

RESEARCH RESULTS

Recent Research Progress in Inorganic Chemistry in China

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Great processes in the basic research of inorganic chemistry have been achieved in recent years as a result of persisting supports by the National Natural Science Foundation of China (NSFC). Many brilliant young experts have showed their talents and gradually established their reputation in the relative fields. On the one hand, they have utilized their scientific productions into practice or market successfully, on the other hand, considerable important papers have been published in international famous journals comparing with the beginning of the 1990s, such as *Science*, *Accounts of Chemical Research*, *Angew. Chem. Int. Ed.* and *J. Am. Chem. Soc.* For example, mainland scholars published 30 papers in *Angew. Chem. Int. Ed.* in the last two years (2000 & 2001) and 16 papers were generated from inorganic chemists, which accounted for 53%. They also published 53 papers in *J. Am. Chem. Soc.* in the last ten years (1991-2001) among which 11 papers written by inorganic chemists, which accounted for 20% although inorganic chemistry is a relatively small branch of chemistry in China. We are fully convicted that in the near future Chinese chemistry will keep on making breakthrough on basic research, starting new field of research and owning some original research works which are internationally leading. Here some aspects of achievements by six China leading groups of inorganic chemistry in recent years are introduced in this paper.

(1) Together with his group, Professor Qian Yitai from University of Science and Technology of China, developed the method of solvothermal synthesis and obtained a series of non-oxide nanomaterials. Compared to the hydrothermal preparation, they used non-aqueous solvents instead of water as the reaction medium in their reactions. By designing appropriate inorganic reactions

in sealed reaction systems, novel materials, especially those with metastable phases and special nanostructures have been synthesized under mild conditions.

Qian Yitai, Xie Yi and their co-workers prepared nanocrystalline GaN in the benzene-thermal system at 280°C through the metathesis reaction of GaCl₃ and Li₃N. The ultrahigh-pressure rock-salt GaN metastable phase, which previously existed at 37 GPa, was obtained at ambient condition. This work was published in *Science*. The referee's comments were that "This interesting paper reports two fairly exciting findings: (1) a solvothermal synthesis (in benzene) of crystalline GaN at a very low temperature, and (2) the observation of rock-salt cubic GaN, which is apparently a kinetic (metastable) product previously observed only at very high pressure". Use the same method, nanocrystalline InAs was synthesized via the co-reduction of InCl₃ and AsCl₃ by using metal zinc at 160°C in toluene, or through reacting InCl₃, elemental arsenic with KBH₄ at 180°C in ethylenediamine. These works were published in *J. Am. Chem. Soc.* and *Chem. Mater.* respectively.

Qian Yitai, Li Yadong and the co-workers synthesized diamond crystallites through a Wurtz-like reaction in reducing CCl₄ by sodium in an autoclave at 700°C. This work was also reported in *Science*. The *C&EN* appraised it as "straw into gold". Similarly, multiwalled carbon nanotubes were synthesized in the solvothermal catalytic reduction of C₆Cl₆ and C₂Cl₄ with metallic potassium at 350 and 200°C respectively. The papers were published in *J. Am. Chem. Soc.* and *J. Phys. Chem.* SiC nanowires were prepared through a solvothermal co-reduction route by reacting SiCl₄ and CCl₄ with sodium at 400°C, and published in *Appl. Phys. Lett.* The referee commended that "this paper reports a new and very interesting synthesis method", "it should stimulate further work in this area".

Qian Yitai and the co-workers also synthesized CdE (E = S, Se, Te) nanorods at temperature below

200°C using ethylenediamine as reaction medium. This work was reported in *Chem. Mater.* The paper won the ISI "Classic Citation Award" for high-impact papers in 1981-1998. They also reported in *Adv. Mater.* that 100 μm \times 40 nm CdS nanowires were synthesized in ethylenediamine at 170°C through the polymer-controlled growth routes. Recently they reported in *Angew. Chem.* a general synthesis of chalcogenide nanorods by using a monodentate ligand n-butylamine as a shape controller. They also made efforts in room-temperature synthesis in organic liquid phases. Semiconductor chalcogenide nanomaterials, such as one-dimensional SnSe and PbSe were prepared at room temperature and published in *J. Am. Chem. Soc.* and *Adv. Mater.*

