at a molecular scale.<sup>30</sup> The  $FeO_r/TiO_2$  structure shows 77 improved visible-light activity and also good UV-light activity. 78 These features came from band gap narrowing and were 79 explained by the presence of the  $FeO_r$  clusters that are 80 responsible for shifting the valence band (VB) maximum of 81 TiO<sub>2</sub>.<sup>31</sup> Further, with SnO<sub>2</sub>-modified TiO<sub>2</sub>, striking differences 82 between the light absorption properties and the visible-light 83 photocatalytic activity of modified rutile and anatase TiO<sub>2</sub> were 84 observed and rationalized with first-principles simula-<sup>85</sup> tions.<sup>32,33</sup>Other examples of heterostructures have included <sup>86</sup> BiOBr–ZnFe<sub>2</sub>O<sub>4</sub>,<sup>27</sup> BiVO<sub>4</sub>–WO<sub>3</sub>,<sup>28</sup> SnO<sub>x</sub>–ZnGa<sub>2</sub>O<sub>4</sub>,<sup>34</sup> and 87 AgI-BiO,35 displaying improved photocatalytic activity com-88 pared to the pure oxides or simple physical mixtures, 89 highlighting the important role of the interface.<sup>35</sup> Further, the 90 Ni<sup>2+</sup> surface modification of rutile TiO<sub>2</sub> by the impregnation 91 method was reported to enhance both the UV- and visible-light 92 activities, whereas the effect is much smaller than that by the 93 Fe<sup>3+</sup> surface modification.<sup>36</sup> Recently, we have shown that the 94 surface modification of TiO<sub>2</sub> with extremely small NiO clusters 95 by the CCC technique (NiO/TiO<sub>2</sub>) causes a high visible-light 96 activity concomitantly with the UV-light activity increased for 97 the decomposition of 2-naphthol.<sup>37</sup> However, the origin of the 98 visible-light response is not fully understood and needs further 99 investigation to facilitate the development of this exciting 100 approach to developing photocatalytic materials.

On the other hand, to understand the origin of the 101 102 experimental findings, density functional theory (DFT) 103 simulations are of great help. Iwaszuk and Nolan have shown 104 that subnanometer diameter  $(TiO_2)_n$  clusters, with n = 2 - 100105 4, adsorbed on the rutile  $TiO_2(110)$  surface, can reduce the 106 band gap compared to pure TiO<sub>2</sub> (although that work was also 107 focused on examining the reactivity of these heterostruc-108 tures).<sup>38</sup> The presence of Ti 3d states of the cluster above the 109 VB will enhance charge separation, and the photocatalytic 110 activities will be improved.<sup>38</sup> Moreover, further work has 111 demonstrated that modification of TiO<sub>2</sub> with other transition 112 metal oxides will also result in potentially useful photocatalytic 113 properties. For example, DFT simulations show that small 114 transition metal oxide nanoclusters, for example, Cr<sub>2</sub>O<sub>3</sub> and 115  $Mo_2O_4$ , deposited on TiO<sub>2</sub> rutile (110) will lead to a band gap 116 reduction<sup>39</sup> and improvement of photocatalytic activities. Thus, 117 the surface modification of the catalyst is an approach that may 118 benefit over doping by reducing formation of localized 119 electronic states and electron/hole recombination that are the 120 key factors for an efficient photocatalyst.

Herein, we report that NiO/TiO<sub>2</sub> (anatase/rutile = 4/1 w/w, specific surface area =  $50 \text{ m}^2 \text{ g}^{-1}$ , P-25, Degussa) exhibits high l23 levels of visible-light activities for 2-naphthol and *p*-cresol l24 degradations concurrently with enhanced UV-light activity. Pl25 25 possesses high UV-light activity for the degradation of most l26 organic compounds. Furthermore, in elucidating the origin of l27 the activity of NiO-modified TiO<sub>2</sub>, we show by spectroscopic l28 measurements and DFT calculations that the visible-light l29 response of modified TiO<sub>2</sub> is induced by the rise in the VB top l30 with NiO surface modification. We investigate the TiO<sub>2</sub> anatase (001) and rutile (110) surfaces modified with NiO nanoclusters <sup>131</sup> using DFT simulations to establish (1) how NiO nanocluster <sup>132</sup> modification of TiO<sub>2</sub> changes the light absorption properties <sup>133</sup> and (2) if there is any sensitivity to TiO<sub>2</sub> crystal form, as <sup>134</sup> observed for SnO<sub>2</sub>.<sup>33</sup> We investigated representative structures <sup>135</sup> of NiO, Ni<sub>2</sub>O<sub>2</sub>, and Ni<sub>4</sub>O<sub>4</sub> nanoclusters deposited on both <sup>136</sup> TiO<sub>2</sub> surfaces. All NiO clusters adsorb strongly on both <sup>137</sup> surfaces; however, adsorption is stronger at the rutile (110) <sup>138</sup> surface due to formation of additional Ni–Ti metallic bonds <sup>139</sup> that are not possible at the anatase (001) surface. The <sup>140</sup> electronic structure shows that the band gap is narrowed and <sup>141</sup> the energy band alignments will give electron and hole <sup>142</sup> separation after light excitation. <sup>143</sup>

### 2. METHODOLOGY

**2.1.** Photocatalyst Synthesis. The NiO/P-25 was 144 prepared by the CCC technique.<sup>30</sup> After P-25 (1 g) had been 145 added to 100 mL of a Ni(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> solution (solvent, 146 ethanol/*n*-hexane = 3:17 v/v), they were allowed to stand for 147 24 h at 298 K. The Ni(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> concentration was 148 changed ranging from  $1 \times 10^{-5}$  to  $\sim 5 \times 10^{-3}$  M. The resulting 149 samples were washed repeatedly with the solvent for the 150 physisorbed complexes to be removed and dried, followed by 151 heating in air at 773 K for 1 h. The complex adsorption and the 152 subsequent heating were repeated to increase the Ni loading 153 amount. The loading amount was shown by the amount of Ni 154 loaded on the unit surface area of P-25 ( $\Gamma$ , ions nm<sup>-2</sup>).

