

MICROSTRUCTURE AND OPTICAL PROPERTIES OF TRANSITION METAL (Co, Ni)-DOPED TiO₂ NANOWIRES SYNTHESIZED BY SOLVOTHERMAL METHOD

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Abstract. *The undoped and transition metal (Co, Ni)-doped TiO₂ nanowires were synthesized by simple and low cost solvothermal method and their microstructure and optical properties were investigated based on the fixed doping concentration of 1 at.%. The X-ray diffractometer and high-resolution transmission electron microscopy demonstrated that the nanowire had a single-crystalline rutile structure and grew along the [001] growth direction. The UV-VIS spectroscopy analysis showed that the optical absorption threshold of transition metal doped-TiO₂ nanowires was the red-shifted to visible light region compare to the undoped nanowires, indicating promise for visible light photocatalytic and dilute magnetic semiconductor applications.*

I. INTRODUCTION

One-dimensional (1-D) TiO₂ nanostructures have been extensively studied for various applications such as photocatalysis, gas sensor and solar cell due to its outstanding photocatalytic properties, non-toxicity, low cost, and chemical stability [1-7]. Recently, several synthesis methods have been developed to grow 1-D TiO₂ nanostructures directly on substrate such as vapor-phase deposition [8], template-assisted method [9,10], and electrochemical approaches such as anodization [4-6]. However, most of them require high growth temperature and post-thermal treatment which increases costs significantly. Very recently, well-aligned rutile TiO₂ nanowires were synthesized by solvothermal/hydrothermal method at low cost, simple process and large-scale on FTO as well as arbitrary substrates and they show a promising potential application in dye-sensitized solar cell (DSSC) [1-3]. Besides, the doping of TiO₂ with other elements such as transition metal (TM) for further applications has been great interest. The doping of TiO₂ with TM cations [7,11] have been explored to enhanced its photocatalytic efficiency by extending its photoresponse from UV region to visible light region, and reducing the recombination rate of photogenerated carriers. Moreover, the doping of TM into TiO₂ system is considered as a potential dilute magnetic semiconductor (DMS) candidate for spintronic device application since Co-doped TiO₂ was shown to be ferromagnetic with T_C up to 400 K [12]. However there are few reports on synthesis of insitu doping of TM on well-aligned rutile TiO₂ nanowires. In this study, we report on the simple and low cost synthesis of

TM-doped TiO₂ nanowires (TM = Co and Ni) with the fixed doping concentration of 1 at. % by solvothermal method. The microstructure and optical properties of TM-doped TiO₂ nanowires were also investigated.

II. EXPERIMENTAL

Undoped and TM (TM = Co and Ni)-doped TiO₂ nanowires were grown directly on Si (100) and glass substrates using solvothermal method. All chemicals used in the experiments were of the highest purity grade available and were purchased from Sigma-Aldrich. In a typical synthesis, the substrates were cleaned by sonication in acetone, methanol and deionized (DI) water and finally dried under N₂ flow. The substrates were placed in a sealed Teflon reactor (50 ml), containing 10 ml H₂O, 10 ml HCl (37 wt.%), 0.5 ml titanium tetrachloride (TiCl₄), 0.5 ml tetrabutyl titanate (Ti(OC₄H₉)₄) and a certain amount of TM chloral hydrate (CoCl₂.xH₂O or NiCl₂.6H₂O). The reaction temperature was 180 °C and reaction time was fixed at 4 h. After reaction period, the nanowire samples were removed and washed with ethanol, then dried in air. For comparison, the same TM/Ti molar ratios were fixed at 1 %. The as-prepared sample was denoted as 1 at. % Co and 1 at. % Ni-doped TiO₂ nanowires.

The morphology and size of the nanowires were characterized using a scanning electron microscopy (SEM, FEI Nova NanoSEM 200). The crystal structure and microstructure of the nanowires was analyzed using an X-ray diffractometer (XRD, Siemens, D5005, Cu K_α radiation) and a high-resolution transmission electron microscopy (HRTEM, Philips CM20-FEG, operated at 200 kV). The optical absorption spectra were obtained on an ultraviolet-visible (UV-VIS) spectroscopy (Agilent, 8453) at room temperature.

III. RESULTS AND DISCUSSION

Fig. 1 presents SEM images of undoped, Co and Ni-doped TiO₂ nanowire samples grown on Si substrate. The undoped and the TM-doped TiO₂ nanowire samples show a similar morphology. The well-aligned nanowires are formed with high density and uniformly. Several TiO₂ nanowires bundle together to form a larger secondary structure, that is a nanowire bundle. The single nanowires are tetragonal in shape with square top facets, which is the typical growth habit for the tetragonal crystal structure. Cross-section SEM images show the length of TiO₂ nanowires of 3 μm (data not shown). Energy-dispersive X-ray spectroscopy (EDX) was used to confirm the presence of doped Co and Ni in TiO₂ nanowires as seen in Fig. 2a and b, respectively. The data indicates that the TM-doped nanowires are composed of Ti, O, and TM (Co and Ni) elements.

