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Synthesis, Characterization and Photocatalytic Activity of Nanocrystalline First Transition-Metal (Ti, Mn, Co, Ni and Zn) Oxide Nanofibers by Electrospinning

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Abstract: In this work, five nanocrystalline first transition-metal (Ti, Mn, Co, Ni and Zn) oxide nanofibers were prepared by electrospinning and controlled calcination. The morphology, crystal structure, pore size distribution and specific surface area were systematically studied by scanning electron microscope (SEM), transmission electron microscope (TEM), surface and pore analysis, and thermo gravimetric analyzer (TGA). The results reveal that the obtained nanofibers have a continuously twisted three-dimensional scaffold structure and are composed of neat nanocrystals with a necklace-like arrangement. All the samples possess high specific surface areas, which follow the order of NiO nanofiber (393.645 m²/g) > TiO₂ nanofiber (121.445 m²/g) > ZnO nanofiber (57.219 m²/g) > Co₃O₄ nanofiber (52.717 m²/g) > Mn₂O₃ nanofiber (18.600 m²/g). Moreover, the photocatalytic degradation of methylene blue (MB) in aqueous solution was investigated in detail by employing the five kinds of metal oxide nanofibers as photocatalysts under ultraviolet (UV) irradiation separately. The results show that ZnO, TiO₂ and NiO nanofibers exhibit excellent photocatalytic efficiency and high cycling ability to MB, which may be ascribed to unique porous structures and the highly efficient separation of photogenerated electron-hole pairs. In brief, this paper aims to provide a feasible approach to achieve five first transition-metal oxide nanofibers with excellent performance, which is important for practical applications.

Keywords: nanocrystalline metal oxide nanofibers; electrospinning; controlled calcination; photocatalytic efficiency

1. Introduction

Transition-metal oxide nanoparticles have been a subject of intense research due to unique optical, electrical, catalytic, spin and electronic properties [1–3]. It has been widely used in energy, sensor, sterilization and photocatalysis [4–7], and is an extremely important part of the research of inorganic functional materials. In the study of transition-metal oxide nanomaterials, preparation technology has an important influence on the microstructure and macroscopic properties of nanomaterials. Up to now, a rich variety of methods, namely the template directed method, solvothermal or hydrothermal

synthesizer, self-assembly and vapor-phase approach [8–11], have been proposed for fabricating transition-metal oxide nanoparticles. Over the past decades, significant progress has been achieved by the aforementioned methods. However, some intractable problems, such as long preparation cycles, high equipment requirements, low yield, and especially the problem of agglomeration [12–15], are still great challenges to overcome. Therefore, it has become an urgent task for scientists to explore simple methods and equipment to prepare transition-metal oxide nanoparticles with uniform size, good dispersibility and high yield.

One-dimensional metal oxide nanomaterials [16,17], as the name implies, refer to materials containing metal oxide nanoparticles in one-dimensional nanostructures. Due to the spatial orientation of one-dimensional structures, nanoparticles can be uniformly dispersed along the axial direction of the nanomaterials, which can effectively be against the agglomeration of nanoparticles. Among the different strategies for producing one-dimensional metal oxide nanomaterials, electrospinning has proved a remarkably simple, straightforward and cost-effective process to obtain long continuous metal oxide nanofibers with a diameter ranging from submicrometre to nanometre scales [18–22]. To date, many groups have focused on designing one-dimensional transition-metal oxide nanofibers composed of nanoparticles. Lu et al. successfully developed a simple strategy for the preparation of $\text{Fe}_3\text{O}_4/\text{N-C}$ hybrid nanofibers as artificial peroxidase mimics combining electrospinning and pyrolysis processes, which have promising potential applications in biosensing, medical diagnostics and environmental monitoring [23]. Kim et al. successfully synthesized aligned TiO_2 nanofibers (NFs) using an electrospinning technique with a two-piece Al collector. They demonstrated that, by controlling the needle-to-collector distance and applied voltage, well-aligned TiO_2 NFs with controllable diameters can be obtained [24]. Xue et al. fabricated Co_3O_4 nanoparticles (NPs) anchored on N-doped mesoporous carbon nanofibers ($\text{Co}_3\text{O}_4/\text{NMCF}$) by electrospinning combined with simple heat treatment. Because of its superior electrochemical performance, $\text{Co}_3\text{O}_4/\text{NMCF}$ composite is a promising choice, serving as an efficient electrocatalyst for oxygen reduction reaction (ORR) [25]. Apparently, transition-metal oxide nanofibers are rich in types and structures, resulting in a variety of properties and applications. Therefore, systematic comparative studies on a series of transition-metal oxide nanofibers, including the composition, morphology and formation mechanism, can effectively analyze the relationship between structure and properties of nanomaterials. In addition, the synthesis of functional materials with expected structures can be controlled according to one's wishes, so as to achieve an excellent performance. Yet, to the best of our knowledge, few studies have been done on this aspect. In addition, it should be noted that the preparation process of one-dimensional transition-metal oxide nanofibers is linear nucleation and growth of nanocrystals in the one-dimensional direction. The properties of the nanofibers are related not only to their structure, but also to the crystal form, grain size and crystallinity of the nanocrystals. Systematic analysis of the formation process of nanocrystals in nanofibers is the key to study the formation mechanism of the transition-metal oxide nanofibers and, more importantly, provides a new way of thinking for the preparation of nanocrystal materials.

