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Highlights on inorganic solid state chemistry and energy materials

LIU AiPing & DONG WenJun*

Center for Optoelectronics Materials and Devices, Department of Physics; Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Engineering Research Center for Eco-Dying & Finishing of Textiles, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, China

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This review highlights the recent research progress on inorganic solid state energy materials in China, from synthesis and fundamental properties to their applications. It describes the significant contributions of Chinese scholars in the field of inorganic solid state chemistry and energy materials including green catalysts, fuel cells, lithium batteries, solar cells, hydrogen storage materials, thermoelectric materials, luminescent materials and superconductors, and then outlines the ongoing rapid progress of novel inorganic solid state materials and the development of reliable and reproducible preparation methods for inorganic solid state materials in China. Finally, we conclude the paper by considering future developments of inorganic solid state chemistry and energy materials in China.

inorganic, solid state materials, energy materials

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Over the past few years, inorganic solid state materials have been given great attention because of the crucial demands for efficient, clean, versatile and renewable energy sources. Numerous studies have focused on designing novel inorganic solid state materials with size-dependent optical, electrical, catalytic and magnetic properties for their potential applications to energy conversion and storage devices. Many research groups in China have given their attention to these hot topics in inorganic solid state chemistry and produced a variety of new materials including green catalysts, fuel cells, lithium batteries, solar cells, thermoelectric materials, luminescent materials and magnetic materials. The journal *Science China Chemistry* with international influence has provided a stage for Chinese scholars to demonstrate their significant contributions to this field. The special topic of inorganic solid state chemistry and energy materials organized by Feng [1] illustrates the ongoing rapid progress in the field of inorganic solid state chemistry and energy materials in China by listing high qualified review papers and research articles in the field.

One of the flourishing themes in novel energy materials is the green catalysts that demonstrate extraordinary properties such as reuse, environmental-friendliness and high catalytic efficiency. The heterogeneous catalysts based on noble metal nanoparticles can efficiently catalyze the conversion of natural energy such as solar energy into chemical energy and degrade many hazardous pollutants through a redox process, indicating their promising application as photocatalysts in energy conversion, information sensing and environmental treatment. Currently, many researchers are devoting their efforts to finding highly active heteronanostructures for a wide variety of applications, including catalysis, photocatalyst, sensing, etc. In this regard, Dong and Feng reviewed the recent research progress in the hetero-nanostructure of silver nanoparticles on MO_x (M=Mo, Ti and Si) (as shown in Figure 1) and described their synthesis technologies and potential applications to photocatalyst and information sensing [2]. Hetero-nano-

*Corresponding author (email: wenjundong@zstu.edu.cn)

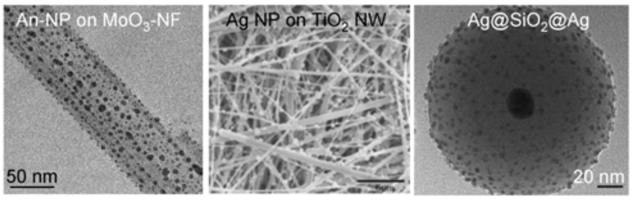

Figure 1 Hetero-nanostructures of silver nanoparticles on MO_x (M = Mo, Ti and Si) [2].

structures of Ag nanoparticles on MoO_3 nanofibers were prepared by a simple one-pot simultaneous redox route [3]. The functionalized hetero-nanostructured material showed excellent gas sensing performance and the H_2 sensing limit could be as low as 400 ppm at room temperature. The porous catalytic membrane based on the Ag/titanate nanowire was also synthesized by ion sputtering and deoxidized reaction processes [4, 5]. The catalytic membrane showed extremely flexible, stable and self-supporting properties, and enhanced photocatalytic degradation efficiency for methamidophos. Li et al. [6] also designed hierarchical nanostructure of Ag@SiO_2@Ag by a facile one-pot synthesis method with polyvinylpyrrolidone as the gentle reducing and protective agent and ammonia as smart catalyst. The unique hierarchical nanostructure of Ag@SiO_2@Ag structure not only displayed predominant catalytic decomposed activity for dye RB but also decreased the Ag nanoparticles losing during the catalytic reaction.