(2) The research group led by Professors Xu Ruren and Feng Shouhua from Jilin University reported a successful hydrothermal synthesis for an inorganic-organic nano-composite material with inorganic helix chains, $\text{M}(4,4'\text{-bipy})_2(\text{VO}_2)_2(\text{HPO}_4)_4$ ($\text{M}=\text{Co}, \text{Ni}$) from much simple reactants. In these two compounds, tetrahedral PO_4 and trigonal bipyramidal VO_4N are alternatively arrayed by corner-sharing oxygen atoms, forming novel inorganic helical chains of $[(\text{VO}_2)(\text{HPO}_4)]_x$. This structure contains both left-handed and right-handed helical chains and these helical chains are alternatively connected by $\text{M}(4,4'\text{-bipy})_2$ fragments to build up a three dimensional open framework. The formation of the helix in this structure partially originates from the coordination force of two rigid bipyridine molecules in $\text{M}(4,4'\text{-bipy})_2$ fragments with the vanadium atoms from adjacent helical chains. The paper entitled "Inorganic-organic hybrid materials constructed from $[(\text{VO}_2)(\text{HPO}_4)]_x$ helical chains and 2^+ ($\text{M}=\text{Co}, \text{Ni}$) fragments" was published in *Angew. Chem. Int. Ed.*, 39 (13): 2325-2327, 2000.

Based on their systematic and creative research in the frontiers of inorganic hydrothermal synthesis internationally. Professors Feng Shouhua and Xu Ruren from the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry at Jilin University were invited by the American Chemical Society to publish their review article entitled "New materials in hydrothermal synthesis" in *Acc. Chem. Res.*, 34(3): 239-247, 2001. In this review, they systematically summarized seven aspects of research achievements in hydrothermal synthesis chemistry of new materials, including microporous crystals, ionic conductors, complex oxides and fluorides, low dimensional aluminophosphates, inor-

ganic-organic hybrid compounds, specially condensed solids, and materials, life, environment and social issues related to hydrothermal chemistry.

(3) Homochiral metal-organic coordination polymers (MOCP) have found a wide of applications in non-linear optical materials, asymmetric catalysis and enantioseparation. So far, the attempts to resolve enantiomers using zeolite beta or zeolite analogues have not proved successful. The enantiopure or homochiral zeolite analogues capable of resolving racemic mixtures of organic molecules still remain extremely unexplored and a great challenge. Now, Xiong Rengen and You Xiaozeng et al., chemistry professors at the Nanjing University, reported that their design strategy—a multichiral centers ligand used as building block reacts with $\text{Cd}(\text{OH})_2$ to assemble the first homochiral 3D MOCP which can efficiently and selectively include (S)-2-butanol or (S)-2-methyl-1-butanol, with an approximately estimated ee value of 98% (*Angew. Chem. Int. Ed.* 2001, 40: 4422, and this paper was selected as a hot paper). The successful design of this kind chiral ligand bears the following merits: a carboxylate binding group that makes the ligand anionic and the framework neutral. This ensures that intraframework voids are not occupied by counterions; A mix of hydrophobic (R-, Ar-etc.) and hydrophilic groups ($-\text{NR}_2$, $-\text{OH}$ etc.) that induce the inclusion of a variety of guests; A pyridyl-type group that is able to satisfactorily complete the coordination sphere of the metal center in the generation of a 3D diamondoid coordination polymer. One candidate that fulfils these requirements is quinine, 6'-methoxyl-(8S,9R)-cinchonane-9-ol-3-carboxylic acid.

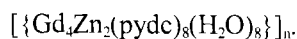
(4) Professors Hong Maochun and Wu Xintao from Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, have published more than 30 papers about nano-materials and inorganic polymers in the high-level international journals, such as *Angew. Chem. Int. Ed.*, *J. Am. Chem. Soc.*, *Chemistry J. Eur.*, *Chem. Comm.*, and *Inorg. Chem.*. Chemists in China and other countries have interested their research works.

Professor Hong and Wu have explored a way to design and prepare novel cages with nanometer-size cavities by the self-assembly reactions of transition metal salts and organic ligands with multi-functions. They designed a multidentate ligand, 2,4,6-tri[(4-pyridyl)sulfanylmethyl]-1,3,5-triazine (tpst), which possesses exo-tridentate bonding sites. By using metal ions with

square planar or octahedral coordination geometry, such as Ni (II), Pd (II), and Pt (II) to link the three pyridyl groups of the tpst ligand. A stable neutral nanometer-sized metallocupramolecular cube cage $[\text{Ni}_6(\text{tpst})_8\text{Cl}_2]$ with O_h symmetry was isolated. The volume of the inner cavity was estimated to be ca. 1000 \AA^3 , implying that the complex can host many solvent molecules. Furthermore, the cage opens twelve windows from the two-fold axis directions of the cube edges. Monitored by ^1H NMR spectra, the solvent-exchange from the cage illustrates that the DMF molecules come out from the cage. (*J. Am. Chem. Soc.* 2000, 122: 4819—4820).