In this article, we report a series of nanocrystalline transition-metal (Ti, Mn, Co, Ni and Zn) oxide nanofibers with controllable structure and uniform morphology by electrospinning and controlled calcination (Figure 1). In the electrospinning process, we selected polyvinylpyrrolidone (PVP) as the utilized stabilizer to assemble transition-metal oxide nanomaterials, because it is water-soluble and perfectly fulfills both steric and ligand requirements for stabilization [26]. Then, the formation process and structural characteristics of metal oxide nanofibers were systematically characterized in detail. In addition, a possible formation mechanism of the nanofibers composed of metal oxide crystals was also investigated. Finally, as electrospun nanofibers are widely used in many fields, such as supercapacitors, lithium batteries, biological devices, piezoelectric devices, photochemistry and photocatalytic fields [27–31], we chose their photocatalytic properties as an example to explore their excellent performance characteristics.

Figure 1. Schematic illustration of the fabrication of nanocrystalline metal oxide nanofibers by electrospinning and controlled calcination.

2. Materials and Methods

2.1. Materials

Polyvinylpyrrolidone (PVP, weight-average molecular weight (M_w) = 30000), manganese (II) acetate tetrahydrate, zinc acetate, nickel (II) acetate tetrahydrate, cobalt (II) acetate tetrahydrate, tetrabutyl titanate, methylene blue (MB) and absolute ethyl alcohol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemical reagents were analytical grade and employed without post-processing. The deionized water used in the experiments possessed a resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$.

2.2. Preparation of Nanocrystalline First Transition-Metal (Ti, Mn, Co, Ni and Zn) Oxide Nanofibers

The organometallic saline solution was added to the uniform and transparent PVP ethanol solution (14 mL, 0.3 g/mL), and the homogeneous liquid was obtained by ultrasonic treatment. For the electrospinning process, the solution was poured into the syringe with a needle of 1 mm diameter at the tip and connected to a high voltage power supply. The needle tip to the collector drum distance was fixed at 15 cm. The nanofibers were spun with a flow rate of 3 mL/h at 17–18 kV, and the obtained nanofibers were dried in an oven for 4 h at 60°C . Finally, the as-spun nanofibers were put into a ceramic crucible and calcined in a muffle furnace with a heating rate of $10^\circ\text{C}/\text{min}$, where the end temperature was 500°C . After many experimental screenings (such as solution viscosity, flow rate, electric field intensity and work distance), the detailed parameters are shown in Table 1. It should be pointed out that the amount of acetate is determined by its solubility in PVP/ethanol solution, and a certain amount of water is necessary. In addition, butyl titanate is a common raw material for the preparation of nano- TiO_2 , but it is easy to decompose in water, so glacial acetic acid is often added to prevent its hydrolysis.

Table 1. The detailed parameters of the preparation of nanocrystalline first transition-metal (Ti, Mn, Co, Ni and Zn) oxide nanofibers.

