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Review Article

Recent Progress of TiO_2-Based Anodes for Li Ion Batteries

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TiO_2-based materials have been widely studied in the field of photocatalysis, sensors, and solar cells. Besides that, TiO_2-based materials are of great interest for energy storage and conversion devices, in particular rechargeable lithium ion batteries (LIBs). TiO_2 has significant advantage due to its low volume change (<4%) during Li ion insertion/desertions process, short paths for fast lithium ion diffusion, and large exposed surface offering more lithium insertion channels. However, the relatively low theoretical capacity and electrical conductivity of TiO_2 greatly hampered its practical application. Various strategies have been developed to solve these problems, such as designing different nanostructured TiO_2 to improve electronic conductivity, coating or combining TiO_2 with carbonaceous materials, incorporating metal oxides to enhance its capacity, and doping with cationic or anionic dopants to form more open channels and active sites for Li ion transport. This review is devoted to the recent progress in enhancing the LIBs performance of TiO_2 with various synthetic strategies and architectures control. Based on the lithium storage mechanism, we will also bring forward the existing challenges for future exploitation and development of TiO_2-based anodes in energy storage, which would guide the development for rationally and efficiently designing more efficient TiO_2-based LIBs anodes.

1. Introduction

Lithium ion batteries (LIBs) are becoming the best choice in portable electronics, implantable devices, power tools, and hybrid/full electric vehicles (EVs) for their high working voltage, low self-discharge rate, long cycle life, high energy, and power density [1, 2]. Using electric vehicles instead of traditional gasoline powered transportation can significantly reduce pollution of combustion gas and increase energy security. More importantly, the high energy efficiency of LIBs also has potential application in various large electric grid applications, including improving the energy efficiency of wind, solar, tidal, and other clean energy; thus LIBs are expected to have a very favorable impact on building an energy-sustainable economy [3, 4]. Figure 1 shows the forecasted evolution of the LIBs demand in the future years [5]; we think we will see economical battery-driven electric vehicles sooner than most people expect.

Up to now, the vast majority of commercial LIBs rely, at the cathode side, on transition metals oxides or phosphates active material ($LiCoO_2$ [6], $LiNiO_2$ [7], $LiMnO_2$ [8], $LiFePO_4$ [9], $LiMnPO_4$ [10], etc.), while graphite is commonly used as anode active material. Figure 2 is the principle of a typical lithium ion battery; both anodes and cathodes could shuttle lithium ion back and forth between them. The electrolyte is usually made of polypropylene/polyethylene which contains lithium salts (i.e., $LiPF_6$) in alkyl organic carbonates. The separator between anode and cathode can allow the diffusion of Li ions from cathode to anode during the charging and the reverse discharging process.

The anode is a crucial part in LIBs; therefore, the research and the development on the current situation of anode materials are one of the most important factors to determine the performance of this device. An ideal anode material shall meet the following requirements [11, 12]: (1) high specific surface area and large exposed surface offering more lithium insertion channels, (2) low volume change during Li ion insertion/desertions process, which is important for good cycling stability, (3) large pore size and short paths for fast lithium ion diffusion with high speed, which is crucial for good rate capability, (4) low internal resistance which leads to fast charging and discharging, (5) low intercalation potential for Li, (6) low price, (7) environment friendly. Based on the

Table 1: Comparison of advantages and limitations of TiO_2 and other anode materials [11–15].

Materials	Theoretical capacity ($mA\,h\,g^{-1}$)	Advantages	Common issues
TiO_2	330	Fast lithium ion diffusion; low cost; environmentally friendly; good safety	Low capacity; low electrical conductivity; poor rate capability
Metal oxides (CuO, NiO, Fe_3O_4, etc.)	500–1200	High capacity; high energy; low cost	Low coulombic efficiency; unstable SEI formation; low electrical conductivity; poor capacity retention
Carbon	372	Good working potential; low cost; good safety	Low coulombic efficiency; high irreversible capacity
Si	4200	High specific capacities	Large irreversible capacity; poor cycling
Sn	990	Good safety; low cost; good electrical conductivity	Poor cycling

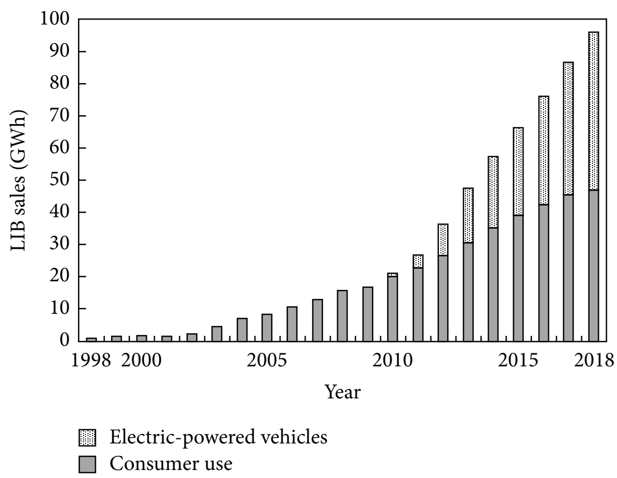


Figure 1: Forecasted expansion in demand for lithium ion batteries. Reprinted from [5].

Li ion storage mechanisms, anode materials can be classified into the following categories: carbon based materials, such as graphite, amorphous carbon, carbon nanotubes, and graphene; alloy/dealloy materials, such as Si, Sn, Ge, Al, and Bi; transition metal oxides (M_xO_y, M = Cu, Mn, Fe, Co, Ni, etc.); metal sulphides; metal phosphides and metal nitrides [13–15]. Figure 3 shows the potential versus Li/Li^+ and the corresponding capacity density of some potential active anode materials. In the whole, transition metal oxides always have relatively higher potential and capacity.

Among these transition metal oxides, TiO_2 is one of the most promising anode candidates for LIBs, which exhibits excellent structural stability, high discharge voltage plateau (more than 1.7 V versus Li^+/Li), excellent cycling stability, environmentally friendly, high safety, and low cost [16, 17]. However, some limitations of TiO_2 exist as well, such as low capacity, low electrical conductivity, and poor rate capability. Table 1 compares advantages and limitations of TiO_2 and other anode materials. The reversible lithium ion insertion and extraction from TiO_2 occur according to the following reaction [18]:

$$x\mathrm{Li}^+ + \mathrm{TiO}_2 + xe^- \longleftrightarrow \mathrm{Li}_x\mathrm{TiO}_2 \quad (1)$$

where x can range between 0 and 1, depending strongly on the TiO_2 polymorph, particle size, and morphology. Therefore, the electrochemical performance of TiO_2 highly depends on their structural parameters such as crystallinity, size, morphology, polymorphs, and specific surface area. Table 2 summarizes the structural and electrochemical profiles of various TiO_2 polymorphs [19]. Amongst these, the anatase, rutile, brookite, and bronze phases of TiO_2 have been reported for LIBs applications. However, there are some problems which exist in practical application, that is, low electrical conductivity (10^{-12}–10^{-7} $s\,cm^{-1}$) and diffusion coefficient of lithium ions (10^{-15}–10^{-9} $cm^2\,s^{-1}$), always leading to the poor rate capability of TiO_2 anodes, which result from their low electric conductivity with the lack of open channels [20–22].