Zhao further summarized the interesting topic of supported noble metal nanoparticles (such as Au/TiO_2, Au/ZrO_2, Ag/AgCl) as efficient photo/sono-catalysts for the selective synthesis of chemicals and degradation of environmental pollutants [7]. Zhao and his collaborators prepared oxides (ZrO_2, Zeolite Y, TiO_2, SiO_2) supported noble metal nanoparticles by photo-reduction strategies [8, 9]. Upon either visible or UV light excitation, the electrons transferred from metal nanoparticles to electron acceptors such as O_2 caused positive charged metal, which captured the electrons from the organic molecules adsorbed on them. The oxidation of benzyl alcohol to benzaldehyde on Au/Zeolite Y and Ag/Zeolite Y catalysts achieved almost 100% under UV light irradiation [10, 11]. The Au/TiO_2 composites were also utilized as efficient sonocatalysts to promote H_2 production in the aqueous solution with methanol at a rate up to 282.3 mol/h [9]. The supported noble metal nanoparticles also decomposed various pollutants, including aldehydes, alcohols, acids, phenolic compounds, and dyes under UV/visible light and ultrasound irradiation, which was highly desirable to guarantee environmental safety [10–13].

Another attractive theme in novel energy materials for energy conversion is fuel cells, lithium-based batteries and solar cells, due to the rapid depletion of fossil fuels and increasingly worsened environmental pollution caused by vast fossil-fuel consumption. Electrochemical energy storage and conversion can generate clean electric energy from the stored chemical energy through the desired electrochemical reactions. Solid oxide fuel cells are considered a promising next-generation electric power source because of their high efficiency, environmental friendliness and fuel flexibility. Ln_2MO_4 oxides with the K_2NiF_4-type structure, as important cathode materials, possess high electrical conductivity and electrocatalytic activity for oxygen reduction reaction, great compatibility with traditional electrolytes, chemical and thermal stability during operation, sufficiently porous channels for oxygen transport and lower operation temperatures. Zhao summaried in detail the effects of different factors on performances of Ln_2MO_4 (Ln = La, Pr, Nd, Sm; M = Ni, Cu, Fe, Co, Mn) as cathodes materials of solid oxide

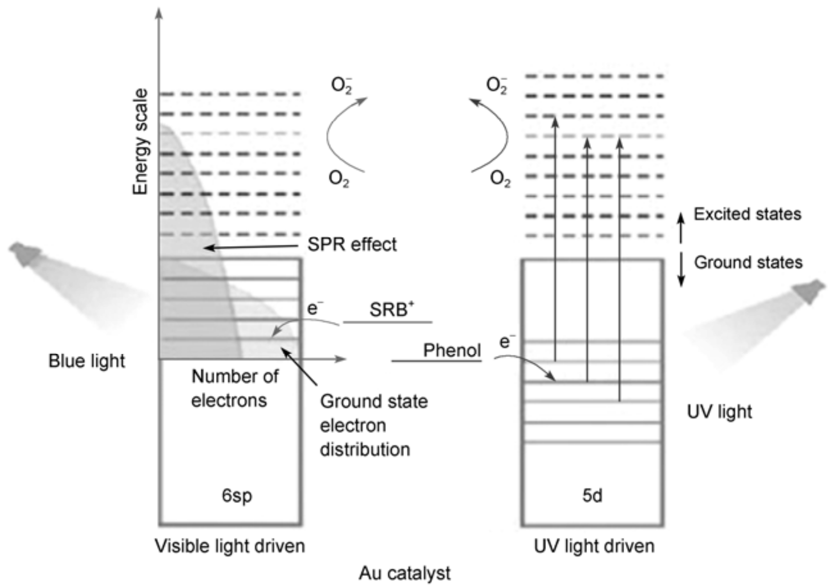

Figure 2 Band structures of Au nanoparticles and the proposed mechanism for photocatalysis using Au nanoparticles [7].

fuel cells [14]. After doping with allovalent elements, $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Sr_xNiO_4$ exhibited improved chemical compatibility with CGO and SDC electrolytes, indicating their promising application as cathode materials for intermediate-temperature solid oxide fuel cell [15, 16]. Li et al. [15] studied the high temperature transport property of Sr doped La_2CuO_4 and found that $La_{2-x}Sr_xCuO_{4-\delta}$ exhibited a metallic conducting behavior. Zhao's group also studied the kinetics of oxygen reduction reaction on cathode material surfaces through the polarization resistance (R_p) of the electrodes [16–18] and found the lowest R_p in the Sr doped $La_{1.7}Sr_{0.3}CuO_4$ [15]. The addition of 5 vol% Ag in $La_{1.6}Sr_{0.4}NiO_4$ resulted in the lowest R_p of 0.21 Ωcm^2 at 700 °C due to the oxygen reduction enhancement by impregnated silver [19]. Yuan et al. prepared pyrochlore materials such as $M_2Sn_2O_7$ (M=La, Bi, Gd or Y), $Bi_2Pb_2O_7$ and $R_2Ru_2O_7$ (R=Pr^{3+}, Sm^{3+}-Ho^{3+}) by a hydrothermal method [20–22]. The synthesized $M_2Sn_2O_7$ stannates were thermally stable and showed ionically conducting properties at high temperatures [20]. The ruthenium pyrochlore oxides $R_2Ru_2O_7$ showed novel conductivity property, thermal and chemical stability, which made them promising candidates as cathode for intermediate-temperature solid oxide fuel cells [22].

