Team of Particulate Materials Chemistry and Engineering
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**Brief Introduction**

Particulate materials have been widely used as raw materials in production of chemicals, pigments, foods, drugs, structural/functional materials and environmental, energy related matters. The Team initially focused on expanding our competence in the large scale production of nanosized particles, and developing their value-added technology and products profiting from the interdisciplinary advantage at IPE. With the scientific and technological advances at nanoscale, we began to extend the interests in innovating and applying new materials using nanostructures as building blocks. Addressing the concerns of new clean energy need, environmental pollution control and insufficient supply of high quality engineering materials in China, we are working along with the entire chain-form particulate materials preparation to engineering applications including the tailored technology solutions as well.

To date, we have developed a series of new materials for solar cell, lithium battery, gas sensor and direct methanol fuel cell. A large number of research papers have been published in prestigious journals and recognized by our international peers. In the field of particle preparation, environmental purification and inorganic-organic nanocomposite, most of the laboratory achievements have been successfully transferred to industry manifesting our competencies in the market. Our high temperature engineering materials have become the powerful backup for the urgent needs in our country, and served as the major supplier for the related indexes of the products. Recently, we are making great efforts to create knowledge and cultivate talent at mesoscale to develop technology platforms that will spur the growth of particulate materials, as well as linking multiple disciplines to lead research breakthroughs that will boost China’s economy in process engineering of materials.

**Research Activities**

1. **Preparation and structure-tailoring of nano/micro sized particles**

   The strategy and approaches we are following in this field cover: (1) synthesis and processing of particulate materials, (2) understanding the physicochemical properties related to the material dimensions and structures, (3) design and fabrication of devices/functional units using particulate materials as building blocks. In recent years, our research and development (R&D) are positioned in the production of uniform and disperse particles (e.g., Al$_2$O$_3$, CeO$_2$, SiO$_2$, SiC, ZrO$_2$), as well as hollow particles by RF thermal plasma hydrothermal and multiphase reaction processes, design and preparation of composite particles composing different natures from inorganic, metallic and even mineral particles ready for coating application, manufacturing of inorganic-organic nanocomposites involving nanoparticles and low even zero VOCs content polymers, and large scale preparation of new materials such as graphene and BN fibers.

2. **Particulate materials for new energy applications**

   The imminent shortage of fossil fuels and current fear of global warming are driving scientists and engineers to develop renewable, highly efficient methods of creating and storing energy without damaging the environment. However, there are many drawbacks in both the production and application of current energy conversion and storage systems (e.g., low efficiency, high cost or considerable environmental damage). This has inspired our interests in such technologies as solar cells, lithium-ion batteries, fuel cells and energy saving. Considering the performance of the energy-related devices
and materials is closely related to their structures, we are making greater efforts in the design of novel materials with manipulated structures such as hollow microspheres with different shell structures, cage-bell nanostructured particles, Si-based composites and the approaches to facilitate electron or ion transport and electrolyte diffusion. On the other hand, how to decrease the energy consumption using new energy-saving materials and technologies becomes equally important as development of new clean energy, so we are paying more attention to the R&D in this field.

3. Particulate materials for environmental applications

Our R&D works in environment field started from the effort to develop new antibacterial materials for suppressing the epidemic viruses, bacteria excess propagation. With the air pollution becoming more and more heavy, we began to pursue effective technology and equipment to reduce SO$_2$, NOx, VOCs pollutants and then the related gas sensor using the innovative particulate materials. Recently, our attention has been paid to develop regenerative thermal oxidizer, regenerative catalytic oxidizer for VOCs, and novel ceramic or metallic filters with the integrated catalytic and dust-collecting coupled functions. From the scientific point of view, some of our research works have been focused on the vacancy and defect manipulation in the particles in addition to preparation and design of nanostructures.

4. Particulate Materials for high temperature applications

The innovation and developments of engineering materials for high temperature applications are not only related to the energy industry but also to a large number of applications such as thermal barrier, oxidation/corrosion resistance and anti-ablation thermal structures. Profiting from our long period efforts in the particulate structure design and application, many kinds of composite powders have being produced and applied in the coating and composite structured materials manufacture. Composite particles lay a solid foundation for high temperature coating preparation, so we set up the massive production platform for nano-structured coatings by hydrothermal/molten salts/plasma process and atmospheric plasma spraying technique. Recent research strategy and approaches have been concentrated on the development of novel engineering materials and techniques such as ultra-high temperature ceramic matrix composites, chemical vapor deposition/infiltration and precursor impregnation and pyrolysis process.