2.2. Photocatalyst Characterization. High-resolution 156 transmission electron microscopy (HRTEM) observation and 157 X-ray energy dispersive spectroscopic measurements were 158 performed using a JEOL JEM-3000F and a Gatan imaging 159 filter at an applied voltage of 300 or 297 kV. UV-visible diffuse 160 reflectance spectra of NiO/TiO2 were recorded on a Hitachi U- 161 4000 spectrophotometer. The spectra were converted to the 162 absorption spectra by using the Kubelka-Munk function. X-ray 163 photoelectron spectroscopic (XPS) measurements were 164 performed using a Kratos Axis Nova X-ray photoelectron 165 spectrometer with a monochromated Al K $\alpha$  X-ray source ( $h\nu = 166$ 1486.6 eV) operated at 15 kV and 10 mA. The takeoff angle 167 was 90°, and multiplex spectra were obtained for Ni 2p, O 1s, 168 and Ti 2p photopeaks. All the binding energies were referenced 169 with respect to the C 1s at 284.6 eV. The photoluminescence 170 spectra were measured with an excitation wavelength of 320 nm 171 at 77 K using a JASCO FP-6000 spectrofluorometer. 172

**2.3. Photocatalytic Reactions.** A 50 mL amount of  $1.0 \times 173$  $10^{-5}$  M 2-naphthol solution (solvent, acetonitrile/water = 1:99 174 v/v) or  $5.0 \times 10^{-4}$  M p-cresol solution (solvent, water) was 175 placed in a double-jacket-type reaction cell made of borosilicate 176 glass, and then, P-25 (Degussa) or NiO/P-25 particles (0.1 g) 177 were added. The reaction cell was irradiated with a Xe lamp 178 (Wacom XRD-501SW) through a band-pass filter (33U, 179 SIGMA KOKI CO., Ltd.) superposed on FTO-coated glass 180 (two pieces of FTO glass for 2-naphthol and a piece of FTO 181 glass for p-cresol) transmitting only the 330–400 nm range for 182 the UV-light photocatalytic activity evaluation and a high-pass 183 filter (L-42, Toshiba) to cut off UV light for the visible-light- 184 induced activity test. The irradiation conditions are as follows: 185 for 2-naphthol UV light, 330 <  $\lambda$  < 400 nm,  $I_{\rm 320-400~nm}$  = 0.5  $_{\rm 186}$ mW cm<sup>-2</sup>, and visible light,  $\lambda > 400$  nm,  $I_{420-485 \text{ nm}} = 1.0$  mW 187 cm<sup>-2</sup>; for *p*-cresol UV light, 330 <  $\lambda$  < 400 nm,  $I_{320-400 \text{ nm}} = 2$  188 mW cm<sup>-2</sup>, and visible light,  $\lambda > 400$  nm,  $I_{420-485 \text{ nm}} = 2$  mW 189 cm<sup>-2</sup>. A 3 mL amount of the solution was sampled every 15 190 min, and the absorbance at  $\lambda = 224$  nm was measured using a 191

<sup>192</sup> spectrometer (UV-1800, Shimadzu) to determine the concen-<sup>193</sup> tration of 2-naphthol. The *p*-cresol concentration was <sup>194</sup> determined by high-performance liquid chromatography <sup>195</sup> (SPD-6A, Shimadzu; column = Fluofix INW425 4.6 mm × <sup>196</sup> 250 mm (NEOS); mobile phase = water-ethanol (3:7 v/v);  $\lambda$ <sup>197</sup> = 277 nm).

**2.4. DFT Simulation.** For modeling  $TiO_2$  rutile (110) and 198 199 anatase (001) surfaces, we use three-dimensional periodic slab 200 models with the VASP code.<sup>40</sup> The valence electrons are 201 described by a plane wave basis set, and the cutoff for kinetic 202 energy is 396 eV. The valence electrons are 4 for Ti, 6 for O, 203 and 10 for Ni, within the PAW approximation, and the 204 exchange-correlation functional is the approximation of 205 Perdew-Wang (PW91).<sup>41,42</sup> The Monkhorst-Pack scheme is 206 used for k-point sampling with a  $(2 \times 2 \times 1)$  sampling grid. 207 The rutile (110) surface is terminated by 2-fold coordinated 208 bridging oxygen atoms, and the next sublayer consists of 6-fold 209 and 5-fold coordinated Ti atoms. The (unreconstructed) (001) 210 surface model of anatase is terminated by 2-fold coordinated oxygen and has 5-fold coordinated Ti ions in the next sublayer. 211 212 We use models of rutile (110) and anatase (001), since (110) is 213 by far the most stable surface of rutile and is well studied, 214 while for anatase, (001) is of great interest as the most 215 photocatalytically active anatase surface.<sup>44,45</sup> We consider the 216 rutile and anatase surfaces in their perfect, stoichiometric form, with consideration of the OH-terminated surfaces that are well 217 known for TiO<sub>2</sub> being the subject of ongoing studies. In order 218 219 to have isolated NiO nanoclusters, we employed a  $(2 \times 4)$ 220 surface supercell for each TiO<sub>2</sub> surface; for the largest NiO 221 nanocluster considered, a  $(4 \times 4)$  rutile (110) surface was also studied to examine the effect of the interaction of NiO clusters 222 with periodic images on the resulting properties, with the larger 223 surface supercell giving a bigger distance between periodic NiO 224 225 images, thus reducing the periodic interactions and modeling 226 more widely separated NiO nanoclusters. NiO nanoclusters with composition NiO, Ni<sub>2</sub>O<sub>2</sub>, Ni<sub>3</sub>O<sub>3</sub>, and Ni<sub>4</sub>O<sub>4</sub> are studied as 2.2.7 228 representative molecular-sized NiO nanoclusters. The super-229 cells and technical parameters for the free nanoclusters are the 230 same as the extended surfaces.

For the calculations we use the DFT+*U* approach<sup>46,47</sup> where are applied U = 4.5 eV on the Ti 3d states. The need to are applied the *U* parameter in order to describe properly electronic states of d or f shells is well known.<sup>46–50</sup> We also applied the +*U* correction for Ni in NiO, since the electronic states of NiO are known to be poorly described with DFT;<sup>46,47,51–53</sup> for Ni, we apply U = 8 eV and J = 1 eV (giving literature, for example, refs 51–53; a check with other values of U, namely, (U - J) = 5 and 6 eV, gives similar results to those are associated electronic structure. The DFT+*U* approach approach states of the electronic of transition metal d states, but still an underestimation of band gap remains, and this depends the band gap of TiO<sub>2</sub> upon modification with NiO, which is 246 more reliable, is our primary focus.

The clusters were deposited on both  $TiO_2$  surfaces and fully relaxed. The adsorption energy was computed from the relaxed following:

$$E^{\text{ads}} = E((\text{NiO})_n - \text{TiO}_2) - \{E((\text{NiO})_n) + E(\text{TiO}_2)\}$$
(1)

251 where  $E((\text{NiO})_n - \text{TiO}_2)$  is the total energy of the NiO 252 nanocluster supported on the surface and  $E((\text{NiO})_n)$  and

250

 $E(\text{TiO}_2)$  are the total energies of the free cluster and the bare 253 surface, respectively. A negative adsorption energy signifies that 254 the cluster adsorption is stable. 255

#### 3. RESULTS

The point of effective surface modification of  $TiO_2$  with metal 256 oxide clusters is the dispersion state and the strict control of the 257 loading amount.<sup>30</sup> The Ni(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> complex is chem- 258 isorbed on P-25 via the partial ligand exchange between the 259 acac ligand and the acidic surface Ti–OH group to yield NiO 260 clusters by postheating.<sup>37</sup> Figure 1 shows HRTEM micrographs 261 fi



**Figure 1.** HRTEM images of NiO/P-25: (A)  $\Gamma$  = 0; (B)  $\Gamma$  = 0.014; (C)  $\Gamma$  = 0.47; (D)  $\Gamma$  = 0.83.