Recently they have studied the syntheses, structures and properties of coordination polymers with new type of metal-organic nano-porous zeolite structures by using transition metal ions and organic bridging ligands. They have isolated a single stranded 1D coordination polymer $[\text{Ag}_7(\text{tpst})_4(\text{ClO}_4)_2(\text{NO}_3)_3]_n$ containing nanometer-sized tubes. The crystallographic analysis of the complex revealed that its structure is a chain polymer containing a basic nanometer-sized tube unit $[\text{Ag}_7(\text{tpst})_4]$. Every ligand bonds to three silver (I) centers by the N atoms of the three pyridyl groups of the tpst ligand and each silver (I) is in turn coordinated by the pyridyl group of the other tpst ligand to form a $[\text{Ag}_3(\text{tpst})_2]$ nanometer-sized cycle. Two such cycles are linked by Ag-N and Ag-S bonds forming the basic nanometer-sized tube unit, accommodating two DMF molecules and two perchlorate anions.

They have prepared a coordination polymer with Zn_4 cluster unit $[\{\text{Zn}_4(\text{OH})_2(\text{bdc})_3(\text{dmsO})_4\} \cdot 2\text{H}_2\text{O}]_n$ (bdc =1,4-benzenedicarboxylate) has been prepared from the self-assembly reaction of $\text{Zn}(\text{ClO}_4)_2$, NaOMe and H_2bdc in dmsO. X-ray diffraction analyses show that the polymer exhibits a zeolite structure with large-pore of ca $10.22 \times 12.29 \text{ \AA}$. By employing hydrothermal reaction method, a series of lanthanide (III)-transition metal coordination polymers with fascinating structures and unusual properties were successfully isolated in their groups. The hydrothermal reactions of lanthanide oxide, transition metal oxide or metal salt and organic ligand resulted in the formation of polymeric complexes. From the hydrothermal reactions of lanthanide oxide, pyridine-2, 5-dicarboxylic acid (H_2pydc), and copper (II) oxide or copper (II) salts, $[\text{Gd}_2\text{Ag}_2(\text{pydc})_4(\text{H}_2\text{O})_4]_n$, $[\{\text{Gd}_2\text{Cu}_3(\text{pydc})_6(\text{H}_2\text{O})_{12}\} \cdot 4\text{H}_2\text{O}]_n$, $[\{\text{Gd}_4\text{Cu}_2(\text{pydc})_8(\text{H}_2\text{O})_{12}\} \cdot 4\text{H}_2\text{O}]_n$, $[\{\text{Gd}_2\text{Zn}_3(\text{pydc})_6(\text{H}_2\text{O})_{12}\} \cdot 4\text{H}_2\text{O}]_n$,



Professor Hong and Wu are interested in the frontier research field of nanoscience and technology, especially in the nano-devices, and have explored a pathway to design and prepare coordination polymers with nano-wire and lamellar structure. Based on organo-sulfur ligands, they have reported a series of polymer $[\text{Ag}(\text{SPy})]_n$ with nano-wire and lamellar structure. From the results of structural characterizations, they have studied the assembly reaction roles, steric structures, electron structures as well as physical and chemical properties, and exploited the relationship between the structure and properties.

The research group lead by Prof. Gao Song at Peking University conducted excellent work in the field of magnetic molecular materials.

Magnetic field dependent unusual magnetic relaxation. Rings of 24 atoms form part of the two-dimensional structure of the novel compounds $[\text{Nd}(\text{M}(\text{bpym})(\text{H}_2\text{O})_4(\text{CN})_6)_3\text{H}_2\text{O}]$ ($\text{M}=\text{Fe}, \text{Co}$; bpym =2,2'-bipyrimidine), which were obtained by the slow diffusion of $\text{K}_3[\text{Fe}(\text{CN})_6]$ or $\text{K}_3[\text{Co}(\text{CN})_6]$ and bpym with $\text{Nd}(\text{NO}_3)_3$ in a 1 : 1 : 1 molar ratio in aqueous solution. These compounds are the first two-dimensional cyano-bridged species containing lanthanide and transition metal centers. The comparison of the variable - temperature magnetic behaviors between the two compounds suggests ferromagnetic interactions between the Nd^{3+} and Fe^{3+} ions. No long-range ordering was observed down to 2 K, and the ac susceptibility of the compounds show normal paramagnetic behavior in zero applied dc field. However, they display a slow magnetic relaxation when applied dc field (1-10 kOe) is present, which is strongly frequency and field dependent, and qualitatively resembles those in single-molecule magnets. The behavior was attributed to the geometrically frustration tentatively. The unusual magnetic relaxation phenomenon was also observed in series magnetic molecular systems with extended structures and weak interaction. The results were partly reported in *Angew. Chem. Int. Ed.* (2001, 40: 434), *Chem. Commun.* (2000, 1685), *Phys. Rev. B* (2001, 63: 054431), and reviewed by *Chem. Rev.* (2002, 102: 2369. Rare Earth Special Issue).