Nanofibers	PVP/Ethanol (0.3 g/mL)	Organometallic Salt (g)	H_2O (mL)	Acetic Acid (mL)
TiO_2	14	3.0	-	2
Mn_2O_3	14	2.0	2	-
Co_3O_4	14	2.0	2	-
NiO	14	1.3	2	-
ZnO	14	1.5	2	-

2.3. Photocatalytic Tests of Nanocrystalline Metal Oxide Nanofibers

The photocatalytic activities of metal oxide nanofibers were studied by the degradation of MB. In this process, 20 mg nanofibers were suspended in 200 mL MB aqueous solution (10 mg/L). The suspension needed to be stirred continuously for 30 min to ensure adsorption/desorption equilibrium in the dark and then exposed to a 40 W UV lamp at room temperature. The supernatant was collected and separated by centrifugation at irradiation time intervals, and then determined by UV spectrophotometer. The degradation efficiency of dye is calculated by the following equation [32]:

$$\text{Degradation}(\%) = \frac{C_0 - C}{C} \times 100 \quad (1)$$

C_0 is the initial concentration of dye before irradiation and C is the concentration of dye after a certain irradiation time. The photocatalytic degradation kinetics were analyzed using pseudo-first-order kinetics:

$$\ln(C_0/C) = kt \quad (2)$$

C is the concentration and C_0 is the initial concentration of the reactant. k refers to the reaction rate kinetic constant and t is the irradiation time.

2.4. Characterization

The morphology of the samples was observed by S-4800 scanning electron microscope (SEM, Hitachi, Tokyo, Japan) and JEM-2100 transmission electron microscope (TEM, JEOL, Tokyo, Japan). The functional groups in the samples were characterized by fourier transform infrared spectroscopy (FTIR) (Bruker Tensor II, Karlsruhe, Germany), and the scanning range of the samples was 4000–400 cm^{-1} . The crystal structures of the samples were determined by X-ray diffraction (XRD, ARL XTRA, Zurich, Switzerland). The scanning rate was 0.1 s/step and the scanning range was 10–80°. Thermogravimetric analysis (TGA, NETZSCH, Selb, Germany) of the samples was measured in air with a heating rate of 10 °C/min. The pore size distribution and specific surface area were obtained by surface and pore analyzer (Quantachrome, Boynton Beach, State, USA) by using nitrogen analysis.

3. Results and Discussion

3.1. Morphologies of Nanofibers before and after Calcination

SEM measurements were performed to study morphology of the nanofibers before and after calcination. Figure 2a–e represents $\text{Ti}(\text{BuO})_4/\text{PVP}$, $\text{Mn}(\text{Ac})_2/\text{PVP}$, $\text{Co}(\text{Ac})_2/\text{PVP}$, $\text{Ni}(\text{Ac})_2/\text{PVP}$ and $\text{Zn}(\text{Ac})_2/\text{PVP}$ blended nanofibers with fiber diameters in the range of 300–700, 200–600, 300–600, 800–1000 and 350–600 nm, respectively. It can be seen that the nanofibers exhibit uniform diameter and continuous long nanofiber smooth morphology. Furthermore, due to unsteady bending of the spinning jet, the nanofibers are arranged in random orientation [33]. Therefore, the nanofibers with a three-dimensional random orientation network structure are finally formed. Figure 2a'–e' represents TiO_2 , Mn_2O_3 , Co_3O_4 , NiO and ZnO nanofibers calcined at 500 °C, respectively. It can be seen that the calcined nanofibers still remain the three-dimensional scaffold, and consist of well-twisted continuous nanofiber structures. Due to the oxidative decomposition of organometallic salt and removal of PVP, the nanofibers show a shape of shrinkage. The diameters of the nanofibers decreased to 200–600 nm for TiO_2 , 190–260 nm for Mn_2O_3 , 150–370 nm for Co_3O_4 , 350–550 nm for NiO and 240–500 nm for ZnO nanofibers. In detail, all five obtained nanofibers are composed of neat nanoparticles with a necklace-like arrangement, and exhibit high spatial orientation and necklace-like porous structure. TiO_2 and ZnO nanofibers are curled irregularly. Mn_2O_3 , Co_3O_4 and NiO nanofibers show straight geometry with granular rough microstructure. In addition, Figure 3a–e exhibits the TEM of TiO_2 , Mn_2O_3 , Co_3O_4 , NiO and ZnO nanofibers, respectively, from which the nanoparticles and the porous surface structures can be clearly reflected.