of NiO/TiO<sub>2</sub> with varying Ni loading amount  $\Gamma$  (ions nm<sup>-2</sup>). 262 Highly dispersed NiO clusters smaller than ~2 nm are observed 263 on the surface of P-25. The strong chemisorption of the 264 complex on the TiO<sub>2</sub>surface (DFT results) prevents 265 aggregation of the small NiO clusters into larger structures 266 during the subsequent heating, thus yielding extremely small 267 adsorbed NiO clusters. 268

2-Naphthol and p-cresol were used as model water 269 pollutants. 2-Naphthol, a starting material of azo-dyes, has no 270 absorption at  $\lambda$  > 330 nm.<sup>54</sup> Both the degradations of 2- 271 naphthol and p-cresol apparently followed the first-order rate 272 law under irradiation of UV light and visible light, and the 273 activity was evaluated by the pseudofirst-order rate constant (k, 274) $h^{-1}$ ). Figure 2A (red circles) shows visible-light activity for the 275 f2 2-naphthol degradation as a function of  $\Gamma$ . The surface 276 modification with NiO clusters endows P-25 with visible-light 277 activity, whereas pristine P-25 has only low activity. The visible- 278 light activity drastically increases with increasing  $\Gamma$ , passing 279 through a maximum at  $\Gamma \sim 0.32$ . The maximum activities of 280 several metal oxide surface modified P-25 are on the order of 281  $NiO > FeO_x > SnO_2 > none$  under the same reaction 282 conditions, and the value of NiO/P25 reaches approximately 283 twice that of the FeO<sub>x</sub>/P-25 system (Table S1, Supporting 284 Information).<sup>30</sup> Figure 2B (red circles) shows UV-light activity 285 for the 2-naphthol degradation as a function of  $\Gamma$ . The UV-light 286 activity further increases by the surface modification with the 287



**Figure 2.** (A) Visible-light and (B) UV-light activities of NiO/P-25 for 2-naphthol (red circles) and *p*-cresol (blue circles) degradations.

288 NiO clusters. The loading at  $\Gamma = 0.47$  affords a maximum 289 activity, which is  $\sim$ 2.8 times the activity of P-25. The maximum 290 activities of several metal oxide surface modified P-25 are on 291 the order of  $\text{FeO}_x > \text{NiO} > \text{SnO}_2 \sim \text{none}$  (Table S1, Supporting Information). We have recently reviewed the 292 difference in the surface modification effect between FeO<sub>x</sub> 2.93 294 and SnO<sub>2</sub> clusters.<sup>55</sup> On the other hand, *p*-cresol widely used as <sup>295</sup> a sterilizer and disinfectant has no absorption at  $\lambda$  > 330 nm. As shown in Figure 2A,B (blue circles), similar trends are also 296 297 observed for the degradation of p-cresol, while the enhancement effect is somewhat smaller as compared to that for the 2-298 299 naphthol degradation.

The effect of the surface modification of P-25 with varying amounts of NiO clusters on the optical property was studied. Ni-doped TiO<sub>2</sub> prepared by the solid-state reaction of TiO<sub>2</sub> with NiO has a broad and weak absorption around 450 nm due to the d-d transition, while the intrinsic absorption edge is invariant.<sup>56</sup> Chemical doping of Cr and N ions into TiO<sub>2</sub> yields sold similar weak shoulders in the visible region due to the formation of localized impurity levels within the band gap.<sup>57</sup>

f3

f4

Figure 3A shows UV-visible absorption spectra of NiO/P-308 309 25 with varying  $\Gamma$ :  $F(R_{\infty})$  is the Kubelka–Munk function. In 310 contrast to the spectra of Ni-doped TiO<sub>2</sub>, band gap narrowing 311 occurs for NiO/P-25, whereas the d-d transition band grows at 312  $\Gamma$  > 0.47. Figure 3B shows plots of  $[F(R_{\infty})h\nu]^{1/2}$  versus  $h\nu$  for 313 NiO/P-25.58 The indirect band gap determined from the 314 extrapolation of the tangent to the abscissa decreases from 3.1 315 eV at  $\Gamma$  = 0 to 2.6 eV at  $\Gamma$  = 0.83. A similar spectral feature is 316 observed for Cr-<sup>59</sup> and N-doped<sup>60</sup> TiO<sub>2</sub> prepared by physical 317 techniques such as ion implantation and magnetron sputtering. 318 Also, the VB-XPS was measured for NiO/P-25 with varying  $\Gamma$ . 319 As shown in Figure 4A, the emission from the VB extends from 320 2 to 9 eV for every sample. Figure 4B magnifies the energy 321 region near the VB maximum. The top of the VB rises with an 322 increase in  $\Gamma$ . The magnitude of the change reaches 323 approximately 0.5 eV at  $\Gamma$  = 0.83, which is comparable with 324 the decrement in the band gap with the surface modification.  $_{325}$  Consequently, the visible-light absorption of TiO<sub>2</sub> by the



**Figure 3.** (A) UV-visible absorption spectra of NiO/P-25 with varying  $\Gamma$ :  $F(R_{\infty})$  denotes the Kubelka-Munk function. (B) Plots of  $(F(R_{\infty}h\nu))^{1/2}$  vs  $h\nu$ .



Figure 4. (A) VB-XPS of NiO/P-25 ( $\Gamma$  = 0, 0.0018, 0.014, 0.16, 0.32, 0.39, 0.47, 0.70, and 0.83 from left to right). (B) Magnified VB-XPS near the VB maximum.

surface modification with the NiO clusters stems from the rise 326 in the top of the VB. 327

To understand the effect of the surface modification with the 328 NiO clusters at an electronic level, DFT simulations were 329 performed for model systems consisting of  $TiO_2$  and NiO 330 nanoclusters adsorbed at rutile and anatase. Figure 5 presents 331 f5 the atomic structure of the NiO, Ni<sub>2</sub>O<sub>2</sub>, Ni<sub>3</sub>O<sub>3</sub>, and Ni<sub>4</sub>O<sub>4</sub> 332 nanoclusters, which are chosen as representative NiO nano- 333 clusters, adsorbed on  $TiO_2$  anatase (001) and rutile (110) 334 surfaces together with the adsorption energies and the 335



Figure 5. Relaxed adsorption structures with adsorption energies given in eV for (a) NiO, (b)  $Ni_2O_2$ , (c)  $Ni_3O_3$ , and (d)  $Ni_4O_4$  clusters on  $TiO_2$  anatase (001) and (d) NiO, (e)  $Ni_2O_2$ , and (f)  $Ni_4O_4$  clusters on  $TiO_2$  rutile (110). The blue spheres are Ni atoms, the gray spheres are Ti atoms, and the red spheres are O atoms. Cluster Ni atoms are numbered.