Superclusters based on sub-units of metal clusters. An extended network, $\{[\text{Dy}_4(\text{OH})_4(\text{asp})_3(\text{H}_2\text{O})_8](\text{ClO}_4)_2 \cdot 10\text{H}_2\text{O}\}_n$, having three-dimensional channels with a space of 11.78 \AA has been prepared by mixing $\text{Dy}(\text{ClO}_4)_3$ and L-aspartic acid in aqueous solution, and subse-

quently adjusting the pH values to about 6.5 using aqueous NaOH solution. This open-framework compound is representative for the assembly of discrete lanthanide cubanes into supercubanes. (*Angew. Chem. Int. Ed.*, 39 (20): 3644, 2000).

Cyano-bridged 3-D ferromagnets. Using stable new kinds of cyano complexes of Ruthenium (III), trans-Ph₄P[Ru^{III}(acac)₂(CN)₂] (Hacac=acetylacetonate), as building blocks, a novel cyano-bridged Mn^{II}Ru^{III} polymer {Mn[Ru(acac)₂(CN)₂]}_n was synthesized, which has a diamond-like structure and exhibits ferromagnetic ordering below *T*_C=3.6 K. (*Angew. Chem. Int. Ed.*, 40 (16): 3031, 2001). A 3D coordination polymer {[Cu(EtOH)₂][Cu(en)]₂[Cr(CN)₆]}_n was obtained by slow diffusion of Cu(en)(H₂O)₂SO₄ in H₂O into K₃[Cr(CN)₆] in a H₂O-EtOH (2 : 1) mixture. The 3D structure is novel, and a long-range ferromagnetic ordering below 57 K was observed. The present complex is the first structurally characterized Cu(II)-containing Prussian blue analogue with spontaneous magnetization. (*J. Am. Chem. Soc.*, 123: 11809, 2001).

(5) Professor Li Yadong and the co-workers from Tsinghua University have made prominent progress in the field of preparation and assembly of novel one-dimension nano-structures. A novel single-crystal multi-well metal nano-tubes, converted from metal bismuth with the characteristic of quasi-layer structure, were observed for the first time by Li's group, and the corresponding outcome was published in *J. Am. Chem. Soc.* (123 (40): 9904—9905, 2001). The observation of bismuth nano-tube, which was the first instance of converting metal into single-crystal nano-tubes, providing new object and task for the mechanism and application research of the inorganic nano-tubes.

With the artificial organic-inorganic layer-structured as precursors, they also successfully synthesized metal tungsten nano-wires and high-quality WS₂ nano-tubes. After investigating the layer-rolling mechanism through the analysis of small-angle X-ray Diffraction and HRTEM (high-resolution transmission electronic microscope) images, they carried out a novel method and idea for the synthesis of one-dimension nano-wires and nano-tubes. The corresponding outcomes of their research were published in *Angew. Chem. Int. Ed.* (41 (2):333—335, 2002) and *J. Am. Chem. Soc.* (124 (7): 1411—1416, 2002).

Much attention is paid to one-dimension oxide

nano-wires, nano-belts and nano-tubes for their promising and wide foreground in application. High-quality α-, β-MnO₂ nano-wires and nano-rods were synthesized under mild conditions by Li's group via liquid phase reaction, and meanwhile controlling the phase of products was achieved. In addition, single-crystal MoO₃ nano-belts and titanate nano-tubes were synthesized by them as well. Part of the results of their research were published in journals such as *J. Am. Chem. Soc.* (124 (12): 2880—2881, 2002), etc.

The above results demonstrated that the most outstanding achievements in inorganic chemistry in China in recent years are on the research of solid materials chemistry and coordination chemistry, which accords with the developing trend of international chemistry. However, research on bioinorganic chemistry and radiochemistry lags behind relatively. For that reason, a "Symposium on Developing Stratagem of Bioinorganic Chemistry" was held in Shenzhen in March 5th to 7th, 2002, which was supported both by Bureau of Policy and Department of Chemical Sciences of NSFC and Department of Chemistry of CAS. In this conference, the development progress of domestic and overseas bioinorganic chemistry and how to promote the powerful drive and trend of life science and chemistry interact and reciprocally were analyzed. Bioinorganic chemistry was started in 1980s in China and at that time trailed international level by about 10 years. In about 10 years' time, bioinorganic chemistry in China took three steps forward through the great efforts of bioinorganic chemists and the constant supports of NSFC. These were enlarging research subjects from biologic little-molecule ligand to biologic big-molecule; establishing research system from separated biologic big-molecule to biologic system and developing research on the level of cell. We have already established relatively research areas on interaction between metallic ligand and biologic big-molecule, structure and function of metallic protein, chemical basis on biologic effect of metallic ions, inorganic pharmic chemistry and biologic mineralization. The researcher teams are become younger, too. However, the general standard of bioinorganic chemistry in China has a widening gap with foreign research. This could be due to less research funds and long research periods and the lack of outstanding young experts.