Infrastructure

Currently, the team has 91 staff, of which 81 are engaged in scientific research and engineering innovations, including 10 full professors, and 20 associate professors. Around 47% of the total staff is 35 years old or younger. More than 50% of the research staff hold doctoral degrees.

The team has established several equipment platforms for preparation of particulate materials (e.g. HF plasma, CVD, CVI, Hydrothermal), preparation and characterization of catalysts for VOCs oxidation. The equipments available in our team can meet the requirement in characterization of particle size, microstructure, thermal, electrical, magnetic, catalytic, mechanical, antibacterial performance. Some pilot plants have also been set up for the development of production lines and processes for particles and functional coatings such as inorganic-organic composite coatings, ceramic coatings for high temperature applications. An engineering center has been built in Langfang industrial zone to promote and expand our competence in engineering research and application of particulate materials.

Research Progress

1. New energy materials highlight the effects of structure design at nano/mesoscale

We developed a general and facile method for synthesizing multiple-shell hollow microspheres (MSHM) of metal oxides
using carbonaceous microspheres as templates (Fig. 1). All of the shells were created by a one-step thermal treatment. The number and composition of shells could be rationally designed by adjusting the heating conditions and the concentration and type of metal salt species used. Different types of MSHM, such as α-Fe$_2$O$_3$, Co$_3$O$_4$, CuO, and ZnO, could be fabricated by soaking the carbonaceous microspheres in solutions with the corresponding metal ion species. Furthermore, heterogeneous metal oxide (ZnO@ZnO/ZnFe$_2$O$_4$@ZnO) and binary metal oxide (ZnFe$_2$O$_4$) MSHM were also prepared by the simultaneous or successive use of different metal ions. The research may open up new opportunities for preparing advanced materials based on MSHM for multipurpose applications.

Nanostructured Si-based composites have been regarded as the anode materials of next generation Li-ion batteries. Our work results are concentrated on: (1) the scalable synthesis of the interconnected porous Si/C composites by Rochow reaction, (2) facile synthesis of Si/C anode nanocomposites via the CVD method using cheap CH$_3$SiCl$_3$ and (CH$_3$)$_2$SiCl$_2$ as Si and C precursors, instead of toxic SiH$_4$ commonly used, (3) low-cost synthesis of porous Si/C microspheres by spray drying technique followed by carbonization using Si nanoparticles and graphitized carbon black nanoparticles, (4) modification of commercial graphite microspheres with Si nanorods via CVD. Till now, some of our synthetic processes are readily scalable, opening a viable way for practical application in future Li-ion batteries.

We developed simultaneously a general approach for synthesizing metal nanomaterials with hollow interiors or cage-bell structures based on the inside-out diffusion of Ag in core-shell structured nanoparticles. It begins with the synthesis of core-shell or core-shell-shell metal nanoparticles with Ag residing in the core or inner shell region in an organic solvent. Ag is then extracted by bis(p-sulfonatophenyl)phenylphosphane, which binds strongly with Ag(I)/Ag(0) to allow the complete removal of Ag, leaving behind an organosol of hollow or cage-bell structured materials. The obtained materials have been proven to be especially relevant to catalysis. For example, cage-bell structured Pt-Ru nanoparticles displays outstanding methanol tolerance for the cathode reaction of direct methanol fuel cells as a result of the differential diffusion of methanol and oxygen in the cage-bell structure.

Recently, graphene is highly attractive for numerous applications. We found that interface tailoring is an effective approach towards high performance graphene/Si schottky-barrier solar cells. Inserting a thin graphene oxide (GO) interfacial layer can improve the efficiency of graphene/silicon solar cells by > 100%. The role of the GO layer is systematically investigated by varying GO film annealing temperature and thickness. It is found that it should be regarded as a p-doped thin layer. The effects of GO film thickness on device response are also studied and there exists an optimal thickness for device performance. A record 12.3% power conversion efficiency is achieved by performance optimization.