336 numbering of the nanocluster Ni atoms. We compute the 337 coverage of the nanoclusters in terms of Ni atoms per unit area, 338 so that for NiO, Ni<sub>2</sub>O<sub>2</sub>, Ni<sub>3</sub>O<sub>3</sub>, and Ni<sub>4</sub>O<sub>4</sub> on anatase (001), the 339 coverages are 0.85, 1.70, 2.55, and 3.41 Ni atoms/nm<sup>2</sup>. On 340 rutile (110), the corresponding coverages are 0.64, 1.28, 1.92, 341 and 2.56 Ni atoms/nm<sup>2</sup>. On the larger  $(4 \times 4)$  surface 342 supercell, the coverage is 1.28 Ni atoms/nm<sup>2</sup>. For Ni<sub>4</sub>O<sub>4</sub>, the size of the nanocluster on a  $(2 \times 4)$  surface supercell will lead 343 to stronger periodic NiO-NiO interactions than for the smaller 344 345 NiO nanoclusters, which will influence the adsorption structure, 346 due to the NiO nanoclusters being essentially in close proximity, and the effect of this on the change in the electronic 347 properties of NiO-modified TiO<sub>2</sub> will be discussed. 348

All structures show negative adsorption energies, ranging so from -3.18 to -6.15 eV giving an indication of a strong interaction between the nanocluster and the surface and the surface and the surface and the surface and the so high stability of individual NiO nanoclusters adsorbed at TiO<sub>2</sub>, so which prevents aggregation of the clusters into larger structures during postheating. For all deposited clusters, detailed information about the geometry is presented in Table 1.

t1

For NiO nanoclusters deposited on anatase, the NiO cluster results in two new bonds with the TiO<sub>2</sub> surface with distances of 1.75 and 1.91 Å. It is important to note that an O atom from the anatase surface is pulled out of the surface by Ni from the cluster by 0.26 Å that distorts the surface of TiO<sub>2</sub> anatase of (001), similar to SnO<sub>2</sub> adsorbed at anatase (001).<sup>32</sup> The same behavior is observed for  $Ni_2O_2$  deposited at anatase (001), 362 where in this case the O atom is pulled out of the surface by 363 0.17 Å upon bonding to Ni. The number of new bonds in 364  $Ni_2O_2$  deposited on TiO<sub>2</sub> anatase (001) is three. The  $Ni_3O_3$  365 cluster presents 11 new bonds when deposited on TiO<sub>2</sub> anatase 366 (001). There are five bonds between Ni and O atoms in the 367 range 1.93-2.20 Å while oxygen atoms from the cluster bond 368 to Ti surface atoms with two bonds that are 1.90 Å long. The 369 Ni<sub>4</sub>O<sub>4</sub> cluster deposited on TiO<sub>2</sub> anatase (001) shows six new 370 bonds. In this case, the surface O atom is pulled out of the 371 surface by 0.19 Å. Within the Ni–O nanoclusters, the Ni–O 372 distances are notably shorter compared to bulk NiO, for 373 example, 1.95 Å in Ni<sub>4</sub>O<sub>4</sub>, compared to 2.10 Å in bulk NiO. Of 374 the NiO nanoclusters adsorbed at anatase (001), only the 375 Ni<sub>3</sub>O<sub>3</sub> nanocluster shows intermetallic Ni-Ti bonds, with Ni- 376 Ti distances in the range 2.71–2.87 Å, which is consistent with 377 those in the intermetallic NiTi alloy.<sup>61</sup> 378

At the TiO<sub>2</sub> rutile (110) surface, the NiO cluster bonds to 379 the surface with six new bonds. The Ni atom from the cluster 380 bonds with two bridging O atoms and one surface O atom, and 381 the fourth metal—oxygen bond is from an O cluster atom that 382 bonds to Ti surface atoms. The Ni<sub>2</sub>O<sub>2</sub> cluster binds to the 383 surface with nine new bonds. Five metal—oxygen bonds are 384 from Ni cluster atoms to surface oxygen, and the last two are 385 from cluster oxygen to surface Ti. Ni<sub>3</sub>O<sub>3</sub> deposition on rutile 386 (110) results in formation of seven new bonds between the 387

Table 1. Surface–Cluster Ni–O Bond Distances for NiO Clusters Adsorbed at the  $TiO_2$  Anatase (001) and Rutile (110) Surfaces<sup>*a*</sup>

	distance (Å)							
	anata	se						
	Ni <sub>c</sub> -O <sub>s</sub>	O <sub>c</sub> – Ti <sub>s</sub>	Ni <sub>c</sub> -Ti <sub>s</sub>	Ni <sub>c</sub> -O <sub>s</sub>	O <sub>c</sub> – Ti <sub>s</sub>	Ni <sub>c</sub> -Ti <sub>s</sub>		
NiO	1.75 (1)	1.91		2.08 (1)	1.80	2.61 (1)		
				1.96 (1)		2.81 (1)		
				2.03 (1)				
$Ni_2O_2$	1.73 (2)	1.99		2.10 (1)	1.96	2.79 (1)		
		2.22		1.92 (1)	1.78	2.70 (1)		
				2.09 (1)		2.58 (2)		
				2.02 (2)				
				2.03 (2)				
Ni <sub>3</sub> O <sub>3</sub>	1.95 (1)	1.90	2.87 (1)	1.97 (1)	1.89	2.73 (3)		
	1.93 (2)	1.90	2.85 (2)	1.96 (2)	1.89	2.87 (3)		
	2.07 (3)		2.71 (3)	2.20 (3)		2.87 (3)		
	2.02 (3)		2.71 (3)	2.20 (3)				
	2.20 (3)			2.05 (3)				
Ni <sub>4</sub> O <sub>4</sub>	1.95 (1)	1.93		2.21 (1)	1.89	2.74 (1)		
	1.92 (2)	1.92		2.22 (1)	1.90			
	1.95 (3)			2.04 (1)				
	1.95 (4)			1.96 (2)				
				1.99 (4)				
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"The numbers in parentheses are the atom numbers of Ni in each NiO nanocluster.

388 cluster and surface. Five bonds are between Ni cluster atoms 389 and surface O atoms with the bond distances from 1.96 to 2.20 390 Å. The other two bonds come from O cluster atoms and Ti 391 surface atoms, and their distance is 1.89 Å. The Ni₄O₄ cluster 392 bonds to the rutile surface with eight new bonds where three of 393 the cluster Ni atoms create four Ni-O bonds with bridging 394 surface O atoms and one surface O atom, with the shortest distance being 1.96 Å and the longest distance being 2.22 Å. 395 396 The other two bonds are from cluster O binding with surface Ti. In each of these structures, surface Ti atoms are pulled out 397 of the surface after bonding to cluster oxygen. For the example 398 of NiO adsorbed at rutile (110), this Ti is displaced by 0.48 Å. 300 At the (110) surface, we also observe the formation of new 400 401 intermetallic Ni-Ti bonds between cluster Ni and surface Ti, 402 with the distances given in Table 1. The Ni-Ti distances we 403 observe are consistent with those in the intermetallic NiTi 404 alloy.<sup>61</sup> Since the adsorption energies of NiO nanoclusters on 405 the rutile (110) surface are more negative compared to those 406 on anatase (001) for a given NiO cluster, we suggest that the 407 presence of the new Ni-Ti bonds plays a role in further 408 stabilization of the heterostructure. The exception is the Ni<sub>3</sub>O<sub>3</sub> 409 nanocluster, where Ni-Ti bonds are formed at both TiO2 surfaces and the adsorption energies are very similar. 410

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<sup>411</sup> Figure 6 shows the electronic density of states projected <sup>412</sup> (PEDOS) on Ni 3d and Ti 3d states for NiO, Ni<sub>3</sub>O<sub>3</sub>, Ni<sub>2</sub>O<sub>2</sub>, <sup>413</sup> and Ni<sub>4</sub>O<sub>4</sub> clusters adsorbed on anatase (001) (Figure 6a–d) <sup>414</sup> and rutile (110) (Figure 6e–h). PEDOS plots for the O 2p <sup>415</sup> states are shown in the Supporting Information (Figure S1); <sup>416</sup> the Ni 3d states lie near the top of the VB in the clusters and <sup>417</sup> are important in this analysis. The DOS of the clean rutile and <sup>418</sup> anatase TiO<sub>2</sub> surfaces (see the Supporting Information) show <sup>419</sup> the well-known O 2p derived VB, with a Ti 3d contribution, <sup>420</sup> while the conduction band is dominated by the Ti 3d states in <sup>421</sup> both anatase and rutile.