Based on the analysis of shortcomings of TiO_2 anodes, several different strategies have been developed to address these issues of TiO_2-based anodes and summarized in this review, such as designing different nanostructured TiO_2, coating or combining TiO_2 with carbonaceous materials and metal oxides to change the physical and chemical surface, and selective doping with heteroatoms to form more open channels and active sites for Li ion transport, as well as increasing the intrinsic conductivity. Indeed, these methods lead to many advantages in improving the capacity, cycling stability, and rate capability of TiO_2.

2. Research on the LIBs Property of TiO_2-Based Anodes

2.1. Different Structures. Different structures usually exhibit unique performance based on their surface and structural properties. Thus, various morphologies of TiO_2 have been synthesized to obtain superior electrochemical properties.

2.1.1. One-Dimensional Nanostructures. One-dimensional (1D) nanostructures including nanorods, nanoneedles,

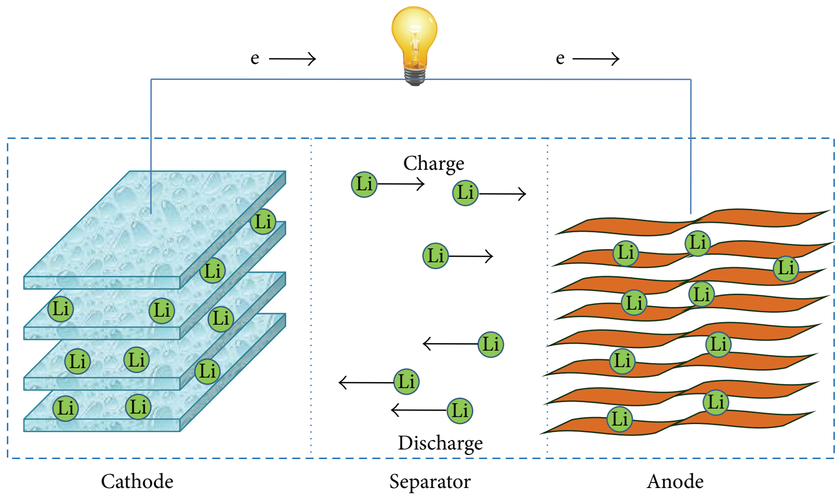


Figure 2: Schematic representation of lithium insertion/deinsertion mechanism for current rechargeable lithium battery.

Table 2: Structural and electrochemical properties of various TiO_2 polymorphs [19].

Structure	Space group	Density (g cm^{-3})	Lattice parameter values	Lithiation quantity (mole)	
				Bulk	Nano
Rutile	Tetragonal *P4₂/mnm* → $P4_2/mnm$	4.13	a = 4.59, c = 2.96	0.1	0.85
Anatase	Tetragonal $14_1/amd$	3.79	a = 3.79, c = 9.51	0.5	1.0
Brookite	Orthorhombic *Pbcv*	3.99	a = 9.17, b = 5.46, c = 5.14	0.1	1.0
TiO_2-B (bronze)	Monoclinic *C2/m*	3.64	a = 12.17, b = 3.74, c = 6.51, β = 107.298	0.71	1.0
TiO_2-II (Columbite)	Orthorhombic *Pbcn*	4.33	a = 4.52, b = 5.5, c = 4.94		
TiO_2-H (hollandite)	Tetragonal *14/m*	3.46	a = 10.18, c = 2.97		
TiO_2-III (baddeleyite)	Monoclinic $P2_1/c$		a = 4.64, b = 4.76, c = 4.81, β = 99.28		
TiO_2-R (ramsdellite)	Orthorhombic *Pbmn*	3.87	a = 4.9, b = 9.46, c = 2.96		
TiO_1-O I	Orthorhombic				
TiO_2-O II	Orthorhombic				

nanotubes, nanofibers, and nanowires could serve as an electron express way along the axial direction for electron collection due to a shorter collection time for the efficient electron transportation [31, 32]. For example, single-crystalline TiO_2 nanowires have an electron mobility of $\sim 1\,cm^2\,V^{-1}\,s^{-1}$, nearly 1-2 orders higher than that of polycrystalline nanoparticles [33, 34]. Thus, 1D nanostructure is conductive to shorten the diffusion length for electrons and lithium, increase the electrode/electrolyte interfacial area, and accommodate volume changes arising from the lithium ion insertion/extraction process [35]. Moreover, due to the unique structural flexibility, 1D material with good mechanical properties has potential in various binder-free and flexible electronics and photonics [36–38].

1D TiO_2 with different nanostructure (Figure 4) including nanotubes, nanofibers, and nanorods has been designed for high performance anodes in LIBs. The significance of 1D TiO_2 on battery performance was demonstrated by several

