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THEORETICAL
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Electronic Properties of Titanium Dioxide Nanotubes Doped with 4*d* Metals

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Abstract—The effect of 4*d*-metal dopants on the densities of states of hexagonal TiO_2 nanotubes has been calculated by the linearized augmented cylindrical wave method. It has been demonstrated that the substitution of Nb, Mo, Tc, or Pd atoms for a part of Ti atoms leads to a decrease in the band gap width of the material due to the formation of impurity levels in the band gap of TiO_2. Doping TiO_2 nanotubes with these metals is a promising way to produce materials for electrodes for electrochemical photolysis of water. Doping with Y, Rh, or Ag leads to the displacement of the absorption edge from the UV to the visible range owing to a considerable broadening of the valence and conduction band edges; Zr, Ru, and Cd have a lower disturbing effect on the electronic levels of TiO_2.

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Water photolysis at titanium dioxide electrodes under sunlight irradiation generates hydrogen [1]. Titanium dioxide has attracted much recent attention as a material for photocatalytic hydrogen production; however, its application is constrained by the large band gap width of TiO_2 crystals. Because of this, the compound exhibits photocatalytic activity only when exposed to UV light, but does not absorb visible light. Modification of the material composition through doping crystals with main-group or transition elements is a natural way to change its electronic properties [2–5]. Doping can lead to the formation of impurity levels in the crystal band gap, as well as to the displacement and broadening of the valence and conduction band edges so that the band gap becomes narrower, the absorption range increases, and the photocatalytic activity is enhanced [6–13]. Another possible way to improve the photocatalytic activity of TiO_2 is going from crystalline titanium dioxide to nanomaterials, which have a large surface area and high adsorptivity. For example, TiO_2 nanotubes can be synthesized through a hydrothermal route or sol–gel process on carbon nanotube matrices [14–20]. Extraneous species, for example, transition metals, are introduced using an ion-exchange technique. There are three structure types of TiO_2 nanotubes that can be constructed by rolling up three-layer O–Ti–O sheets of rutile (110), anatase (101), or (111) hexagonal fluorite.

In this work, we have calculated the densities of states of hexagonal titanium dioxide nanotubes doped with 4*d* metals; it supplements available data concerning the effect of third period elements on the properties of such nanotubes [20]. Earlier, the stability and band structure of undoped single-wall and multiwall TiO_2 nanotubes based on anatase, rutile, and hexagonal structure [21–25], as well as the effect of doping

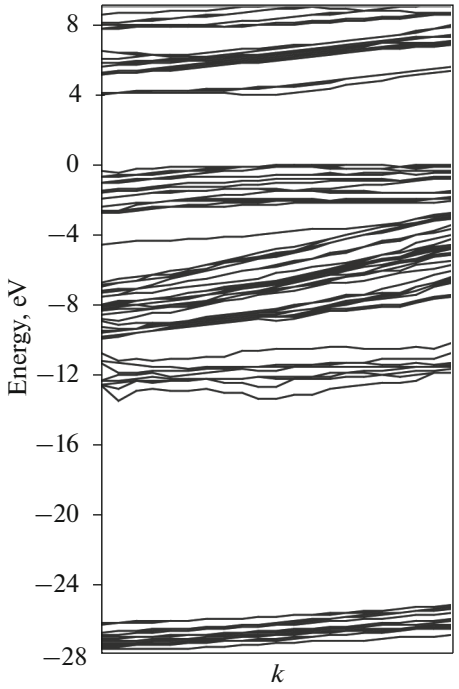

Fig. 1. Band structure of the hexagonal (4,4) TiO_2 nanotube. Energies are counted from the top of the valence band.