Examination of the PEDOS shows clearly that, upon 422 modification of TiO<sub>2</sub> with NiO nanoclusters, NiO cluster 423 derived states are found laying above the top of the VB edge of 424 the rutile and anatase surfaces, which pushes the VB edge of the 425 composite system to higher energy compared to the bare 426 surfaces. The conduction band of the NiO-modified surfaces 427 can show some dependence on the crystal form of TiO<sub>2</sub>. For 428 modified rutile (110), the bottom of the conduction band is 429 dominated by surface Ti 3d states. Interestingly, this is in 430 contrast to the  $SnO_2$ /rutile TiO<sub>2</sub> system, where the DOS near 431 the conduction band minimum increases, with the VB 432 unmodified.<sup>32</sup> A close inspection of the conduction band states 433 for anatase indicates that, in some cases, for example, Ni<sub>2</sub>O<sub>2</sub>, 434 empty NiO cluster levels are generated near the conduction 435 band minimum. 436

In the NiO/TiO<sub>2</sub> system, the shift of the VB to higher energy 437has the consequence that the overall band gap of the composite 438 is reduced compared to unmodified TiO2. We find in the DFT 439 calculations a maximum band gap reduction of 0.8 eV (for 440  $Ni_4O_4$  at anatase (001)) compared to the unmodified anatase 441 surface, and this shift is qualitatively comparable to the value 442 determined by the VB-XPS, in Figure 4B. This can further be 443 compared with SnO<sub>2</sub>/TiO<sub>2</sub>, where anatase modification leads 444 to no band gap change, but rutile modification can reduce the 445 band gap.<sup>32</sup> The narrowing of the band gap will induce visible- 446 light absorption in the composite as shown in Figure 3. Thus, 447 upon modification with NiO nanoclusters, NiO states appear 448 above the VB edge of the TiO<sub>2</sub> surface, which pushes the VB up 449 in energy. There is a case in Figure 6, where the Ni<sub>2</sub>O<sub>2</sub> 450 nanocluster on anatase appears to also show some empty 451 NiO states just below the anatase conduction band. In general, 452 we can conclude that the NiO modification of TiO2 will reduce 453 the energy gap by pushing the VB edge up in energy. 454

We show in Figure 7 the atomic structure and PEDOS of a 455 f7 Ni<sub>4</sub>O<sub>4</sub> nanocluster relaxed on the rutile (110) surface with a (4 456  $\times$  4) surface supercell, which has a coverage of 1.28 Ni atoms/ 457 nm<sup>2</sup> and an adsorption energy of -4.50 eV. In this case, 458 although the effect of the smaller coverage of NiO at the surface 459 on the final adsorption structure of the nanocluster at this 460 surface is clear compared to Figure 5*f*, namely, that the Ni<sub>4</sub>O<sub>4</sub> 461 cluster takes a different adsorption structure, the PEODS shows 462 that the impact of modifying TiO<sub>2</sub> with NiO is unchanged, 463 namely, that there are NiO-derived states found at the top of 464 the VB, which will reduce the energy gap compared to 465 unmodified TiO<sub>2</sub>.

The oxidation state of the metal oxide surface modifier can 467 also affect the photocatalytic activity of  $\text{TiO}_2$ .<sup>33</sup> A Bader charge 468 analysis<sup>62</sup> on Ni for the NiO nanoclusters deposited on both 469 surfaces gives net charges on Ni ranging from 8.7 to 8.9 470 electrons, which are consistent with a Ni<sup>2+</sup> oxidation state. 471 Moreover, in TiO<sub>2</sub>, the computed net Bader charges are 472 approximately +1.3 electrons, which is typical for the Ti<sup>4+</sup> 473 oxidation state. The oxidation states of Ni and Ti are in 474 agreement with those determined by XPS.<sup>37</sup>

On the basis of these results above, the NiO surface 476 modification effect on the photocatalytic activity of P-25 can be 477 rationalized as follows and indicated in Figure 8. NiO clusters 478 f8 possess a strong interaction with the anatase and rutile surfaces 479 through Ni-O-Ti bonds for anatase and rutile and additional 480 Ni-Ti bonds for rutile. As a result of the mixing of the Ni 3d 481 levels, the VB maximum of TiO<sub>2</sub> rises significantly, while new 482 vacant levels are generated near the conduction band minimum 483 of anatase that is the major phase of P-25.



Figure 6. Spin polarized PEDOS on Ni 3d and Ti3d states for (a) NiO, (b)  $Ni_2O_2$ , (c)  $Ni_3O_3$ , and (d)  $Ni_4O_4$  clusters supported on the anatase (001) surface and for (e) NiO, (f)  $Ni_2O_2$ , (g)  $Ni_3O_3$ , and (h)  $Ni_4O_4$  clusters supported on the TiO<sub>2</sub> rutile (110) surface.



Figure 7. (a) Atomic structure and (b) PEDOS for a  $Ni_4O_4$  cluster adsorbed at the rutile (110) surface in a (4 × 4) surface supercell.

<sup>485</sup> Upon visible-light irradiation of NiO/P-25, the electrons in <sup>486</sup> the surface Ni 3d sub-band are excited to the TiO<sub>2</sub> conduction <sup>487</sup> band. This surface-to-bulk interfacial electron transfer (IET) <sup>488</sup> enhances the charge carrier separation. The holes generated at <sup>489</sup> the surface d sub-band oxidize adsorbed 2-naphthol and *p*-<sup>490</sup> cresol. On the other hand, the electrons in the TiO<sub>2</sub> conduction band are consumed by  $O_2$  reduction. This process can be the  $_{491}$  key to increasing photocatalytic activity in the oxidative  $_{492}$  decomposition of organic pollutants.<sup>63,64</sup> Figure 8 suggests  $_{493}$  that the excited electrons in the anatase conduction band can  $_{494}$  be transferred to the surface levels of the NiO species, which  $_{495}$  further assists the electron transfer to  $O_2$  as previously  $_{496}$ 



Figure 8. Energy band diagram for NiO-modified TiO<sub>2</sub>.