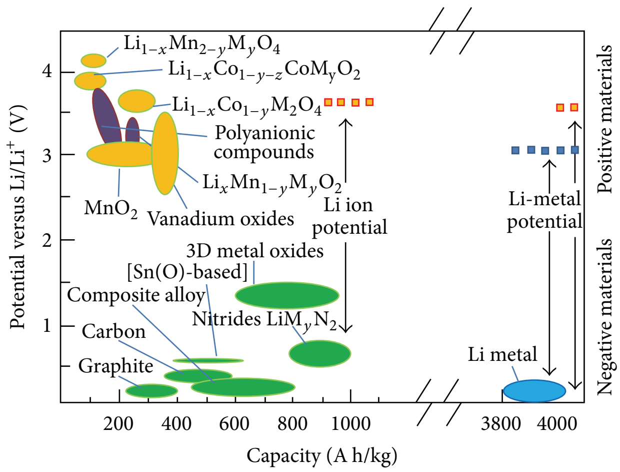


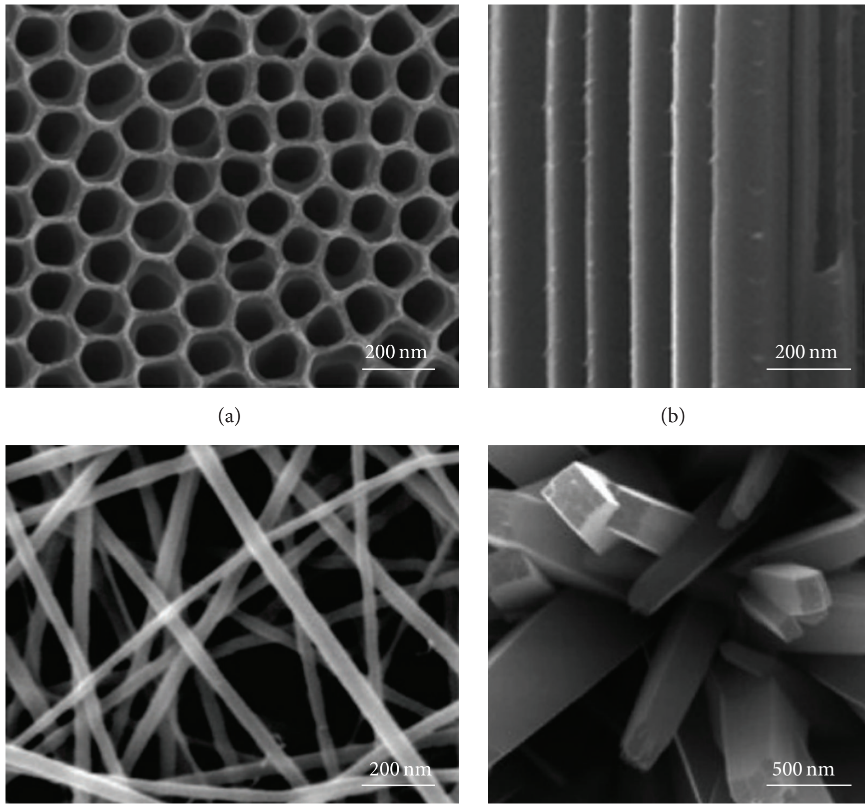
Figure 3: Comparing of some potential anode materials for lithium ion batteries.

groups. Tammawat and Meethong reported that anatase TiO_2 nanofiber anodes were directly used as an anode active material in LIBs without an additive or a binder. The nanofibers exhibited a high lithium storage capacity, a stable cycle life, and good rate capability [39]. The enhanced reversible capacity and cycling performance of the anatase TiO_2 nanofibers are attributed to the large surface area of the nanofibers, small nanocrystalline size, large Li nonstoichiometric parameters, and the increased electronic conductivity. Armstrong et al. prepared TiO_2 nanowires; these unique structures gave a higher capacity of 305 mA h g^{-1} compared to 240 mA h g^{-1} of bulk TiO_2 [40–42]. The enhanced capacity closely related to the good electronic conductivity and large surface area. Wei et al. reported a highly ordered anodic TiO_2 nanotube arrays with a tube length of 9 mm. These nanofibers exhibited significantly better microbattery performance (i.e., areal capacities, rate capability, and cycling stability) than both previously TiO_2-based electrodes and other 3D microbattery electrodes. They suggested that the enhanced performance depends strongly on the long range ordering and crystallinity of the nanotube structures [18]. Wang et al. prepared a hybrid Li ion capacitor based on TiO_2 nanobelt array and graphene hydrogels cathode. It is found that the densities of the capacitor can reach an energy density of 21 W h kg^{-1} and a high power density of 19 kW kg^{-1} [43]. The above studies also show that self-ordered 1D nanoarchitectures grown directly on a current collector are helpful to have a regularly oriented property and good contact with the current collector, enhancing the lithium ionic and electrical conductivities. Designing 1D structure is an effective way to improve the Li storage properties of TiO_2.

2.1.2. Two-Dimensional Structure. Two-dimensional (2D) nanomaterials often have large exposed surfaces and specific facets, which is very effective in high energy storage applications such as LIBs and supercapacitors. More importantly, 2D nanostructures can offer short ion diffusion length and open charge transport channel for electrolyte penetration and buffer the volume variations during the Li ion intercalation/deintercalation process [45–48]. Lithium insertion in this kind of material is just like surface lithium storage; both sides of 2D structure can store lithium ion, which can meet the requirement of fast and more lithium storage. A large number of 2D nanomaterials have been explored as anodes for LIBs, including graphene [49, 50], transition metal dichalcogenides (MoS_2, WS_2) [51, 52], ternary transition metal carbides (Ti_3C_2, Ti_2C) [53–55], and metal oxides (V_2O_5, MoO_3) [56, 57].

For TiO_2, 2D structures could provide stable framework, effective grain boundaries, and short path for lithium ion diffusion and storage compared with 0D nanoparticles and 1D nanostructures. Significant efforts have been made on the fabrication of 2D TiO_2 materials. Li et al. synthesized mesoporous TiO_2 nanoflakes with size of 10–20 nm via hydrothermal methods using $Ti(SO_4)_2$ as titanium source and NaOH solution as alkaline medium. The result of electrochemical performance test shows that the prepared TiO_2 nanoflakes with shorter calcining time have high discharge specific capacity (261.5 mA h g^{-1}) and good cycling performance [25]. In the process of heat treatment, longer calcining time results in uneven nanometer size and obvious reunion phenomenon. Shorter calcining time usually leads to more stable structure and higher specific surface area. Thus, both the lithium storage specific capacity of TiO_2 and the cycling stability of the battery can be improved [25]. Zhu et al. first synthesized the mesoporous single-grain layer anatase TiO_2 nanosheets using a simple and easily reproducible method. The obtained TiO_2 nanosheets exhibited a discharge capacity of 73 mA h g^{-1} with obvious voltage plateaus over 4000 cycles, highlighting them as promising anode material for long-term LIBs [58]. Wu et al. demonstrated a simple and green approach for the synthesis of anatase petal-like TiO_2 nanosheets; the unique structure showed high capacity and good cycling stability. This is because obtained petal-like TiO_2 nanosheets showed a comparative surface area of 28.4 m^2 g^{-1}, which should provide shorter diffusion distance for Li ions and should be beneficial for electrochemical performance of the electrode [29]. Some typical TiO_2 nanosheets used in the lithium storage were listed in Table 3. It can be seen that 2D TiO_2 nanosheets exhibit the superior capacities, improved cycling stability and rate capabilities, owing to unique exposed facets, shortened path, and reserved porous structures.

