

# A Highly Efficient Route for Selective Phenol Hydrogenation to Cyclohexanone

Science reported the results of selective phenol hydrogenation to cyclohexanone on November 27, 2009 (Science 2009, 326, 1250-1252) obtained by researchers at the Institute of Chemistry, Chinese Academy of Sciences.

Cyclohexanone is a key raw material in the synthesis of many useful chemical intermediates, such as caprolactam for nylon 6 and adipic acid for nylon 66. The phenol hydrogenation is one of the main routes for producing cyclohexanone. However, the attainment of high selectivity at elevated conversion with a satisfactory rate is a great challenge, because the cyclohexanone product can be further hydrogenated to cyclohexanol under the reaction conditions.

Researchers at the Institute found that common commercial palladium catalysts (supported on carbon, alumina, or NaY zeolite) and a Lewis acid such as aluminum chloride could synergistically promote this reaction, and a preliminary mechanism was proposed on the basis of kinetic and spectroscopic studies. A Lewis acid itself could not catalyze the reaction, but it could make the benzene ring of phenol more active. At the same time, acid-base interaction between the Lewis acid and cyclohexanone inhibits further hydrogenation to cyclohexanol. The conversion and selectivity could approach 100% simultaneously under mild conditions, and therefore all of the phenol could be converted into the product and the separation process was simple. Further study demonstrated that the reaction conducted in compressed CO<sub>2</sub> was more efficient and environmentally benign, and the reaction efficiency could be tuned by controlling the phase behavior of the reaction system.

The work was financially supported by the National Science Foundation of China and some other organizations in China.

# A Novel Mechanism Employed by KSHV to Maintain the Latent Infection was Revealed

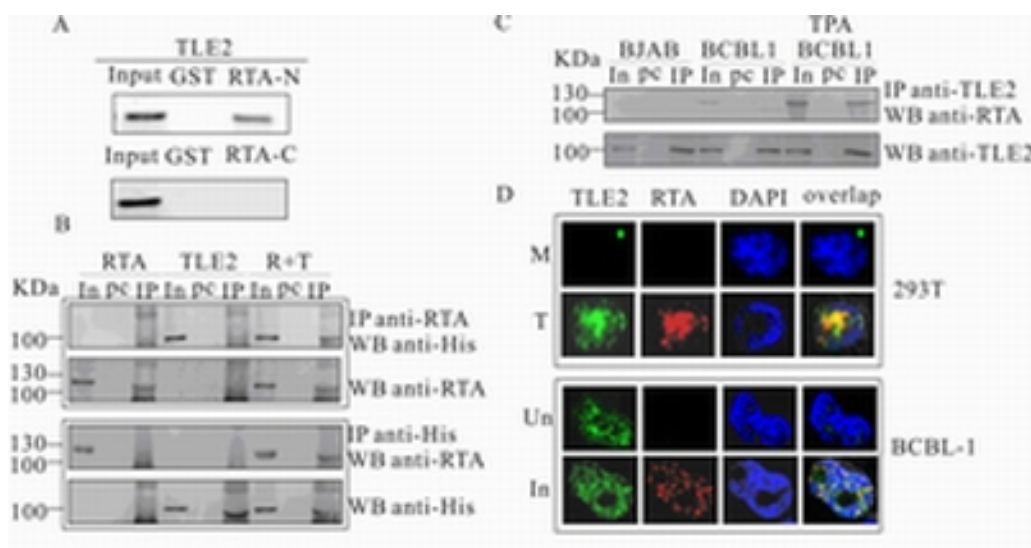
Kaposi's sarcoma (KS) is one of the most common malignant diseases among AIDS patients. KSHV which is the pathologic agent of KS could establish latent infection in host cells and could not be eradicated. The sero-prevalence of KSHV in general population is about 5%. It is important to reveal the mechanism of latent infection maintenance.

On November, 2009, the top virology journal "Journal of Virology" has published online research progress on cellular factors involved in KSHV latent infection. This research project was conducted by Ph.D candidate He Zhiheng, under supervision of Dr. Ke Lan, the Principal Investigator of Tumor Virology Unit of Institute Pasteur of Shanghai, Shanghai Institutes for Biological Sciences, Chinese Academy of Sciences.