To investigate the size and microstructure of the nanowires, the electron microscopy techniques study including bright field TEM (BF-TEM), high-resolution TEM (HRTEM) and selected area electron diffraction (SEAD) was carried out. Fig. 3a, b and c show TEM images of the undoped, Co and Ni-doped nanowires. The TEM images confirm several nanowires bunch together to form a bunch of nanowires. The width of single nanowires is ~ 8 - 12 nm. Fig. 3d shows the HRTEM image and SEAD of the Co-doped TiO₂ nanowires, respectively. The lattice image (Fig. 3d) shows a lattice spacing of 0.32 nm, which corresponds to the (110) plane of the TiO₂ rutile structure. The SEAD pattern

of HRTEM (Fig. 3d) confirms that the nanowire was grown along the [001] direction. It was reported that the growth rate in the [001] direction is the highest in the TiO₂ rutile structure [1,2].

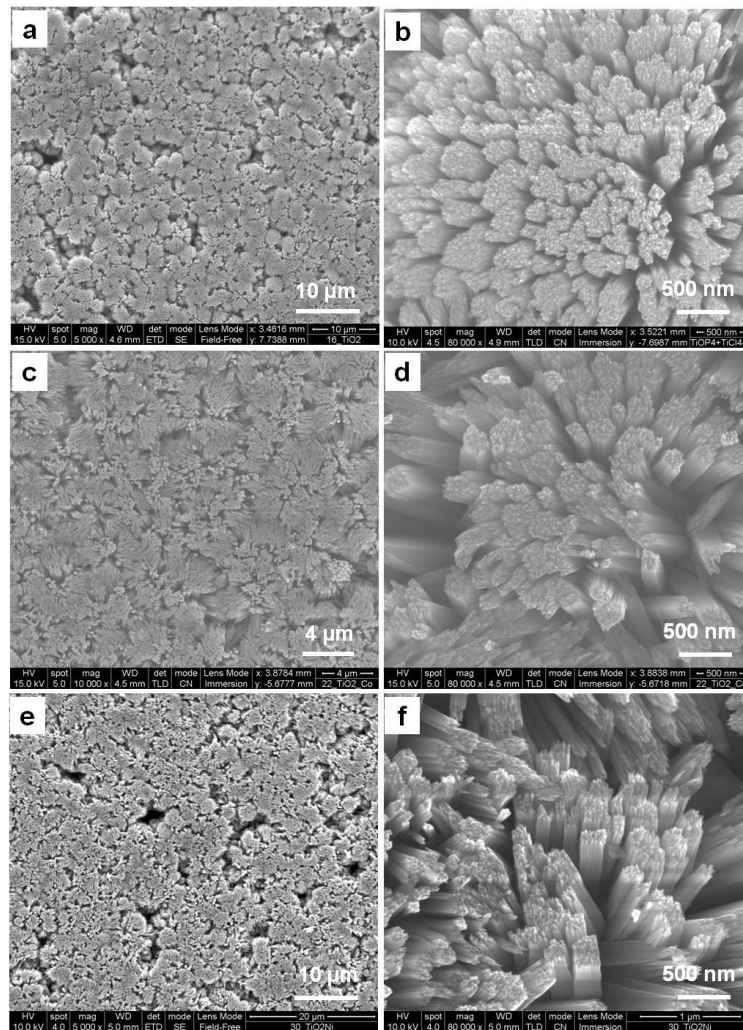


Fig. 1. FESEM images of the undoped and TM doped-TiO₂ nanowire samples grown on Si: (a,b) undoped, (c,d) 1 at.% Co, (e,f) 1 at.% Ni-doped TiO₂ nanowires.

Fig. 4 shows XRD patterns of undoped and TM-doped TiO₂ nanowire samples. The undoped and TM-doped TiO₂ nanowire samples exhibit a similar XRD pattern. The discernible peaks can be indexed as tetragonal rutile TiO₂. The significantly enhanced (002) peak indicates that the nanowire is well crystallized and grows along the [001] direction with the growth axis perpendicular to the substrate, which agrees well with the HRTEM and SEAD data. No obvious peaks corresponding to secondary phases such as metallic