2.1.3. Three-Dimensional Porous Structure. Recently, three-dimensional (3D) porous structure materials exhibiting interesting electrochemical performance in LIBs have attracted more attention, due to their special nature including highly exposed skeleton, tunable pore size, high porosity, high specific surface area, and low bulk density [59, 60]. As described, first, the unique structure is conductive to enhance the diffusion kinetics for its short diffusion paths for Li ions. Second, the pores are beneficial to enable easy infiltration of electrolyte and fast liquid-phase Li ion diffusion, reducing the concentration polarization and increasing rate performance and capacity of the cell. Third, the continuous network of 3D porous structure can provide better electrical conductivity



(a) (b)

(c) (d)

Figure 4: SEM images of different kinds of 1D TiO_2 nanostructures. Thin wall TiO_2 nanotubes ((a) and (b)), nanofibers (c), and nanorods (d). Reprinted from [18, 38, 44].

Table 3: The capacity of reported 2D TiO_2 materials for lithium storage.

Number	Structures	Performance		Ref.
		Reversible capacity	Charge/discharge rates	
1	Carbon-supported ultrathin anatase TiO_2 nanosheets	~150 mA h g^{-1}	850 mA g^{-1}	[23]
2	Anatase TiO_2 nanosheets	~150 mA h g^{-1}	1675 mA g^{-1}	[24]
3	TiO_2 nanoflakes	~261 mA h g^{-1}	33 mA g^{-1}	[25]
4	2D rutile TiO_2-MoO_3 hybrid structure	~240 mA h g^{-1}	600 mA g^{-1}	[26]
5	Mesoporous TiO_2 nanobelts and graphene sheets	~430 mA h g^{-1}	1500 mA g^{-1}	[27]
6	TiO_2 hollow spheres	~148 mA h g^{-1}	850 mA g^{-1}	[28]
7	Mesoporous anatase TiO_2 sheets/rGO	~161 mA h g^{-1}	335 mA g^{-1}	[12]
8	petal-like TiO_2 nanosheets	~180 mA h g^{-1}	400 mA g^{-1}	[29]
9	Sandwich-like, stacked ultrathin titanate nanosheets	~170 mA h g^{-1} ~155 mA h g^{-1} ~135 mA h g^{-1}	850 mA g^{-1} 1700 mA g^{-1} 3400 mA g^{-1}	[30]

compared to loosely connected particles. Forth, the porosity in 3D structure should help in accommodating volume change during charging/discharging process and maintaining the structural integrity of the electrode [61, 62]. Up to now, different hollow structures such as hollow spheres, nanoboxes, and nanotubes are explored to be used as high performance LIBs anodes [63–66]. And the same happens for TiO_2; the introduction of porosity into TiO_2 nanomaterials also can improve the cycling stability and increase the capacity at high charge-discharge rates due to the increased contact surface area and shortened path length for diffusion of Li ions [67–70]. Highly crystalline, nonordered mesoporous

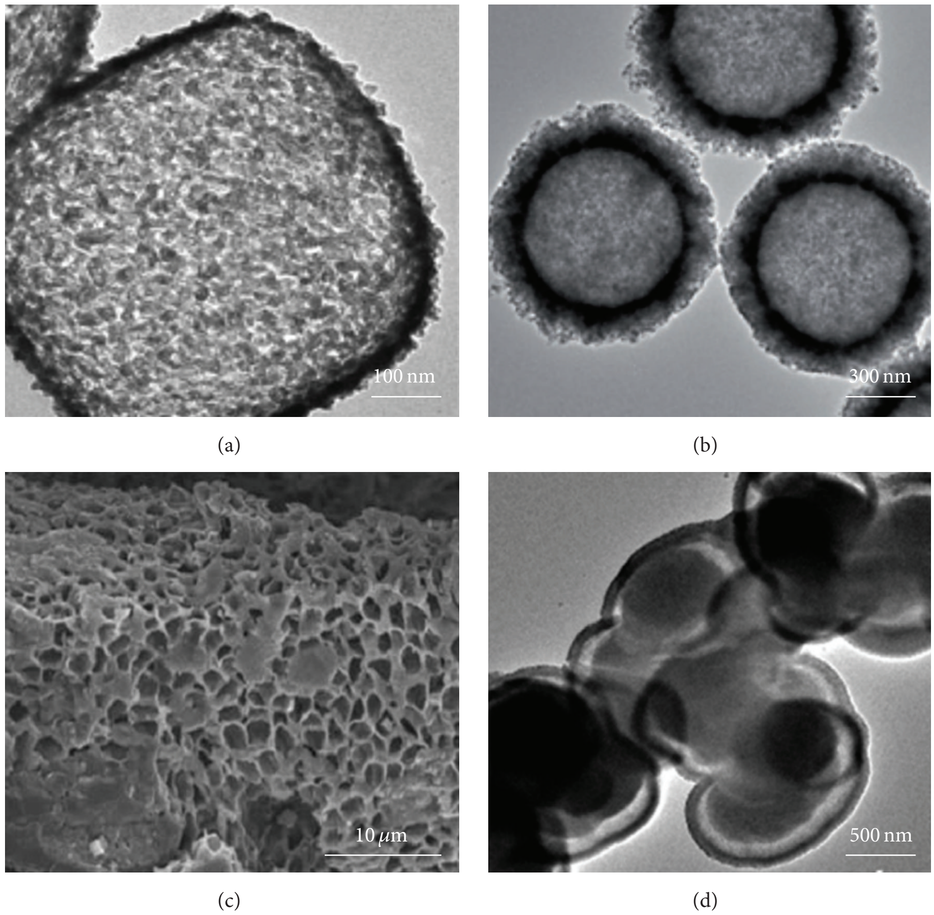
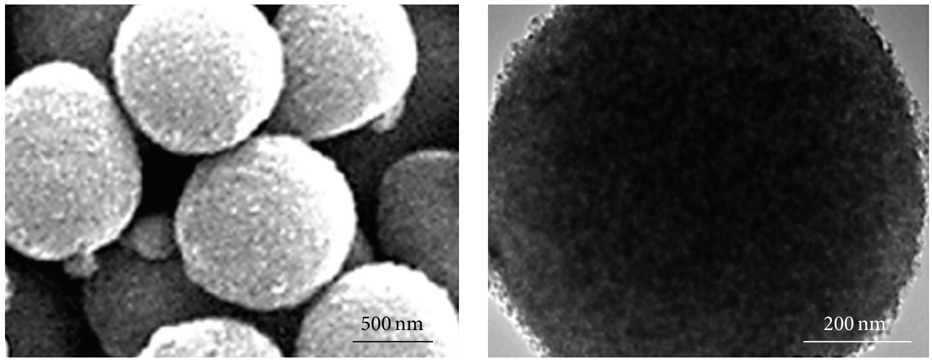


Figure 5: The morphology of different hollow TiO_2 structures. Reprinted from [67, 68, 73, 74].