2. A series of new environmental materials have been developed and exhibited wide application potentials in industry

The high efficiency, fast, and harmless antibacterial materials are highly desired in the scientific and industrial fields. In recent years, our efforts have been deepened into the defect-controlling chemistry in tailoring the antibacterial activity of bulk nanostructured materials. MgO-based antibacterial nanomaterials were investigated and well developed. The key progresses have been made in the tunable antibacterial properties on the basis of the defect engineering of MgO nanocrystals, and pilot-scale manufacturing platform of MgO nanocrystals has been set up. NOx emission cause serious damage to both human health and environmental safety. One strategy is to develop new
selective catalytic reduction catalysts with good low temperature catalytic ability (e.g. 150 °C). We prepared a series of binary oxide of CrO\(_x\)/CeO\(_2\). The as-made materials were surprisingly effective in catalyzing reduction reaction of NO\(_x\) by NH\(_3\) at 150 °C in the presence of CO, which made it a very promising material to eliminate NO\(_x\) in low temperature waste gas. The research results have been confirmed in a pilot application in iron making process.

Volatile organic compounds (VOCs) emitted from industrial process and fossil fuels' combustion can cause many environmental problems, such as ozone generation, photochemical smog. In our research, three advances have been made on improving the catalytic activities of nanomaterials: (1) Hierarchical nanostructure manganese oxides were fabricated and used for catalytic removal of VOCs. The novel materials exhibit high surface area and well-developed porous structure which are favourable for catalytic reaction, (2) hydrothermal and flame spray method were applied to prepare Mn-Ce mixed oxides and the best ratio of Ce/Mn has been established. It is found that the strong synergistic interaction between Ce and Mn formed during the synthesis is responsible for its promoted activity (Fig. 2), (3) co-nanocasting approach was developed for synthesis of Cu-Mn mixed oxides. The synergistic effect was promoted because of the confinement effect in nanoscale, and the sintering of the particles is restricted, the obtained materials have high surface area and special nanostructure. The catalytic activities for removal of benzene were enhanced significantly.

The fast determination of VOCs will facilitate air quality assessment. Compared with the conventional complicated procedures using instruments, metal oxide semiconductor (MOS) gas sensors provide the real-time detection, fast response. We synthesized ZnO, In\(_2\)O\(_3\), Fe\(_2\)O\(_3\) nanomaterials with different structures for formaldehyde and benzene sensor. The strategies include assembling hierarchical nano/micro structures from nanoparticles and nanorods and tailoring different crystallography structures such as crystal defects, exposed reactive planes with specific orientations (Fig. 3). With the help of advanced technology such as plasma enhanced chemical vapor deposition, templating method and hydro/solvothermal synthesis, VOCs sensors with extremely high sensitivity and fast response/recovery time are fabricated with series of articles published. Specifically, the CdO activated Mn-doped ZnO nanorods hold the record for formaldehyde gas sensor with sensitivity of 25/ppm and response/recovery time within 5 min below 300°C. These results show the potential in MOS gas sensors in fast monitoring and treating the VOCs pollutants.

3. The developed composite structured materials advanced the domestic engineering application at high temperatures

Yttria-stabilized zirconia (YSZ) has excellent thermal and mechanical properties, making it one of the most suitable materials for thermal barrier coatings. We have successfully prepared pyrochlore-type La\(_2\)Zr\(_2\)O\(_7\) particles by molten
salts method, and nano-structured La–Zr oxide coatings were deposited by air plasma spraying with reconstituted nanostructured powders (Fig. 4). The microstructure, porosity and pore size distribution of the ceramic coatings were investigated, and thermophysical properties, such as thermal diffusivity and thermal conductivity of these novel coatings exhibited great improvements compared to traditional YSZ.