<sup>497</sup> confirmed by the electrochemical experiments.<sup>37</sup> This action 498 mechanism of the NiO clusters should also operate under UV-499 light irradiation. Consequently, the NiO surface modified P-25 500 causes the high activities under illumination of visible light and 501 UV light. A final point is that, in the experiments, an optimum 502 Ni loading for photocatalytic activity is found (Figure 2A,B), 503 although above this loading, the NiO-TiO<sub>2</sub> system displays a 504 continuous decrease in the band gap. With the results of this 505 work showing that the increased loading of NiO results in a rise 506 in the VB edge of the composite system compared to 507 unmodified TiO<sub>2</sub>, we can explain this finding as follows. The 508 low VB edge in unmodified TiO<sub>2</sub> imparts good oxidative power 509 to the holes formed after light excitation, while an upward shift 510 of the VB edge will weaken the oxidation power of the holes. 511 Thus, with an increase in NiO loading, the VB edge is shifted 512 upward (Figures 3, 4, and 6), which therefore weakens the 513 oxidative power of the holes and results in an optimal loading 514 of NiO on TiO<sub>2</sub>. A similar result has been found for other metal 515 oxide nanocluster modified  $TiO_{2r}^{30-33}$  indicating that this 516 phenomenon is quite general; that is, there will be an optimum 517 loading of a second metal oxide on TiO<sub>2</sub> that shifts the VB edge 518 such that visible-light absorption is realized but that the 519 oxidative power of the photoexcited holes is not reduced too 520 much.

#### 4. CONCLUSIONS

521 We have shown that the surface modification of P-25 (anatase/ s22 rutile = 4:1 w/w with NiO clusters gives rise to high visible-523 light activities for 2-naphthol and p-cresol concomitantly with 524 significant increases in the UV-light activities. We have 525 presented DFT simulations of nickel oxide clusters adsorbed 526 on  $TiO_2$  anatase (001) and rutile (110) surfaces to understand 527 the origin of visible-light activity in these heterostructures. We 528 find that NiO clusters are deposited on TiO<sub>2</sub> surfaces with large s29 adsorption energies ranging from -3.18 to -6.15 eV, with 530 metallic Ni-Ti bonds leading to extra stabilization on rutile 531 (110) compared with anatase (001). The deposited clusters 532 cause the narrowing of the TiO<sub>2</sub> band gap, which pushes the 533 photoactivity into the visible region due to the presence of NiO s34 states at the top of the valence band of  $TiO_2$ . The present 535 energy level alignments enhance the charge separation and the Article

efficiency enhancement. These results are consistent with 537 538

#### ASSOCIATED CONTENT

electron transfer to  $O_{2}$ , which are the origins of photocatalytic 536

#### Supporting Information

experimental data.

Photocatalytic activities of metal oxide surface modified P-25 541 (Degussa) for 2-naphthol degradation; Ni 3d and O 2p PEDOS 542 for NiO nanocluster modified TiO<sub>2</sub>; electronic DOS for 543 unmodified rutile (110) and anatase (001) surfaces. This 544 material is available free of charge via the Internet at http:// 545 pubs.acs.org. 546

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REFERENCES

(1) Nie, X. L.; Zhou, S. P.; Maeng, G.; Sohlberg, K. Doping of TiO<sub>2</sub> 568 Polymorphs for Altered Optical and Photocatalytic Properties. Int. J. 569 Photoenergy 2009, No. 294042. 570

(2) Nowotny, J. Titanium Dioxide-Based Semiconductors for Solar- 571 Driven Environmentally Friendly Applications: Impact of Point 572 Defects on Performance. Energy Environ. Sci. 2008, 1, 556-572. 573 (3) Asahi, R.; Morikawa, T.; Ohwaki, K.; Aoki, K.; Taga, Y. Visible- 574

Light Photocatalysis in Nitrogen-Doped Titanium Oxides. Science 575 2001, 293, 269-271. 576

(4) Di Valentin, C.; Finazzi, E.; Pacchioni, G.; Selloni, A.; Livarghi, S.; 577 Paganini, M. C.; Giamello, E. N-Doped TiO2: Theory and Experiment. 578 Chem. Phys. 2007, 339, 44-56. 579

(5) Di Valentin, C.; Pacchioni, G.; Selloni, A. Origin of the Different 580 Photoactivity of N-Doped Anatase and Rutile TiO2. Phys. Rev. B 2004, 581 70, 085116/1-085116/4. 582

(6) Barolo, G.; Livraghi, S.; Chiesa, M.; Paganinin, M. C.; Giamello, 583 E. Mechanism of the Photoactivity under Visible Light of N-Doped 584 Titanium Dioxide. Charge Carriers Migration in Irradiated N-TiO, 585 Investigated by Electron Paramagnetic Resonance. J. Phys. Chem. C 586 2012, 116, 20887-20894. 587

(7) Ceotto, M.; Lo Presti, L.; Cappelletti, G.; Meroni, D.; 588 Spadaveccia, F.; Zecca, R.; Leoni, M.; Scardi, P.; Bianchi, C. L.; 589 Ardizzone, S. About the Nitrogen Location in Nanocrystalline N- 590 Doped TiO<sub>2</sub>: Combined DFT and EXAFS Approach. J. Phys. Chem. C 591 2012, 116, 1764-1771. 592

(8) Wu, G.; Nishikawa, T.; Ohtani, B.; Chen, A. Synthesis and 593 Characterization of Carbon-Doped TiO2 Nanostructures with 594 Enhanced Visible Light Response. Chem. Mater. 2007, 19, 4530-4537. 595

567

539 540

548

553

599 (10) Di Valentin, C.; Pacchioni, G.; Selloni, A. Theory of Carbon 600 Doping of Titanium Dioxide. *Chem. Mater.* **2005**, *17*, 6656–6665.

(11) Graciani, J.; Ortega, Y.; Sanz, J. F. Carbon Doping of the TiO<sub>2</sub>
(110) Rutile Surface. A Theoretical Study Based on DFT. *Chem. Mater.* 2009, 21, 1431–1438.

604 (12) Wang, H.; Lewis, J. P. Second-Generation Photocatalytic 605 Materials: Anion-Doped TiO<sub>2</sub>. *J. Phys.: Condens. Matter* **2006**, *18*, 606 421–434.

607 (13) Wang, H.; Lewis, J. P. Effects of Dopant States on Photoactivity 608 in Carbon-Doped TiO<sub>2</sub>. *J. Phys.: Condens. Matter* **2005**, *17*, L209– 609 L214.

(14) Di Valentin, C.; Pacchioni, G.; Onishi, H.; Kudo, A. Cr/Sb CoDoped TiO<sub>2</sub> from First Principles Calculations. *Chem. Phys. Lett.* 2009, 612 469, 166–171.

613 (15) Yu, J. G.; Xiang, Q. J.; Zhou, M. H. Preparation, Character-614 ization and Visible-Light-Driven Photocatalytic Activity of Fe-Doped 615 Titania Nanorods and First-Principles Study for Electronic Structures. 616 *Appl. Catal., B* **2009**, *90*, 595–602.