TiO_2 nanocrystalline with high specific surface area and having anatase as the dominant phase have been reported by Gerbaldi and other researchers, which showed very high rate capability and excellent stability upon very prolonged cycling [71, 72]. Besides, the storage characteristics of the mesoporous samples in lithium test cells were reported, and a close correspondence between the structural properties of materials and the electrochemical performance was studied. The presence of mesopores is thought to be important for high rate performances and favorable for electrolyte ions transport. Lou's group recently reported the TiO_2 hollow spheres and submicroboxes, owing to the high surface area, porous shells, and small primary nanoparticles; these TiO_2 hollow structures possess significantly improved lithium storage properties with superior lithium storage properties in terms of high specific capacity, long-term cycling stability, and excellent rate capability [73, 74]. Figure 5 shows the typical morphology of different hollow TiO_2 structures, all of which exhibit outstanding electrochemical performance.

2.2. Coating or Combining TiO_2 with Carbonaceous Materials. Carbon materials such as active carbon, carbon nanotubes, and graphene have been extensively used for sorption, sensing, photocatalyst, electrocatalyst, and energy storage applications, owing to their abundance, accessibility, low health risk, suitable surface areas, and extreme chemical and thermal stabilities [75–80]. Especially in LIBs and supercapacitors, carbon materials are very popular for their superior conductivity, good chemical stability, and mechanical property [81–84].

2.2.1. Carbon Coating. Carbon coating is an effective and common approach to improve the electrochemical performance of the anode materials. The role of carbon has also been studied, such as reducing the charge transfer resistance and improving the Li ions diffusion, enhancing electron transport, buffering the large volume changes during the charge/discharge process, and acting as a passivation layer to prevent the aggregation of active materials [66, 85, 86]. Some research has proved that the SEI (solid electrolyte interphase) film for carbon coated materials was found to be much thinner than the SEI film on uncoated active materials; thus, initial charge-discharge efficiency can be greatly enhanced [87, 88]. For example, Xia et al. investigated the effect of carbon coating on TiO_2; these TiO_2/carbon hybrids could enhance electronic conductivity and provide flexible space for suppressing the large volume expansion during cycling [89]. E. Portenkirchner reports that the anatase TiO_{2-x}-C nanotubes demonstrate a superior Li storage capacity as high as 320 (±68) mA h g^{-1}, nearly twice as high as pure TiO_{2-x}.



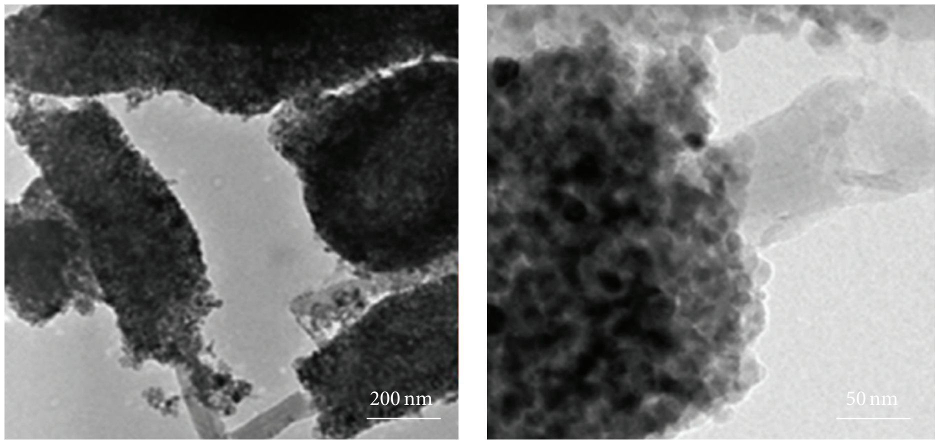
(a) (b)

FIGURE 6: The morphology of carbon coated TiO_2 spheres and their cycling performance. Reprinted from [91].

Electrochemical impedance spectroscopy reveals smaller charge transfer resistances for TiO_{2-x}-C nanotubes at the solid/liquid interface which improves the transfer of lithium ions from the electrolyte into the electrode [90]. Besides, the composites also showed higher initial charge-discharge efficiency compared to pure TiO_2; the reason can be ascribed to the formation of thinner SEI films. Zheng and coworkers prepared nitrogen-containing carbon modified porous TiO_2 composites. The as-prepared composites also exhibited enhanced rate performance and superior cyclability for LIBs compared to pure TiO_2 (Figure 6). The study indicates that N doping is favorable to improve the electronic conductivity and the composites possessed much lower charge transfer resistance than that of TiO_2 [91].

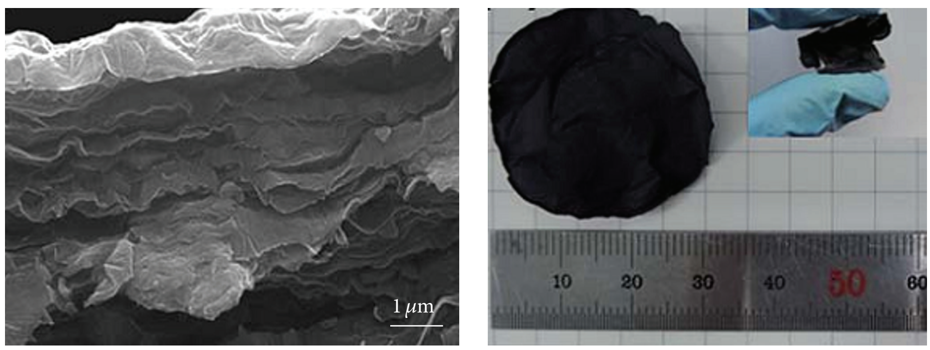
2.2.2. Combining TiO_2 with Carbon Nanotubes (CNTs). In recent years, CNTs have been approved to be a good anode material for lithium batteries due to their unique 1D structure, high conductivity (10^6 S m^{-1} for single-walled carbon nanotubes and $>10^5$ S m^{-1} for multiwalled carbon nanotubes), low gravity (0.8–1.8 g cm^{-3}), high mechanical properties (Young's modulus of the order of 1.2 TPa), and high surface area (>100 m^2 g^{-1}) [92–96]. Some studies showed that CNTs could exhibit reversible capacities anywhere from 300 to 1000 mA h g^{-1} after chemical treatment; the value is significantly higher than the theoretical capacity of graphite (320 mA h g^{-1}) [97–100]. Numerous CNTs conjugated with a variety of nanostructured materials and metal oxides have been synthesized to obtain good electrochemical performance [101–103]. For example, CNTs@TiO_2 composites have been synthesized by controlled hydrolysis of titanium isopropoxide over CNTs (as shown in Figures 7(a) and 7(b)). When CNTs are used as lithium ion battery electrodes, their inclusion is beneficial for an extreme enhancement of the rate capability of lithium ion uptake and release in TiO_2; it also favors the interfacial lithium ion intake from the solution by reducing the inherent charge transfer resistance. CNTs efficiently provide electrons to the nanostructure through the formation of Ti-C bonds, then effectively assisting lithium ion incorporation [104]. Zhao's group synthesized TiO_2/CNTs composite through chemical vapor deposition method. The in situ synthesized composite showed better electrochemical performance (high specific capacity and long-term cycling stability) than the pristine TiO_2. This is because CNTs in the composites not only supply an efficient conductive network but also keep the structural stability of the TiO_2 particles, ultimately resulting in the improved electrochemical performance [105].