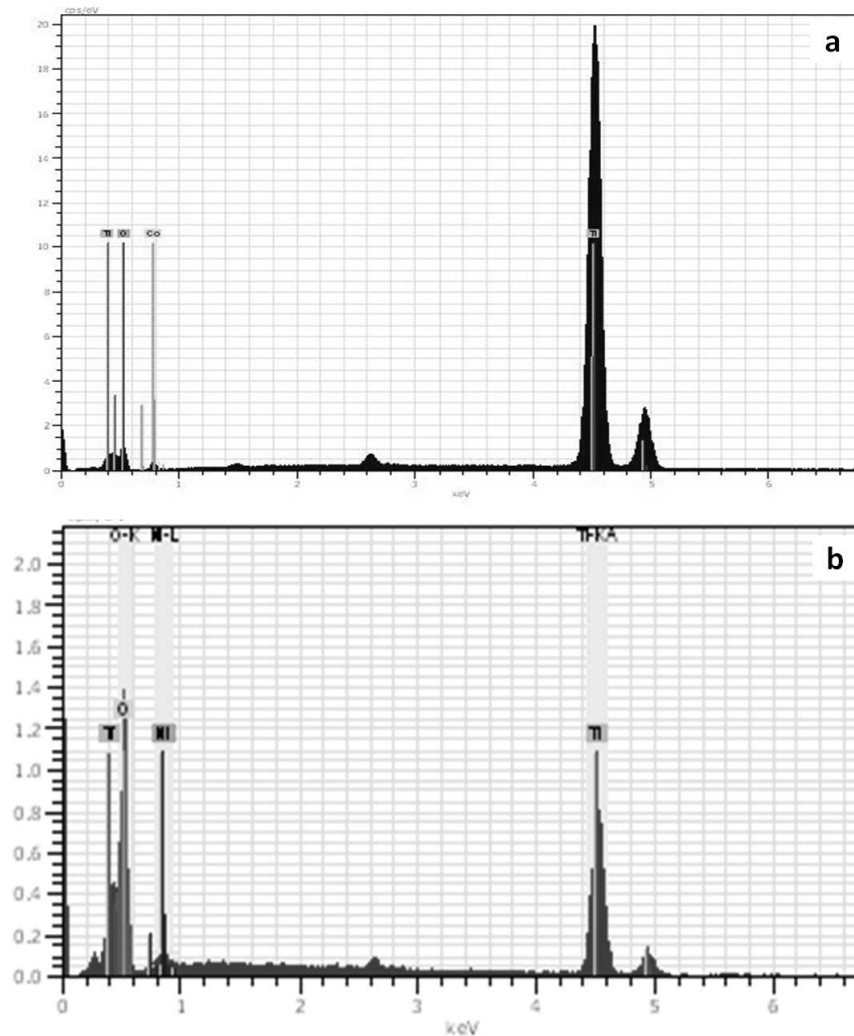


Fig. 2. EDX spectrum of (a) 1 at. % Co and (b) 1 at.% Ni-doped TiO_2 nanowires.

TM (cobalt and nickel) are observed. This may either indicate that the concentration of secondary phases formed in the samples is too low to detect by XRD measurement or TM ions are doped into TiO_2 matrix.

The optical properties of the undoped and TM-doped TiO_2 nanowires were investigated using UV-VIS spectroscopy. Fig. 5 shows the optical absorption spectra of the nanowire samples grown on glass substrate. The undoped TiO_2 nanowire sample show an optical absorption threshold at 2.85 ± 0.01 eV (point A) which is red-shifted compared to the standard bulk rutile phase (~ 3.12 eV). This can be contributed to high density of surface defects which form on high specific surface area of the undoped TiO_2 nanowires. Surface defects on TiO_2 nanowires are well known as point defects that exist as oxygen

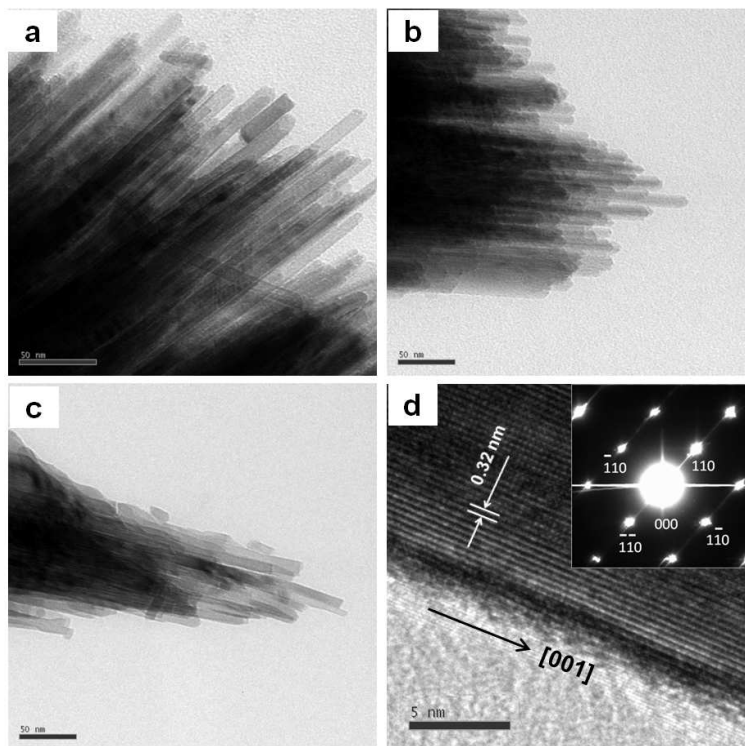


Fig. 3. TEM images of the undoped and TM doped-TiO₂ nanowire samples: (a) undoped, (b) 1 at.% Co, (c) 1 at.% Ni, and (d) HRTEM image and its SEAD patterns of the 1 at. % Co-doped nanowires, respectively.