Figure 2. SEM (scanning electron microscope) images of the electrospun nanofiber (a) $\text{Ti}(\text{BuO})_4/\text{PVP}$, (b) $\text{Mn}(\text{Ac})_2/\text{PVP}$, (c) $\text{Co}(\text{Ac})_2/\text{PVP}$, (d) $\text{Ni}(\text{Ac})_2/\text{PVP}$, (e) $\text{Zn}(\text{Ac})_2/\text{PVP}$ and the nanofibers calcined at 500 °C (a') TiO_2 nanofiber, (b') Mn_2O_3 nanofiber, (c') Co_3O_4 nanofiber, (d') NiO nanofiber, (e') ZnO nanofiber).

Figure 3. TEM and high resolution transmission electron microscopy (HRTEM) images of (a,a') TiO₂ nanofiber, (b,b') Mn₂O₃ nanofiber, (c,c') Co₃O₄ nanofiber, (d,d') NiO nanofiber, (e,e') ZnO nanofiber.

The grains are densely packed along the nanofiber length. Specifically, it can be seen that the TiO_2 and NiO nanoparticles have a uniform and compact arrangement with an average diameter of 10 and 20 nm, respectively. While, the sizes of Mn_2O_3 , Co_3O_4 and ZnO nanoparticles are relatively large, with sizes of 80–100, 60–80, 50–75 nm, respectively. In addition, the edges of Mn_2O_3 , Co_3O_4 and ZnO nanofibers are rough, and the arrangement of Mn_2O_3 particles is relatively dispersed. It is obvious that the crystallinity of TiO_2 and NiO nanofibers is different from others. After careful consideration, we think the possible reasons are as follows. Due to the different solubility of these five metal salts in PVP solution, only the electrospun precursors of TiO_2 and NiO nanofibers are clear and transparent, while the other three precursors are homogeneous emulsions. In the calcination process, when the temperature rises above the decomposition point of organometallic salts, a small amount of metastable nucleations appears in the amorphous region, and the nanocrystal grains with smaller size are formed as the surrounding atoms are adsorbed to the crystal nucleus. However, the particles of $\text{Mn}(\text{Ac})_2$ and $\text{Co}(\text{Ac})_2$, $\text{Zn}(\text{Ac})_2$ are relatively large, the sizes of Mn_2O_3 , Co_3O_4 and ZnO nanocrystal grains are much larger than that of TiO_2 and NiO during nucleation, and have a relatively loose arrangement. Therefore, the crystallinity of TiO_2 and NiO nanofibers is different from the others.

3.2. FTIR Characterization of TiO_2 , Mn_2O_3 , Co_3O_4 , NiO and ZnO Nanofibers

In order to determine the composition and structural changes of nanofibers before and after calcination, FTIR was carried out. It can be seen from Figure 4a that there is a weak broad peak at about 3447 cm^{-1} , which is the $-\text{OH}$ stretching vibration peak of the water molecule adsorbed on the surface of PVP nanofibers. The peaks at 2951 , 1422 and 1286 cm^{-1} correspond to the $-\text{CH}_2$ asymmetric addition. There is a strong absorption peak at 1661 cm^{-1} , which is attributed to the CH_2 stretching vibration in PVP [34]. In addition, the broad hump around 1000 cm^{-1} is probably due to the uneven baseline, which may be caused by poor particle size and poor transparency of the sample. From Figure 4b, we can see that the infrared characteristic peaks of PVP disappear after calcination at $500\text{ }^\circ\text{C}$, indicating that the PVP is completely oxidized and decomposed. There is a wide peak at 532 cm^{-1} in TiO_2 nanofibers, which is caused by the stretching vibration of $\text{Ti}-\text{O}-\text{Ti}$. It has been proven that TiO_2 nanocrystals are formed [35]. The peaks at 670 and 578 cm^{-1} in the infrared peak of Mn_2O_3 nanofibers are caused by the longitudinal optical (LO) mode and the transverse optical (TO) mode in the tensile vibration ($\text{Mn}-\text{O}$) of Mn_2O_3 , respectively, while the peak at 529 cm^{-1} is caused by the bending vibration ($\text{Mn}-\text{O}$) of Mn_2O_3 [36]. Co_3O_4 nanofibers exhibit strong absorption peaks at 666 and 573 cm^{-1} , which is related to the tensile vibration of the $\text{Co}-\text{O}$ band [37]. The single peak at 466 cm^{-1} in NiO nanofibers and 437 cm^{-1} in ZnO nanofibers can be assigned to $\text{Ni}-\text{O}$ and $\text{Zn}-\text{O}$ vibrational peaks respectively [38,39]. In brief, it can be seen that nanocrystalline metal oxide nanofibers are formed by calcination.