Furthermore, rechargeable Li-ion batteries have attracted great attention for their widespread applications in various portable electronic devices and electric vehicles. Chen summarized their progress in battery development using a combination of lightweight elements and nanostructured materials (Figure 3), and highlighted the benefits of nanostructured active materials for advanced green batteries with large capacity, high energy and power density, and long cycle life [23, 24]. Cui et al. [25] synthesized SnO_2@polypyrrole (PPy) nanocomposites by a one-pot oxidative chemical polymerization method. The SnO_2@PPy nanocomposites exhibited high discharge/charge capacities and favorable cycling when employed as anode materials for rechargeable lithium-ion batteries. Zhang et al. [26] also prepared spinel $Li_4Ti_5O_{12}$ submicrospheres assembled with nanoparticles by a facile hydrothermal synthesis method. The spinel $Li_4Ti_5O_{12}$ submicrospheres displayed high rate capability, excellent cycling reversibility, and enhanced lithium diffusion kinetics, indicating their promising applications as anode materials for rechargeable Li-ion batteries.

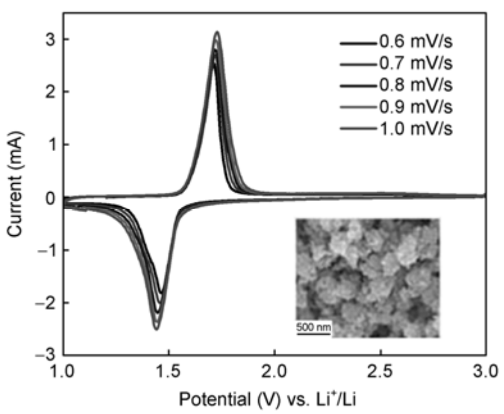

Figure 3 $Li_4Ti_5O_{12}$ submicrospheres and their application as anode materials of rechargeable lithium-ion batteries [26].

Besides, dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO_2 films and organic dyes have attracted considerable interests because of their relatively low cost and high efficiency for the photoelectrical conversion. Wang's group prepared a hierarchically ordered macro-mesoporous TiO_2 film (Ti-Ma-Me) on a fluorine-doped tin oxide substrate and improved the capacity of TiO_2 anode for absorbing dyes and enhanced scattering light [27]. Due to the large specific surface area of macroporous TiO_2 film, the photovoltaic conversion efficiency can be improved from 3.04% to 5.55%. Yang et al. introduced graphene as 2D bridges into the TiO_2 electrodes of dye-sensitized solar cells, which brought faster electron transport, lower recombination and higher light scattering [28].

It is worth mentioning that Li presented a critical review on the studies of defect chemistry of oxide nanoparticles for creating new functionalities pertinent to energy applications including dilute-magnetic semiconductors, giant-dielectrics, or white light generation [29]. The relationships between the internal structures and defective surfaces of oxide nanoparticles were discussed in detail, as well as their synergy in tailoring the materials properties from structural fundamentals of bulk oxides to structural features of simple oxide nanoparticles distinct from the bulk, and to new functions achieved through extending the defect chemistry concept to the assembled architectures or multi-component oxide nanoparticles. It is concluded that the understanding of defect chemistry can provide diverse possibilities to manipulate electrons in oxide nanoparticles for functionalities in energy-relevant applications [30–32]. Wu's group prepared monodispersed magnetite Fe_3O_4 and hematite α-Fe_2O_3 nanocrystals in co-solvents of alcohol and water [33, 34]. Either the shape or the size of the nanocrystals could be easily controlled. It is demonstrated that these iron oxide nanocrystals are soft ferromagnetic at room temperature and α-Fe_2O_3 has a more effective catalytic effect on the thermal decomposition of ammonium perchlorate than Fe_3O_4. It was found that the magnetic and catalytic properties of these nanocrystals depended not only on the size and shape but also on the surface structure of the nanocrystals (Figure 4).