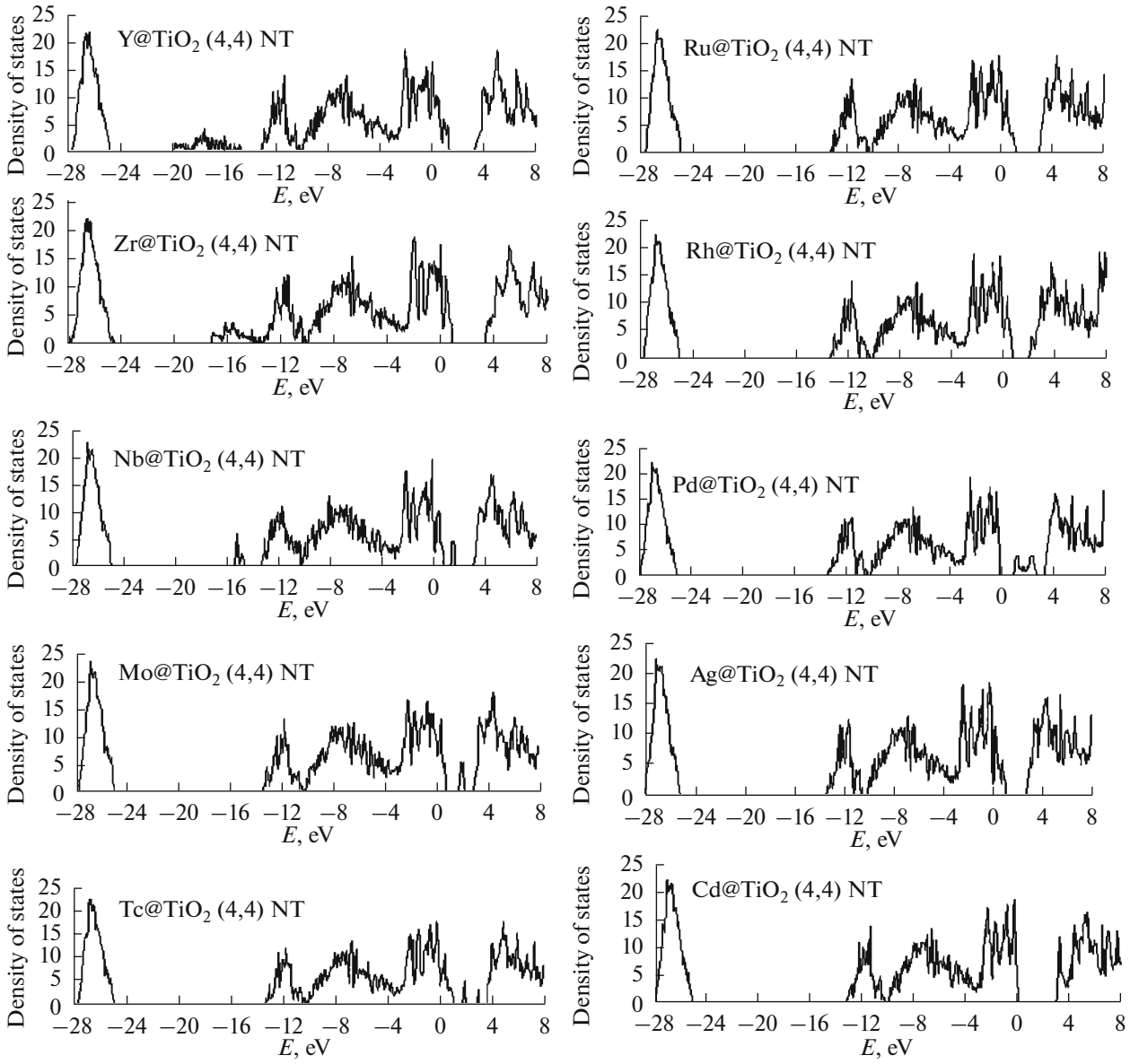

Fig. 2. Total densities of states in $MTiO_2$ nanotubes containing one impurity atom M in a Ti position in unit cells of the (4,4) TiO_2 nanotube.

with B, C, N, S, and Fe on their properties [26–31], have been studied by ab initio quantum-chemical methods.

COMPUTATIONAL DETAILS

All calculations were performed by the linearized augmented cylindrical wave (LACW) method and with the use of the supercell technique for the (4,4) TiO_2 nanotube comprising 24 atoms per translational unit cell with one dopant atom in a titanium position in each unit cell, which corresponds to a dopant content of about 4 at %. The method and its application to various nanotubes have been described in original papers [32–35] and reviews [36, 37]. The key approximations used in this theory are the local density functional approximation and the muffin-tin approximation of the electron potential.

RESULTS AND DISCUSSION

Figure 1 shows the band structure of a perfect undoped (4,4) TiO_2 nanotube, and Fig. 2 shows the densities of states for ten doped (4,4) $M@TiO_2$ nanotubes. The valence band of titanium dioxide is formed by a narrow inner 2*s*(O) band and a broad 2*p*(O) band near the top of this band, which is separated by a band gap of 4 eV from the conduction band mainly made of

vacant 3*d*(Ti) orbitals. The substitution of 4*d* metals for one Ti atom causes a sharp change in the electronic structure of the nanotube in the region of the optical gap. From the viewpoint of the possibility of using nanotubes in photocatalysis, it is essential that the introduction of Nb, Mo, Tc, and Pd dopants leads to the formation of an impurity band in the center of the band gap of the TiO_2 tube so that the optical gap of the material drops to nearly 2 eV. In all cases, the introduction of an impurity leads to the broadening of the valence and conduction band edges. This effect is especially pronounced in the compound doped with Y, Rh, and Ag, for which an extended series of bands forms near the bottom of the conduction band and the top of the valence band; as a result, the optical gap noticeably decreases. Doping TiO_2 nanotubes with these metals seems to be a promising method to produce materials for electrodes for electrochemical photolysis of water. Zr, Ru, and Cd dopants have a lower disturbing effect on the electronic levels of TiO_2.

Thus, hexagonal TiO_2 nanotubes doped with transition metals of the fourth period have been studied by quantum-chemical methods. The calculated densities of states show that the substitution of Nb, Mo, Tc, and Pd for a part of Ti atoms is responsible for a decrease in the optical gap from 4 to 2 eV due to the formation of impurity levels in the band gap of TiO_2. Such nanotubes are promising materials for design of electrodes for electrochemical photolysis of water.

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