2.2.3. Combining TiO_2 with Graphene. Graphene is a single atomic plane of graphite and consists in a honey comb network of sp^2 carbons bonded into two-dimensional sheets with nanometer thickness, due to its unique properties, including high intrinsic carrier mobility (200 000 cm^2 V^{-1} s^{-1}), relevant mechanical strength, excellent conductivity (5000 W m^{-1} K^{-1}), high optical transmittance (~97.7%), large theoretical specific surface area (2630 m^2 g^{-1}), and superior mechanical strength which make graphene a suitable anode material for LIBs [105–111]. Besides, the rich functional groups on the surface of graphene make it an appealing 2D substrate for the anisotropic growth of different kinds of active materials [112, 113]. For example, Fang el al.'s group prepared novel mesoporous graphene nanosheets with an excellent reversible capacity of 833 mA h g^{-1} after 60 cycles [114]; this capacity is much higher than the theoretical lithium storage of graphite. This can be ascribed to the high contact surface area for lithium ion adsorption and intercalation, as well as edges and other defects. Thus, many synthetic strategies have been reported for TiO_2/rGO hybrid nanostructures; Ti-C bond in the hybrids is crucial for rapid interfacial charge transferring. Etacheri et al. chemically bonded mesoporous TiO_2 nanosheets to rGO sheets through a photocatalytic reduction method, resulting in the formation of Ti^{3+}-C bonds between TiO_2 and rGO. These TiO_2/rGO hybrid nanostructures demonstrate superior specific capacity, excellent rate capability, and capacity retention compared to a physical mixture of TiO_2 and rGO [115]. The reason can be attributed to the higher electrochemical performance of TiO_2/rGO hybrid nanostructures to efficient interfacial charge transfer between TiO_2 nanosheets and rGO, which is fostered by Ti^{3+}-C bonds. Figure 8 shows the SEM and digital images of TiO_2/rGO hybrid films; insets in Figure 8(b) display the flexibility of the corresponding films upon bending. The high flexibility of graphene could be an



(a) (b)

Figure 7: (a) and (b) are the TEM images of CNTs@TiO_2 nanocomposite material. Reprinted from [105].



(a) (b)

Figure 8: (a) and (b) are the SEM and digital images of TiO_2/rGO hybrid films, respectively. Insets display the flexibility of the corresponding films upon bending. Reprinted from [116].

excellent supporting matrix or coating layer to accommodate the volume change during the charge/discharge process. This is crucial for maintaining the good cycling stability [116].

2.3. Combining Metal Oxides with TiO_2. Combining different physical and electrochemical properties of components with TiO_2 and utilizing the respective advantage to increase the capacitance are a feasible method, such as using high conductive materials (conducting polymers) [117, 118], increasing the surface area (carbon nanotubes) [104, 105], and using high performance redox-active transition metal oxides (MnO_2) [119]. Among the above materials, metal oxide coatings can efficiently improve the capacitive performance of the materials through intruding synergistic effects into an electrode system, such as in SnO_x@TiO_2 core-shell composites, due to the nearly zero volume change of TiO_2 in insertion of Li^+ ions process, making it suitable as a backbone or protective layer for SnO_x to restrain the pulverization and achieve an excellent high rate cycling ability and good cycling stability [120–123]. Recently, synergistic TiO_2-MoO_3 core-shell nanowire arrays were prepared via a facile hydrothermal growth of ordered TiO_2 nanowires followed by a subsequent controllable electrodeposition of nano-MoO_3. The composites exhibited high gravimetric capacity, good rate performance, and cycling stability. Figure 9 is the SEM images of the pristine TiO_2 nanowire array and optimized TiO_2-MoO_3 hybrid array anode with different magnifications. The strong synergistic effect existing in this design can be summarized as follows: (1) nearly negligible lattice changes during Li ion insertion/extraction, which is crucial to maintain excellent cycling stability. (2) The electrodeposited MoO_3 shell provides both reversible large capacity and good electrical conductivity for its nanosize effect and intrinsic characteristics. (3) The TiO_2 nanowire array can provide direct electron transport pathway between active material and current collector; Li ions can easily intercalate into the composites, manifesting an excellent rate capability and a significantly improved cycling performance [124]. Other transition metal oxides coating TiO_2 composites were also deeply investigated, such as TiO_2-V_2O_5, TiO_2-CoO, and TiO_2-SnO_2 [125–128].

2.4. Doping with Ion or Atom Dopants. For the low electrical conductivity and ion diffusivity of TiO_2, doping with appropriate ions or atoms is advantageous since this method can improve the intrinsic nature of TiO_2 by adjusting its electronic structure, increase the internal surface area and