617 (16) Long, R.; English, N. J. First-Principles Calculation of 618 Synergistic (N, P)-Codoping Effects on the Visible-Light Photo-619 catalytic Activity of Anatase TiO<sub>2</sub>. *J. Phys. Chem. C* **2010**, *114*, 11984– 620 11990.

621 (17) Zheng, J. W.; Bhattcahrayya, A.; Wu, P.; Chen, Z.; Highfield, J.; 622 Dong, Z. L.; Xu, R. The Origin of Visible Light Absorption in 623 Chalcogen Element (S, Se, and Te)-Doped Anatase TiO<sub>2</sub> Photo-624 catalysts. J. Phys. Chem. C **2010**, 114, 7063–7069.

625 (18) Peng, H. W.; Li, J. B.; Li, S. S.; Xia, J. B. First-Principles Study of 626 the Electronic Structures and Magnetic Properties of 3d Transition 627 Metal-Doped Anatase TiO<sub>2</sub>. *J. Phys.: Condens. Matter* **2008**, *20*, 628 125207.

629 (19) Bian, L.; Song, M. X.; Zhou, T. L.; Zhao, X. Y.; Dai, Q. Q. Band 630 Gap Calculation and Photo Catalytic Activity of Rare Earths Doped 631 Rutile TiO<sub>2</sub>. *J. Rare Earths* **2009**, *27*, 461–468.

632 (20) Kubacka, A.; Fernandez-Garcia, M.; Colon, G. Advanced 633 Nanoarchitectures for Solar Photocatalytic Applications. *Chem. Rev.* 634 **2012**, *112*, 1555–1614.

635 (21) Primo, A.; Corma, A.; Garcia, H. Titania Supported Gold 636 Nanoparticles as Photocatalyst. *Phys. Chem. Chem. Phys.* **2011**, *13*, 637 886–910.

638 (22) Herrmann, J. M. Detrimental Cationic Doping of Titania in 639 Photocatalysis: Why Chromium  $Cr^{3+}$ -Doping is a Catastrophe for 640 Photocatalysis, Both under UV- and Visible Irradiations. *New. J. Chem.* 641 **2012**, 36, 883–890.

(23) Tada, H.; Mitsui, T.; Kiyonaga, T.; Akita, T.; Tanaka, K. AllSolid-State Z-Scheme in CdS-Au-TiO<sub>2</sub> Three-Component Manojunction System. *Nat. Mater.* 2006, *5*, 782-786.

645 (24) Williams, G.; Seger, B.; Kamat, P. V. TiO<sub>2</sub>-Graphene 646 Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene 647 Oxide. *ACS Nano* **2008**, *2*, 1487–1491.

648 (25) Murakami, N.; Chiyoya, T.; Tsubota, T.; Ohno, T. Switching 649 Redox Site of Photocatalytic Reaction on Titanium(IV) Oxide 650 Particles Modified with Transition-Metal Ion Controlled by Irradiation 651 Wavelength. *Appl. Catal., A* **2008**, *348*, 148–152.

652 (26) Yu, H.; Irie, H.; Shimodaira, Y.; Hosogi, Y.; Kuroda, Y.; 653 Miyauchi, M.; Hashimoto, K. An Efficient Visible-Light-Sensitive 654 Fe(III)-Grafted TiO<sub>2</sub> Photocatalyst. *J. Phys. Chem. C* **2010**, *114*, 655 16481–16487.

656 (27) Hong, S. J.; Lee, S.; Jang, J. S.; Lee, J. S. Heterojunction BiVO<sub>4</sub>/
657 WO<sub>3</sub> Electrodes for Enhanced Photoactivity of Water Oxidation.
658 Energy Environ. Sci. 2011, 4, 1781–1787.

659 (28) Kong, L.; Jiang, Z.; Xiao, T.; Lu, L.; Jones, M. O.; Edwards, P. P.
660 Exceptional Visible-Light-Driven Photocatalytic Activity over BiOBr–
661 ZnFe<sub>2</sub>O<sub>4</sub> Heterojunctions. *Chem. Commun.* 2011, 47, 5512–5514.

(29) Libera, J. A.; Elam, J. W.; Sather, N. F.; Rajh, T. M.; Dimitrijevic,
N. M. Iron(III)-Oxo Centers on TiO<sub>2</sub> for Visible-Light Photocatalysis. *Chem. Mater.* 2010, 22, 409–413.

(30) Tada, H.; Jin, Q.; Nishijima, H.; Yamamoto, H.; Fujishima, M.; 665 Okuoka, S.-i.; Hattori, T.; Sumida, Y.; Kobayashi, H. Titanium(IV) 666 Dioxide Surface-Modified with Iron Oxide as a Visible Light 667 Photocatalyst. *Angew. Chem., Int. Ed.* **2011**, *50*, 3501–3505. 668

(31) Jin, Q.; Fujishima, M.; Tada, H. Visible-Light-Active Iron Oxide- 669 Modified Anatase Titanium(IV) Dioxide. J. Phys. Chem. C 2011, 115, 670 6478–6483. 671

(32) Fujishima, M.; Jin, Q.; Yamamoto, H.; Tada, H.; Nolan, M. Tin 672 Oxide-Surface Modified Anatase Titanium(IV) Dioxide with 673 Enhanced UV-Light Photocatalytic Activity. *Phys. Chem. Chem. Phys.* 674 **2012**, *14*, 705–711. 675

(33) Jin, Q.; Fujishima, M.; Nolan, M.; Iwaszuk, A.; Tada, H. 676 Photocatalytic Activities of Tin(IV) Oxide Surface-Modified Titanium- 677 (IV) Dioxide Show a Strong Sensitivity to the TiO<sub>2</sub> Crystal Form. J. 678 Phys. Chem. C 2012, 116, 12621–12626. 679

(34) Boppana, V. B. R.; Lobo, R. F.  $SnO_x$ -ZnGa<sub>2</sub>O<sub>4</sub> Photocatalysts 680 with Enhanced Visible Light Activity. ACS Catal. **2011**, 1, 923–928. 681

(35) Cheng, H.; Huang, B.; Dai, Y.; Qin, X.; Zhang, X. One-Step 682 Synthesis of the Nanostructured AgI/BiOI Composites with Highly 683 Enhanced Visible-Light Photocatalytic Performances. *Langmuir* **2010**, 684 26, 6618–6624. 685

(36) Murakami, N.; Chiyoya, T.; Tsubota, T.; Ohno, T. Switching 686 Redox Site of Photocatalytic Reaction on Titanium(IV) Oxide 687 Particles Modified with Transition-Metal Ion Controlled by Irradiation 688 Wavelength. *Appl. Catal., A* **2008**, 348, 148–152. 689

(37) Jin, Q.; Ikeda, T.; Fujishima, M.; Tada, H. Nickel(II) Oxide 690 Surface-Modified Titanium(IV) Dioxide as a Visible-Light-Active 691 Photocatalyst. *Chem. Commun.* **2011**, 47, 8814–8816. 692