Using polymeric precursor infiltration and pyrolysis technique (PIP) to produce SiC matrix was pioneered by Yajima and others, which now is modified and becomes one of the major production methods of C/SiC. However, C/ZrC or C/ZrB₂ composite prepared by this method has not been reported except our recent work. C/C-ZrC-SiC composites based on PIP was developed in IPE for the first time, and then followed by others. These kinds of composite exhibits excellent mechanical properties with flexural strength above 150MPa and fracture toughness of 9MPa/m² (for a 2D perform), even higher bending strength of 325MPa using a 3D woven perform. Both of 2D and 3D composites exhibit excellent ablation resistance at temperatures around 2200–3000°C. Considering attractive merits of ZrB₂ based materials, extensive studies have also been performed in our team to synthesize a series of novel polymeric precursors of ZrB₂/HfB₂ other than ZrC/HfC precursors. With these precursors it is possible to produce a three phase matrix of ZrB₂-ZrC-SiC and their composite in a large amount and maybe at low cost. Because all these precursors can be dissolved into benzene and its compounds, ZrB₂-ZrC-SiC or HfB₂-HfC-SiC matrix can be formed simply by one-step infiltration and pyrolysis. Highly densificated composite can therefore be obtained by repeating this step as those for manufacturing of SiC matrix CMC. Major aims of our studies are to evaluate the possibility of producing the nanosize dispersed ZrB₂-ZrC-SiC matrix using these complex polymeric precursors, which are expected to exhibit improved oxidation and ablation resistance.

Selected Publications and Achievements

1. Room temperature catalytic oxidation of formaldehyde, antibacterial materials and their application in air purifier, The second class award of State Technological Invention Award, 2011
5. Photoluminescence investigation on the gas sensing property of ZnO nanorods prepared by plasma-enhanced CVD method, Sensors Actuators B, 2010, 145; 114-119
8. Accurate control of multishelled Co₃O₄ hollow microspheres as high-performance anode materials in lithium-ion batteries, Angew. Chem. Int. Ed. 2013, 52; 6417-6420
9. Catalytic removal of benzene over CeO₂-MnOₓ composite oxides prepared by hydrothermal method, Applied Catalysis B: Environmental, 2013, 138-139; 253-259
10. Scalable synthesis of interconnected porous silicon/carbon composites by the rochow reaction as high-performance anodes of lithium-ion batteries, Angew. Chem. Int. Ed. 2014, 53; 5165-5169
**Research Professors**

**Prof. Yunfa Chen (Team Leader),** born in 1965, received his Ph.D. from University of Louis-Pasteur Strasbourg I in France in 1993. He joined Institute of Process Engineering (IPE), CAS in 1994. He became a full professor in 1998 and now serves as the deputy director of IPE. He has published more than 200 peer reviewed papers, 1 co-authored monographs, and applied 60 patents with 30 granted.

**Affiliation**
Co-Editor, *J. Sol-gel Sci. & Tech.* (Springer)
Member, Chinese National Steering & Coordination Committee of Nanoscience and Nanotechnology
President, Chinese Society of Particuology
Member of the expert group for pollution control, National High Technology Research & Development Program (863), China
Member of Consulting Expert Committee, GEB, Chinese Securities Regulatory Commission.

**Research Interests**
Synthesis of nanoparticles; Nanostructured environmental materials and applied technology; Preparation of inorganic-organic nanocomposites; Gas sensor.

**Professor Weigang Zhang,** born in 1968, received his Ph.D. from Institute of Metal Research (IMR), CAS in 1998. After then, he studied and carried out research in the Institute of Chemical Technology (ICT) at University Karlsruhe Germany till 2004. He was engaged as a professor in IPE, CAS via “Hundred Talents Program” in 2004. He published more than 90 research papers and one book titled “Chemical Vapor Deposition”.

**Affiliation**
Director of the special ceramics branch of the Chinese Ceramic Society
Member of micro- and nano-scaled composite materials committee of the Chinese Society of Composite Materials
Member of the thermal spraying technology committee of China Surface Engineering Association
Counselor and evaluation expert of the State Commission of Science and Technology for National Defense Industry of the Ministry of Industry and Information
Expert of the technology committee of the Silicon Material Industry Innovative Strategy Union of Jiangsu.

**Research Interests**
Chemical vapor deposition of film and composites, Chemical reaction technology of dispersed micro scale materials; Thermal spray and functional coatings
Prof. Dan Wang, born in 1969, received his Ph.D. from Yamanashi University (Japan) in 2001. He was engaged as a professor in IPE, CAS via “Hundred Talent Program” in 2004 and got National Science Fund for Distinguished Young Scholars in 2013. He has published over 100 peer reviewed papers in SCI journals. As the corresponding author, he has published a series of papers in well-known international journals, such as Chem. Soc. Rev., Adv. Mater., Angew. Chem. Int. Ed., ACS Nano, Energy Environ. Sci. and J. Am. Chem. Soc...