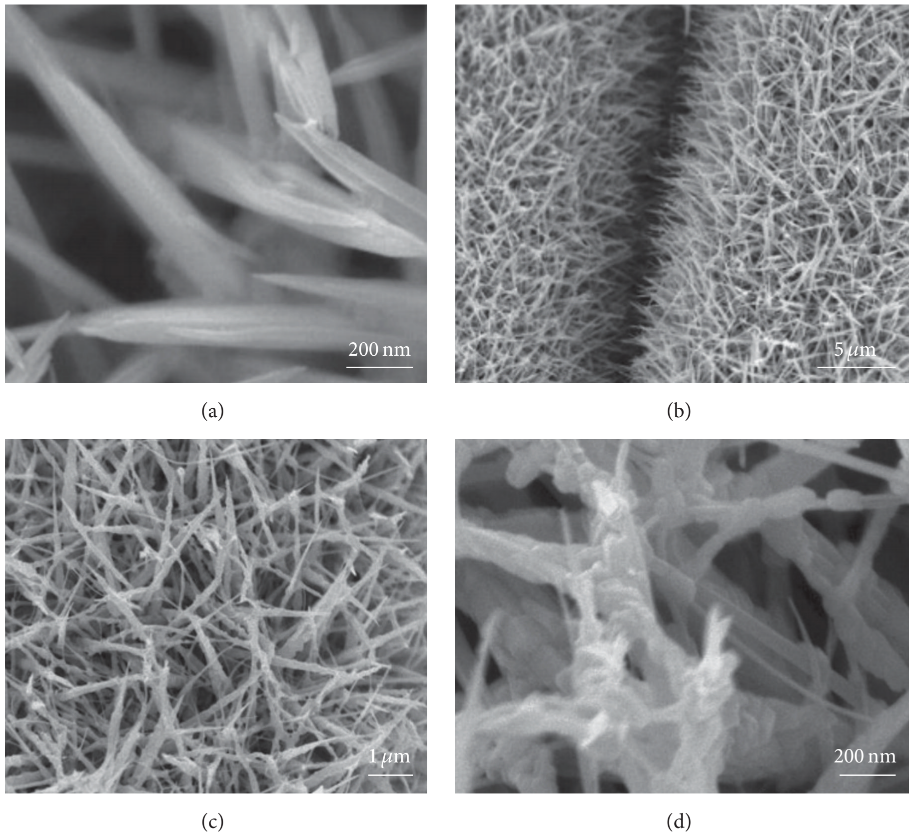


Figure 9: (a) SEM images of the pristine TiO_2 nanowire array. (b)–(d) SEM images of the optimized TiO_2-MoO_3 hybrid array anode with different magnification. Reprinted from [124].

electrical conductivity, and form more open channels and active sites for Li ion transport via the expanding interplanar spacing of TiO_2 lattices [129, 130]. The reported dopants include Fe^{3+} [131], Ti^{3+} [132], Sn^{4+} [133], B [134, 135], and N [136], all of which show beneficial effect on increasing the electrical conductivity more or less.

2.4.1. Ion Dopants. Doping Ti^{3+} in the TiO_2 structure can provide conduction band electrons and undoubtedly improves its conductivity, which also helps to increase the reversible capacity. Ren et al. presented a simple and controllable method to prepare the Ti^{3+} doped TiO_2 by a solvothermal process at lower temperature. The doped TiO_2 nanoparticles showed much enhanced electrochemical performance in reversible capacity, rate performance, and stability comparing with the pure TiO_2 [132]. This is because Ti^{3+} doping can increase the electrical conductivity of TiO_2. Liu et al. synthesized Ti^{3+} doped TiO_2 nanotube arrays which also exhibited excellent lithium ion intercalation performance with an initial discharge capacity of 101 mA h g^{-1} at a high current density of 10 A g^{-1} [137]. The much improved lithium ion intercalation properties were attributed to the easy phase transition promoted by the surface defects, that is, Ti-C, Ti^{3+}, and O^{2-} vacancies, which could serve as nucleation centers. In addition, the rate performance was also improved due to the enhanced electrical conductivity. Sn^{4+}, Fe^{3+}, and other metal ions were also investigated as dopants to improve the electrochemical performance [133, 138]. Kyeremateng and coworkers reported that the Sn doped TiO_2 nanotubes delivered much higher capacity values compared to simple TiO_2 nanotubes. The outstanding electrochemical behaviour is proposed to be related to the enhanced lithium diffusivity evidenced with Cottrell plots (Figure 10) and the rutile-type structure imparted with the Sn doping. The results showed that lithium ion insertion into Sn doped TiO_2 is about 40 times faster than into undoped TiO_2 [133].

2.4.2. Atom Dopants. Atoms doping is also a useful technique to increase the internal surface area and electrical conductivity of anode materials. For example, boron (B) and nitrogen (N) doping had been proven to be an effective strategy for improving the electrochemical performance of carbon materials [139–143]. For example, B doped graphite has a larger lattice constant value, a_0, and a smaller d_{002} distance than ideal graphite, due to replacement of the carbon atoms with boron [144], leading to increases in both the crystallinity and electronic property of carbon as a Li-host material. Jeong et al. synthesized B doped TiO_2 materials through a simple one-pot process. The doped sample containing a relatively large amount of B possesses cylindrical pores that are favorable for lithium ion transfer, leading to the highest diffusion coefficient. Consequently, the doped anodes exhibit significantly improved cyclic capacities compared to the

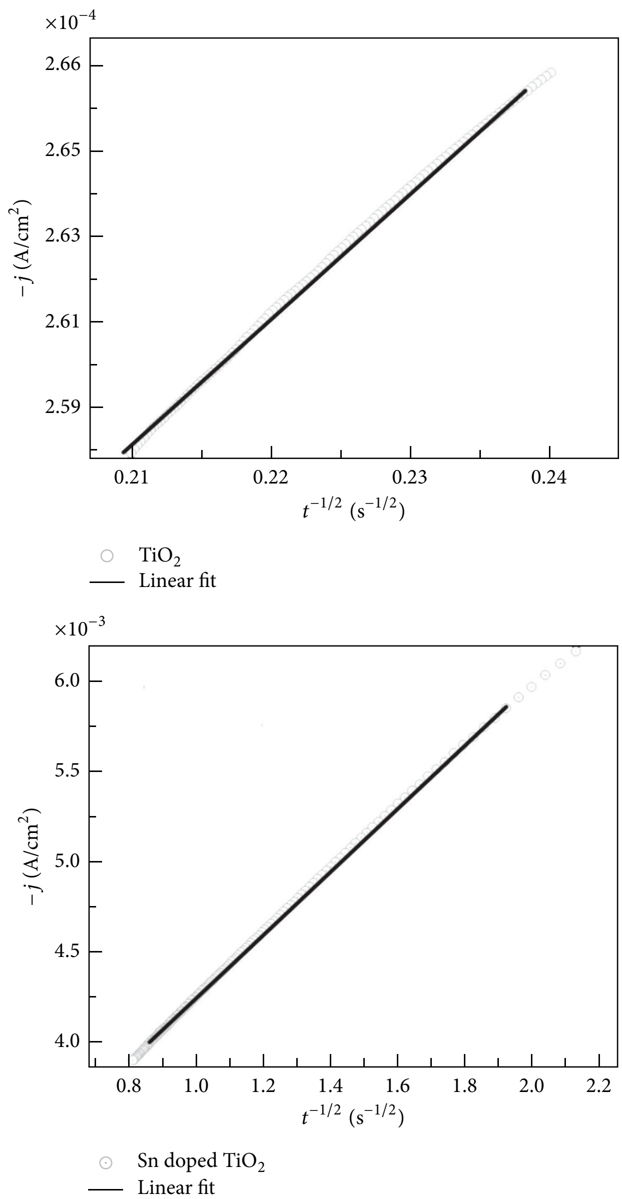


Figure 10: Cottrell plots for the determination of Li^+ diffusion coefficients in TiO_2 and Sn doped TiO_2. Reprinted from [133].

nondoped TiO_2 sample [134]. Furthermore, nitrogen doping has been proven to be an effective strategy for improving the capacity of TiO_2. This is because nitrogen doping can improve the electric conductivity as well as the ionic conductivity; after introducing the N atoms, the distortion of Ti-O lattice can affect the electrochemical reactions on the interfaces between electrodes and the electrolyte, as well as lithium ion diffusion in the Ti-O lattice [68, 145–147].