Figure 4. FTIR spectra of (a) the as-spun nanofibers and (b) electrospun nanofibers calcined at $500\text{ }^\circ\text{C}$.

3.3. XRD Characterization of TiO_2 , Mn_2O_3 , Co_3O_4 , NiO and ZnO Nanofibers

For determining the crystalline phase of the calcined nanofibers, the samples were characterized by XRD. Figure 5a–e represents TiO_2 , Mn_2O_3 , Co_3O_4 , NiO and ZnO nanofibers, respectively. It indicates that diffraction peaks appearing at 2θ of 25.3° , 37.9° , 48.1° and 62.9° in the XRD pattern are well attributed to the anatase phase with a tetragonal structure of TiO_2 (JCPDS card no. 21-1272), corresponding to its (101), (004), (200) and (204) facets, respectively. In addition, the peaks at 2θ of 27.4° , 36.1° , 41.2° , 44.0° , 54.4° , 56.6° , 64.0° and 69.0° in the XRD pattern belong to the tetragonal rutile phase of TiO_2 . This reveals that there were two kinds of crystal forms in the obtained TiO_2 nanofibers. As shown in Figure 5b, the formation of Mn_2O_3 is revealed by the diffraction peaks at 2θ values of 23.2° , 33.0° , 38.3° , 45.4° , 49.4° , 55.2° , 60.7° , 64.1° , 65.9° and 67.6° corresponding to the (211), (222), (400), (332), (431), (440), (611), (541), (622) and (631) crystal planes of Mn_2O_3 (JCPDS card no. 41-1142), respectively [36]. As observed in Figure 5c, all diffraction peaks are well indexed to pure Co_3O_4 with the structure of JCPDS card no. 65-3103, where the diffraction peaks at 2θ values of 18.9° , 31.3° , 36.9° , 38.6° , 44.9° , 59.4° and 65.3° are ascribed to the reflections of (111), (220), (311), (222), (400), (511) and (440) planes of the Co_3O_4 , respectively [40]. Figure 5d,e indicate the phase of NiO and ZnO . The formation of NiO is revealed by the diffraction peaks at 2θ values of 37.3° , 43.3° , 62.9° , 75.3° and 79.2° corresponding to (111), (200), (220), (311) and (222) crystal planes of NiO , respectively [41], while the diffraction peaks at 2θ values of 31.9° , 34.5° , 36.4° , 47.7° , 56.7° , 63.1° , 66.2° , 68.0° , 69.2° , 72.6° and 77.3° correspond to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) crystal planes of ZnO , respectively [42].

Figure 5. X-ray diffraction (XRD) spectra of a: TiO_2 nanofiber, b: Mn_2O_3 nanofiber, c: Co_3O_4 nanofiber, d: NiO nanofiber, e: ZnO nanofiber.

In addition, to verify the XRD results, the HRTEM diagrams of the nanofibers are shown in Figure 3a'–e' respectively. As presented in Figure 3a', the interplanar distances between lattice fringes of 0.350 nm and 0.327 nm correspond to the anatase phase (101) and the tetragonal rutile phase (110) in TiO_2 , respectively. The lattice fringes with a spacing of 0.276 nm can be clearly observed in Figure 3b', which is in agreement with the spacing of (222) planes of Mn_2O_3 . Figure 3c' shows clear lattice fringes of 0.279 nm corresponding to the crystallographic (111) plane of Co_3O_4 , which indicates that the sample was structurally uniform and well crystallized. As shown in Figure 3d',e', the interplanar distances between lattice fringes of 0.240 and 0.279 nm correspond to the facet (101) of NiO and the facet (110) of ZnO , respectively. The results of XRD and HRTEM analysis suggest that the calcined nanofibers are composed of metal oxide nanocrystals.