vacancy sites in conjunction with the conversion of Ti⁴⁺ to Ti³⁺ located within the bridging oxygen rows of the TiO₂. Surface states were shallow intragap states placed at ~ 0.1 eV below the conduction band edge [14]. The high density of surface states can form a surface state band. This band can overlap with the bulk bandgap and reduce the bandgap of TiO₂ nanowires [13]. The narrowed bandgap of TiO₂ nanowires of ~ 0.27 eV is lower than that of two-dimensional phase of TiO₂ of 0.9 eV [15]. Moreover, the absorption threshold of TM-doped TiO₂ nanowires is shifted towards lower energies to point B (2.78 ± 0.01 eV) for Ni doping and C (2.76 ± 0.01 eV) for Co doping. The red-shifted absorption threshold of TM-doped TiO₂ nanowires, which corresponds to the decreased bandgap energy, is likely originated from sp-d exchange interactions between the band electrons and localized d electrons of TM ions substituting Ti⁴⁺ cations [16-18]. It is clear that the variation of the absorption threshold depends on various TM dopants at the same concentration. Moreover, the Co doping shows the more effective to reduced bandgap energy of TiO₂ nanowires than Ni dopant. We noted that the absorption threshold of the 1 at. % Co-doped nanowires is red-shifted of 14 ± 1 nm (0.09 ± 0.01 eV) compared to that of the undoped nanowires. It was reported that the doping of Co into TiO₂ nanoparticles with doping concentration in range of 3 to 8 % was reduced its bandgap energy of (0.07-0.16

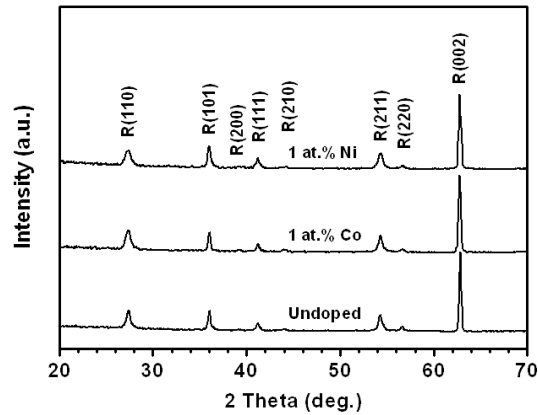


Fig. 4. XRD patterns of the undoped and TM-doped TiO_2 nanowires.

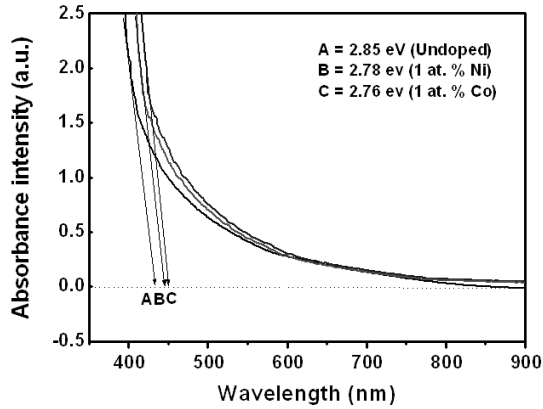


Fig. 5. UV-VIS spectra of the undoped and TM-doped TiO_2 nanowires.

eV) [16]. These results suggest that TM-doped TiO_2 nanowires could possible used for visible light photocatalysis and dilute magnetic semiconductor applications.

IV. CONCLUSION

Simple and low cost solvothermal synthesis of undoped and TM (Co, Ni)-doped TiO_2 nanowires, their microstructure and optical properties were investigated based on the fixed doping concentration of 1 at.%. The X-ray diffractometer and high-resolution transmission electron microscopy demonstrated that the square nanowire of $\sim 8\text{-}12$ nm in size had a single-crystalline rutile structure and grew along the [001] direction. Compared

to the undoped nanowires, the transition metal doped-TiO₂ nanowires showed the red-shifted optical absorption due to the incorporation of transition metal ions in TiO₂ matrix as the UV-VIS spectroscopy analysis. The results show a big potential for visible light photocatalytic and dilutes magnetic semiconductor applications.

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