(38) Iwaszuk, A.; Nolan, M. Reactivity of Sub 1 nm Supported 693 Clusters:  $(TiO_2)_n$  Clusters Supported on Rutile  $TiO_2$  (110). *Phys.* 694 *Chem. Chem. Phys.* **2,011**, *13*, 4963–4973. 695

(39) Nolan, M. Surface Modification of TiO<sub>2</sub> with Metal Oxide 696 Nanoclusters: a Route to Composite Photocatalytic Materials. *Chem.* 697 *Commun.* **2011**, 47, 8617–8619. 698

(40) Kresse, G.; Hafner, J. Ab Initio Molecular-Dynamics Simulation 699 of the Liquid-Metal-Amorphous-Semiconductor Transition in Germa- 700 nium. *Phys. Rev. B* **1994**, *49*, 14251–14269. 701

(41) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* 702 **1994**, *50*, 17953–17979. 703

(42) Perdew, J. P. In *Electronic Structure of Solids* '91; Ziesche, P., 704 Eschrig, H., Eds.; Akademie Verlag: Berlin, Germany, 1991. 705

(43) Diebold, U. The Surface Science of Titanium Dioxide. Surf. Sci. 706 Rep. 2003, 48, 53–229. 707

(44) Liu, M.; Piao, L.; Zhao, L.; Ju, S.; Yan, Z.; He, T.; Zhou, C.; 708 Wang, W. Anatase  $TiO_2$  Single Crystals with Exposed {001} and 709 {110} Facets: Facile Synthesis and Enhanced Photocatalysis. *Chem.* 710 *Commun.* **2010**, 46, 1664–1666. 711

(46) Anisimov, V. I.; Zaanen, J.; Andersen, O. K. Band Theory and 716
 Mott Insulators: Hubbard U instead of Stoner I. *Phys. Rev. B* 1991, 44, 717
 943–954.

(47) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; 719 Sutton, A. P. Electron-Energy-Loss Spectra and the Structural Stability 720 of Nickel Oxide: An LSDA+U Study. *Phys. Rev. B* **1998**, 57, 1505–721 1509. 722

(48) Morgan, B. J.; Watson, G. W. A DFT+ U Description of Oxygen 723 Vacancies at the TiO<sub>2</sub> Rutile (110) Surface. *Surf. Sci.* **2007**, *601*, 5034–724 5041. 725

(49) Ganduglia-Pirovano, M. V.; Hofmann, A.; Sauer, J. Oxygen 726 Vacancies in Transition Metal and Rare Earth Oxides: Current State of 727 Understanding and Remaining Challenges. *Surf. Sci. Rep.* **2007**, *62*, 728 219–270. 729

(50) Nolan, M.; Grigoleit, S.; Sayle, D. C.; Parker, S. C.; Watson, G. 730
W. Density Functional Theory Studies of the Structure and Electronic 731
Structure of Pure and Defective Low Index Surfaces of Ceria. *Surf. Sci.* 732
2005, 576, 217–229.
733

- (51) Ferrari, A. M.; Pisani, C.; Cinquini, F.; Giordano, L.; Pacchioni,
  G. Cationic and Anionic Vacancies on the NiO(100) Surface: DFT+U
  and Hybrid Functional Density Functional Theory Calculations. J.
- 737 Chem. Phys. 2007, 127, 174711.
  738 (52) Long, R.; English, N. J.; Mooney, D. A. Electronic Structures of
  739 N- and C-Doped NiO from First-Principles Calculations. Phys. Lett. A
- 740 2010, 374, 1184–1187.
  741 (53) Yu, N.; Zhang, W.-B.; Wang, N.; Wang, W.-F.; Tang, B.-Y.
  742 Water Adsorption on a NiO(100) Surface: A GGA+U Study. J. Phys.
- 743 Chem. C 2008, 112, 452–457.
- 744 (54) Tada, H.; Matsui, H.; Shiota, F.; Nomura, M.; Ito, S.; Yoshihara,
- 745 M.; Esumi, K. Heterosupramolecular Photocatalysis: Oxidation of 746 Organic Compounds in Nanospaces between Surfactant Bilayers
- 747 Formed on TiO<sub>2</sub>. Chem. Commun. 2002, 1678–1679.
- 748 (55) Nolan, M.; Iwaszuk, A.; Tada, H. Molecular Metal Oxide
  749 Cluster-Surface Modified Titanium(IV) Dioxide Photocatalysts. *Aust.*750 J. Chem. 2012, 65, 624–632.
- 751 (56) Niishiro, R.; Kato, H.; Kudo, A. Nickel and Either Tantalum or
- 752 Niobium-Codoped  $TiO_2$  and  $SrTiO_3$  Photocatalysts with Visible-Light 753 Response for H<sub>2</sub> or O<sub>2</sub> Evolution from Aqueous Solutions. *Phys. Chem.* 754 *Chem. Phys.* **2005**, 7, 2241–2245.
- 755 (57) Liu, G.; Wang, L.; Yang, H. G.; Cheng, H. -M.; Lu, G. Q.
- 756 Titania-Based Photocatalysts—Crystal Growth, Doping and Hetero-757 structuring. J. Mater. Chem. 2010, 20, 831–843.
- (58) Serpone, N.; Lawless, D.; Khairutdinov, R. Size Effects on the
  Photophysical Properties of Colloidal Anatase TiO<sub>2</sub> Particles: Size
  Quantization versus Direct Transitions in This Indirect Semiconductor. J. Phys. Chem. 1995, 99, 16646–16654.
- 762 (59) Anpo, M.; Takeuchi, M. The Design and Development of 763 Highly Reactive Titanium Oxide Photocatalysts Operating under 764 Visible Light Irradiation. *J. Catal.* **2003**, *216*, 505–516.
- (60) Kitano, M.; Funatsu, K.; Matsuoka, M.; Ueshima, M.; Anpo, M.
   766 Preparation of Nitrogen-Substituted TiO<sub>2</sub> Thin Film Photocatalysts by
- 767 the Radio Frequency Magnetron Sputtering Deposition Method and 768 Their Photocatalytic Reactivity under Visible Light Irradiation. *J. Phys.*
- 769 Chem. B **2006**, 110, 25266–25272.
- 770 (61) Nolan, M.; Tofail, S. A. M. Density Functional Theory 771 Simulation of Titanium Migration and Reaction with Oxygen in the 772 Early Stages of Oxidation of Equiatomic NiTi alloy. *Biomaterials* **2010**, 773 *31*, 3439–3448.
- (62) Henkelman, G.; Arnaldsson, A.; Jónsson, H. A Fast and Robust
  Algorithm for Bader Decomposition of Charge Density. *Comput. Mater. Sci.* 2006, 36, 354–360.
- 777 (63) Wang, C. M.; Heller, A.; Gerischer, H. Palladium Catalysis of O<sub>2</sub>
- 778 Reduction by Electrons Accumulated on TiO<sub>2</sub> Particles during
- 779 Photoassisted Oxidation of Organic Compounds. J. Am. Chem. Soc. 780 **1992**, 114, 5230–5234.
- 781 (64) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W.
- 782 Environmental Application of Semiconductor Photocatalysis. *Chem.* 783 *Rev.* **1995**, *95*, 69–96.