3.4. N_2 Adsorption-Desorption Isotherms and Pore Size Distribution of TiO_2 , Mn_2O_3 , Co_3O_4 , NiO and ZnO Nanofibers

To characterize these porous nanofibers further, the N_2 adsorption-desorption isotherms and the pore diameter distributions of all the samples are shown in Figure 6, and a summary of the specific surface area, pore volume and average pore diameter data is shown in Table 2. According to the classification of international union of pure and applied chemistry (IUPAC), all the samples exhibit characteristic type IV isotherms with H3-type hysteresis loops, indicating the presence of uniform microporous structure. The pore size distributions of TiO_2 , Mn_2O_3 , Co_3O_4 , NiO and ZnO nanofibers are 3.823, 3.820, 3.834, 3.816 and 3.407, respectively, which is consistent with the pore size distributions of the corresponding samples obtained from the desorption data of isotherms. The pore volume of the TiO_2 , Mn_2O_3 , Co_3O_4 , NiO and ZnO nanofibers are 0.079, 0.072, 0.082, 0.328 and 0.081 m^3/g , respectively, and the specific areas are 121.445, 18.600, 52.717, 393.645 and 57.219 m^2/g , respectively. Obviously, NiO nanofibers have the largest specific surface area compared with other nanofibers, which agrees with the result of the TEM. The specific surface area ascribes to the porous structure and the small particle size [43–45], and the smaller the particle size, the larger specific surface area. Therefore, among the five nanofibers, the NiO nanofibers with the smallest particle size (10 nm) have the largest specific surface area (393.645 m^2/g).

Figure 6. (a) N_2 adsorption-desorption isotherms and (b) pore diameter distribution of electrospun nanofibers calcined at 500 °C.

Table 2. Specific area distribution, pore volume distribution and pore diameter distribution of the metal oxides nanofibers.

Nanofibers	TiO_2	Mn_2O_3	Co_3O_4	NiO	ZnO
Specific area (m^2/g)	121.445	18.600	52.717	393.645	57.219
Pore volume (m^3/g)	0.079	0.072	0.082	0.328	0.081
Pore diameter (nm)	3.823	3.820	3.834	3.816	3.407

3.5. Possible Mechanism Analysis of Metal Oxide Nanofibers

In order to explore the formation mechanism of nanocrystalline metal oxide nanofibers, TGA experiments of each nanofiber were evaluated in air. As shown in Figure 7, the five nanofibers are roughly divided into three stages during the calcination process from 35 to 500 °C. The first stage is at about 35–180 °C, and in this stage, the weight loss is relatively small (<10%), mainly caused by the residual organic reagents in the nanofiber and the evaporation of water. The second stage is at approximately 150–350 °C, which is caused by the decomposition of acetate and the side chain of PVP. The third stage is at 350–500 °C, which is mainly caused by the decomposition of residual PVP and crystal formation [46]. The specific data are shown in Table 3. On the basis of the aforementioned experimental analysis, a possible formation mechanism of the nanocrystalline metal oxide nanofibers

can be explained as follows. During the calcination process, the PVP in the nanofiber will undergo intermolecular and intramolecular thermal decomposition and be accompanied by nucleation and growth of grains, which will result in a corresponding change in surface morphology. Specifically, when the temperature rises above the decomposition point of organometallic salts, a small amount of metastable nucleations appears in the amorphous region due to the low concentration of metal ions in the nanofibers, and the nanocrystal grains with smaller size are formed as the surrounding atoms are adsorbed to the crystal nucleus. At this time, the PVP molecules become flexible but do not decompose, so the small nanocrystal grains will move gently with the PVP molecules. As the probability of the movement toward each orientation is equivalent, the particles are uniformly dispersed in the PVP nanofibers. Then, when the temperature continues to increase, the PVP molecules move dramatically and begin to decompose, which is the main reason for the bending of the calcined nanofibers. At this moment, the newly formed nanocrystal grains grow larger, and have a better crystallinity. Furthermore, due to the limitation of the one-dimensional morphology of nanofibers, the annexation and growth of the grains can be limited in the axial direction of the nanofibers that retain the morphology of the original shape. Finally, when the PVP molecules are completely decomposed, the grains become coarser and connected with each other in the process of heat preservation, and the nanocrystalline metal oxide nanofibers with porous structure are finally formed. It is worth noting that according to the analysis of the above process, temperature plays a crucial role. As shown in Figure 2a',e', the obtained TiO_2 and ZnO nanofibers are curled irregularly and are uneven in thickness, which may be due to the dramatic movement, collapse and adhesion of PVP caused by the excessive temperature rise. In addition, the appearance of two crystal forms of TiO_2 is also related to temperature. TiO_2 is mainly composed of the anatase phase at a relatively low temperature stage. When the temperature is elevated, the anatase phase is unstable and then gradually converted into the rutile phase [47].