Affiliation
Executive member of International Solvothermal & Hydrothermal Association
Council member and vice secretary general of the Chinese Society of Particuology
Advisory boards for Energy & Environmental Science, Advanced Materials Interface and Materials Research Express
Director of Foshan Gaoming (CAS) Center for Novel Materials
Fellow of the Royal Society of Chemistry.

Research Interests
Functional inorganic materials, Solar energy conversion & photocatalysis; Energy storage materials & secondary batteries, Gas sensor

Prof. Fangli Yuan, born in 1967, received his Ph.D. degree from Institute of Plasma Physics, CAS in 1996. After being a postdoctoral fellow in IPE, CAS (1996-1998), he joined IPE in 1998. He was a visiting research fellow in Korean Research Institute of Chemical Technology, Korean Institute of Geosience and Mineral Resources and Saitama University in 2003, 2007 and 2009. He has been a professor since 2010. He has published more than 60 peer reviewed papers, 2 co-authored monographs and held 8 patents.

Affiliation
Committee member of Plasma Science and Technology, The Chinese Society of Theoretical and Applied Mechanics
Committee member of Metallurgical Physical Chemistry, The Chinese Society for Metals
Editor board member of The Chinese Journal of Process Engineering.

Research Interests
Synthesis and application of functional powder using thermal plasma; Spherical powders, Powders applied in thermal conductive resin, Porous ceramics and composite materials

Prof. Yongping Zhu, born in 1965 received his Ph.D. degree in metallurgy from Beijing University of Science and Technology in 1995. He worked as a visiting research fellow in Kochi University and Research Institute of Innovative Technology for the Earth, Japan (2000-2003). He has been a professor of IPE since 2010. He has published more than 30 papers and held 8 patents.

Affiliation
Guest Professor of the Key Laboratory of Science and Technology on Scramjet.

Research Interests
Hydrothermal synthesis; Preparation and application of nano-micro materials; Plasma spray; Thermal protection coatings
Prof. Jun Yang, born in 1972, received his Ph.D. from National University of Singapore (with Professor Jim Yang LEE) in 2006. After postdoctoral research at Boston College and University of Toronto, he joined the Institute of Bioengineering and Nanotechnology, Singapore in 2007. He was engaged as a professor in IPE, CAS via “Hundred Talent Program” in 2010. He has published more than 35 peer reviewed papers.

Affiliation
Member of American Chemical Society and American Nano Society.

Research Interests
Applied catalysis, Nanocomposites for energy conversion, Synthesis and application of novel nanocrystalline materials, Separation techniques

Prof. Yu Wang, born in 1978, received his Ph.D. degree in Institute of Chemistry, CAS in 2008. He joined as a research fellow chemistry department, National University of Singapore since 2008. He was engaged as a professor in IPE, CAS via “Hundred Talent Program” in 2012. To date, He has authored over 50 peer-reviewed journal articles and held over 30 patents.

Research Interests
Manufacturing technology of two-dimensional materials, Solar energy-transfer process, Metal anti-corrosion science, Thermal energy dissipation technology.

Prof. Ning Han, born in 1982, received his Ph. D. degree from IPE, CAS in 2010. He was a postdoctoral fellow in Department of Physics and Materials Science in City University of Hong Kong in 2010-2014, and was engaged as a professor in IPE, CAS via “Hundred Talent Program” in 2014. He has published more than 40 peer reviewed journal articles, 2 chapters in monographs, and held one Chinese patent.

Research Interests
Preparation of metal oxide semiconductors, III-V compound semiconductors and applications in gas sensors, Electronics and optoelectronics

Prof. Xiaofeng Wu, born in 1976, received his Ph. D. degree in IPE, CAS in 2008. Then he conducted his postdoctoral research in National Chonbuk University of Korea in 2008. He returned to IPE in 2009, and was promoted to professor in 2014. He has published 45 peer reviewed papers, and applied 19 patents with 6 granted.

Research Interests
Controllable synthesis of nanomaterials and their technical applications