3. Conclusions and Outlook

In summary, this review showed the amount of research efforts towards the development and improvement of TiO_2-based anode materials for LIBs. Several elegant strategies aiming to boost the electrochemical performance and promote the practical application of TiO_2 have offered, including fabrication of nanostructures with different morphologies and sizes, modification by various coating materials (carbon materials and metal oxides), elements doping. The unique design allows achieving high lithium storage and good cycling stability based on the high lithium ion flux at the electrode/electrolyte interface, low internal resistance, short paths for fast lithium ion diffusion, and low volume change during Li ion insertion/desertions process. When combining these exquisite features together, it is possible for maximizing their electrochemical advantages to meet the present energy demands.

Firstly, the performance of TiO_2 depends strongly on its particle size and morphology. Therefore, different structures of TiO_2 are explored to improve the electrochemical performance of TiO_2. In a second category, combining TiO_2 with carbonaceous materials such as active carbon, CNTs, and graphene, the composite anode materials can obtain moderate conductivity, large surface area, good chemical stability and mechanical property. In the third, metal oxides such as Fe_2O_3, SnO_2, and MnO_2 can provide larger capacities and high energy density compared to pure TiO_2, which had been combined to improve the overall anode performance. Fourthly, for the low electrical conductivity and ion diffusivity of TiO_2, doping with appropriate ions or atoms is advantageous since this method can improve the intrinsic nature of TiO_2 by adjusting its electronic structure and forming more open channels and active sites for Li ion transport via the expanding interplanar spacing of TiO_2 lattices.

Finally, from this short review, we can conclude that high energy density, high cycle life, and high efficiency battery will still be the mainstream in the future growth of lithium batteries. In order to utilize the TiO_2-based materials as effective anodes in commercial LIBs, interdisciplinary effort in this area is however required.

Although considerable advances have been achieved in improving the Li ion storage performance of TiO_2, several fundamental issues are still needed to be solved. For example, nanomaterials usually show large surface area, which leads to more significant side reactions and results in low coulombic efficiency. Besides, nanopowder has lower density compared to the block material, which would reduce the volumetric energy density of battery. The following two possible strategies may be helpful to solve the abovementioned problem: (1) adopting surface modification or coating to reduce unnecessary side reactions; (2) designing hierarchical structures to enhance the tap density of anode materials.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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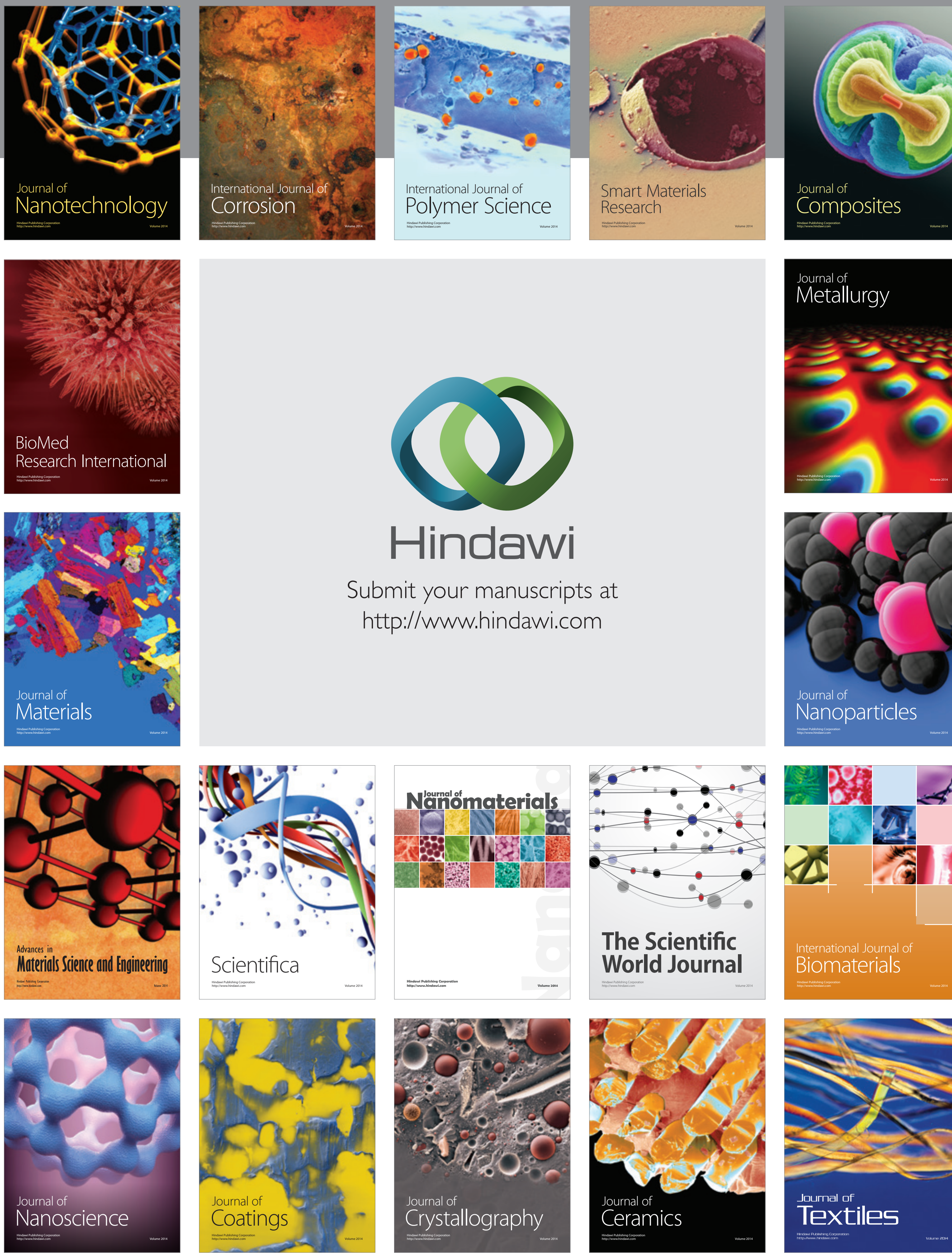
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