Figure 7. Thermogravimetric analysis (TGA) curve of electrospun $\text{Ti}(\text{BuO})_4/\text{PVP}$, $\text{Mn}(\text{Ac})_2/\text{PVP}$, $\text{Co}(\text{Ac})_2/\text{PVP}$, $\text{Ni}(\text{Ac})_2/\text{PVP}$ and $\text{Zn}(\text{Ac})_2/\text{PVP}$ nanofibers.

Table 3. Decomposition of fibers during calcination.

Nanofibers	First Stage: Evaporation of Alcohol and Physisorbed Water		Second Stage ¹ : Decomposition of Acetate and a Fraction of PVP		Third Stage: Decomposition of Residual PVP and the Formation of Crystals	
	T (°C)	Weight Loss (%)	T (°C)	Weight Loss (%)	T (°C)	Weight Loss (%)
Mn_2O_3	35–156	4.5	156–334	22.3	334–500	58.3
Co_3O_4	35–173	8.5	173–344	32.3	344–500	47.2
NiO	35–180	6.8	180–328	45.9	328–500	40.8
ZnO	35–187	5.8	135–346	44.7	346–600	40.6
TiO_2	35–155	6.5	155–285	16.7	285–500	62.0

¹ The second stage of TiO_2 nanofiber is the decomposition of tetrabutyl titanate and a fraction of PVP.

3.6. Photocatalytic Activities of Metal Oxide Nanofibers

Finally, in order to verify the excellent properties of the prepared nanocrystalline metal oxide nanofibers, the photocatalytic experiments were carried out. Figure 8a–e presents the absorption spectra of MB aqueous solution in the presence of the ZnO, TiO₂, NiO, Mn₂O₃ and Co₃O₄ nanofibers under exposure to UV light for different durations. In Figure 8a–c, with the increase of the irradiation time, the absorption peak corresponding to MB at 664 nm diminishes gradually, testifying the degradation of MB. It indicates that MB can be degraded by ZnO, TiO₂ and NiO nanofibers, respectively. However, the absorption peak of MB remained relatively unchanged in Figure 8d,e, indicating that Mn₂O₃ and Co₃O₄ could not induce the degradation of MB. As shown in Figure 8f, under dark conditions, MB dye was decolorized about 3.7%, 5.5% and 4.5% in the presence of ZnO, TiO₂, NiO nanofibers due to adsorption of the dye. After irradiation with UV light for 150 min, 97.6% of MB was decomposed by using the ZnO nanofiber as the photocatalyst, while at the same time TiO₂ and NiO nanofibers revealed 93.8% and 86.7% degradation. Table 4 shows a summary of TiO₂, ZnO and NiO nanofibers employed in the photocatalysis of a wide range of dyes and pollutants. The results indicate that the prepared TiO₂, ZnO and NiO nanofibers in the paper have good photocatalytic properties, especially NiO nanofibers.

Figure 8. Adsorption spectra of methylene blue solution under UV light in the presence of (a) TiO₂ nanofiber, (b) Mn₂O₃ nanofiber, (c) Co₃O₄ nanofiber, (d) NiO nanofiber, (e) ZnO nanofiber, and (f) photocatalytic MB dye degradation activity.

Table 4. Summary of commonly employed TiO₂, ZnO and NiO nanofibers for photocatalysis.

Photocatalysts	Raw Materials (Concentration)	Dye	Light Source	Degradation (%)	Time (min)	Ref.
TiO ₂ nanofiber	Ti rods	Malachite green (10 ^{−5} M)	Ultraviolet lamp	93%	240	[48]
TiO ₂ nanofiber	Titanium tetraisopropoxide/PVP	Methylene blue (20 mg/L)	Visible light, 150 W	25%	80	[49]
TiO ₂ @CNFs nanofiber	TiO ₂ /polyacrylonitrile (PAN)	Rhodamine (10 mg/L)	Ultraviolet lamp, 250 W	98.2%	60	[50]
ZnO nanofiber	Zn(CH ₃ COO) ₂ ·2H ₂ O/polyvinyl alcohol (PVA)	Methylene blue (10 mg/L)	Mercury lamp, 50 W	50%	360	[51]
ZnO nanofiber	Zn rods	Malachite green (10 ^{−5} M)	Ultraviolet lamp	91%	240	[48]
ZnO nanofiber	ZnCl ₂ /PVP	Methylene blue (10 mg/L)	Ultraviolet lamp, 500 W	98.6%	100	[43]
NiO nanofiber	Ni(CH ₃ COO) ₂ ·4H ₂ O/polyethersulfone (PES)	Methyl orange (10 mg/L)	Ultraviolet lamp, 12 W	40%	150	[52]
NiO nanofiber	Ni(CH ₃ COO) ₂ ·4H ₂ O/PAN	Rhodamine B (10 mg/L)	Ultraviolet lamp, 50 W	46.2%	50	[53]
NiO nanofiber	Ni(CH ₃ COO) ₂ /PVP	Methylene blue (10 mg/L)	Ultraviolet lamp, 300 W	47.3%	80	[54]