Furthermore, metal-oxide-based and metal-iodates-based noncentrosymmetric compounds have shown a great interest due to their good piezoelectricity, pyroelectricity, and ferroelectricity. Especially, the second-harmonic generation (SHG) properties make them as promising SHG materials with wide transparency wavelength regions, large SHG coefficients and high optical-damage thresholds as well as high thermal stability [35, 36]. Mao's study indicated that

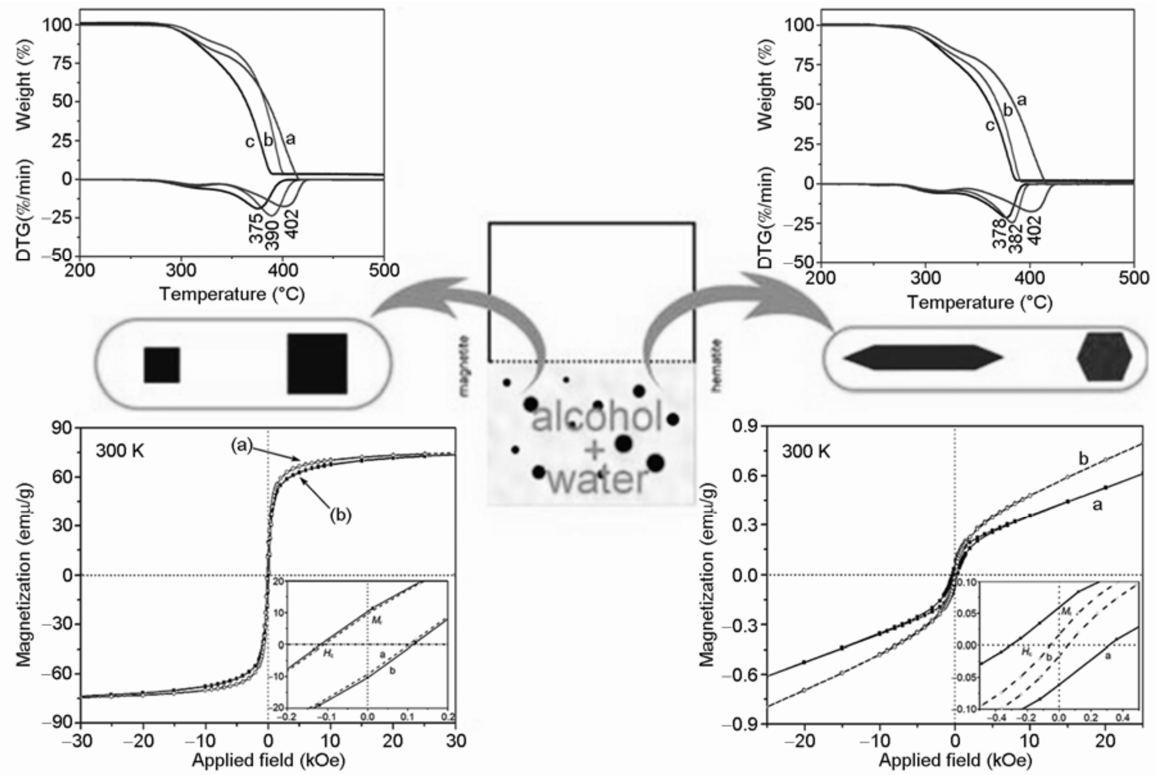

Figure 4 Shape and size-controlled growth of uniform magnetite and hematite nanocrystals with tunable properties [33].

the combination of d_0 transition metal ions with iodate anions enhanced the SHG responses by means of additive polarizations of both types of asymmetric units [37]. The combination of lone-pair cations (Pb^{2+} and Bi^{3+}) with iodate cations were able to emit strong luminescence in the visible or near-IR regions [38, 39].

Overall, current developments in inorganic solid state chemistry and energy materials research in China are bringing forward reliable and reproducible methods for preparing new functional nanomaterials with novel properties. Future research should focus on chemical reactions, synthetic/preparative methods and techniques, chemical composition and structure, structure-property relationships of solid materials, particularly the valence and defects in solids and their influence on the physical and chemical properties of solid materials [1]. More original results will be expected to publish in the journal of *Science China Chemistry* by Chinese researchers, which is a timely reflection of the ongoing rapid development in inorganic solid state chemistry in China.

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