In order to further investigate the photocatalytic activities of these samples, the photocatalytic degradation kinetics were analyzed. From Figure 9a, the samples exhibit a good linear relationship between $\ln(C/C_0)$ and irradiation time t . The reaction rate constants (slope of the fitting line) of ZnO, TiO₂ and NiO nanofibers are 0.02447, 0.01874 and 0.01269 min^{−1}, respectively. In addition, the recycle ability of ZnO, TiO₂ and NiO nanofibers were also studied (Figure 9b), after the third recycle, the photocatalytic efficiency remains 95.9%, 87.1% and 65.4%, respectively, which indicates that ZnO and TiO₂ nanofibers have an excellent catalytic cycling ability. Many researchers have explained the mechanism of photolysis [55–58]: when the ZnO, TiO₂ and NiO are excited by UV light with energy higher than or equal to their band gaps, electrons (e[−]) in the valence band (VB) can be excited to the conduction band (CB), leaving corresponding holes (h⁺) in the VB. Photogenerated electrons (e[−]) on the surface of nanoparticles are easily captured by electronic acceptors such as oxygen dissolved in water to form superoxide radicals (·O₂[−]). At the same time, photo-induced holes (h⁺) can oxidize the organic chemicals adsorbed on the surface of metal oxides or be trapped by electronic donors like OH[−] and H₂O to produce ·OH. The oxidation ability of ·OH and ·O₂[−] are very strong, which can make the combination bond of various organic compounds break, so that MB can be oxidized to obtain CO₂ and H₂O. The process is as follows:

Figure 9. (a) Fitted curves with pseudo-first order kinetic model of nanofibers under the UV light irradiation. (b) Three successive cycles of photocatalytic experiments under UV light irradiation.

Furthermore, it should be pointed out that the photocatalytic degradation is actually a free radical reaction. The photodegradation efficiency is mainly due to electron-hole pair recombination inhibition by charge transfer processes. In the previous study, the particle sizes of Co₃O₄ and Mn₂O₃ were relatively large. When Co₃O₄ and Mn₂O₃ are excited by UV light, electrons (e^-) are easily recombined with holes (h^+) in the process of reaching the conduction band and starting to move toward the surface of the particles, which are emitted in the form of heat [59]. Therefore, $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ cannot be formed in this process, so methyl blue cannot be degraded by Co₃O₄ and Mn₂O₃ nanofibers.

4. Conclusions

In this study, five nanocrystalline first transition-metal (Ti, Mn, Co, Ni and Zn) oxide nanofibers with regular microstructure and lattice structures were fabricated by electrospinning and controlled calcination. The obtained nanofibers composed of metal oxide nanocrystals have continuously twisted three-dimensional scaffold structures. Metal oxide nanocrystals with a grain size lower than 100 nm grow uniformly and orderly along the original nanofiber direction, showing a high individual independence and spatial orientation. The special structure can effectively prevent their own aggregation. Moreover, the calcined nanofibers have a high specific surface area and uniform porous structure, which follow the order of NiO nanofiber ($393.645 \text{ m}^2/\text{g}$) > TiO₂ nanofiber ($121.445 \text{ m}^2/\text{g}$) > ZnO nanofiber ($57.219 \text{ m}^2/\text{g}$) > Co₃O₄ nanofiber ($52.717 \text{ m}^2/\text{g}$) > Mn₂O₃ nanofiber ($18.600 \text{ m}^2/\text{g}$). Due to these special structures, the nanofibers expose many active sites, which can effectively improve the application performance. In addition, we used nanofibers to perform a photocatalytic reaction of methyl orange, which shows that ZnO, TiO₂ and NiO nanofibers have excellent catalytic activity and catalytic cycling. Therefore, we have reason to believe that nanocrystalline metal oxides nanofibers prepared by electrospinning and controlled calcination could have excellent properties in their respective fields.

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