Replication and transcription activator (RTA) encoded by ORF50 of Kaposi's sarcoma-associated herpesvirus (KSHV) is essential and sufficient to initiate lytic reactivation. In this study, researchers identified transducin-like enhancer of split 2 (TLE2) as a novel RTA binding protein by using yeast two hybrid screening of a human spleen cDNA library. This interaction recruited TLE2 to RTA bound to its recognition sites on DNA, and inhibited the induction of lytic replication and virion production driven by RTA. RBP-J $\kappa$  has been shown previously to bind to RTA, and this binding can be subject to competition by TLE2. In addition, TLE2 can form a complex with RTA to access the cognate DNA sequence of RRE (RTA responsive element) at different promoters.

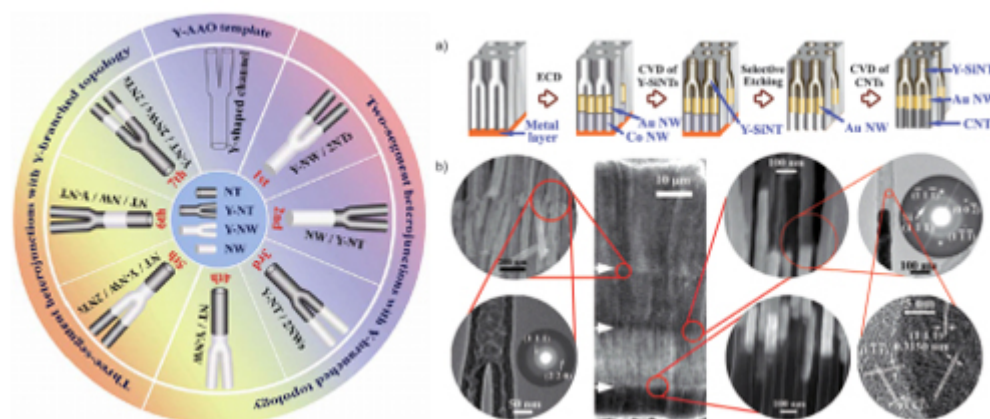
In this study, researchers identified a new RTA binding protein, TLE2, and demonstrated that TLE2 inhibited replication and transactivation mediated by RTA. This provides another potentially important mechanism for maintenance of KSHV viral latency through interaction with a host protein.

This project was supported by National Natural Science Foundation of China, the "100 Talent Program" of CAS and Sanofi-Aventis-SIBS Scholarship (SA-SIBS SCHOLARSHIP) Program.



**Figure.** GST binding assay, co-immunoprecipitation and immunofluorescence indicate that TLE2 interacts with RTA in vitro and in vivo

# Breakthrough in the Synthesis of Interconnected NW/NT and NT/NW/NT Heterojunctions with Branched Topology



*Fig. (Left) Schematics of the NT/NW and NT/NW/NT hybrid architectures with Y-branched topology. (Right) One of the heterostructures: Y-SiNT/2AuNWs/2CNTs architecture. (a) The fabrication procedure; (b) structural characterization.*

Recent researches on one-dimensional (1D) nanostructures show that segmented hybrid structures of nanotube (NT) and nanowire (NW) could provide novel building blocks for fabricating nanoscale electronics and photonics devices, and have a wide variety of other applications in barcodes, optical readout, biology, catalysis, self-assembly and magnetic manipulation. A wide variety of segmented nanoscale heterojunctions, such as segmented NWs of metal/polymer, semiconductor/semiconductor, metal/semiconductor and metal/metal, hybrid NTs of metal/metal, carbon NT/NW, and tree-like nano-heterojunctions, etc., have been reported. However, all these studies have exhibited limited control over the geometry and complexity of 1D nanoscale heterojunctions that can be ultimately essential for building nanodevices. It has been a very challenging and significant task to develop a generic approach for precisely controlled fabrication of high yield interconnected two-segment nanotube/nanowire (NT/NW) and three-segment nanotube/nanowire/nanotube (NT/NW/NT) hybrid architectures with branched topology.

By using Y-shaped nanochannels of anodic aluminum oxide (Y-AAO) template, breakthrough on NT/NW/NT heterojunctions with branched topology has been achieved in Guowen Meng's group at the Institute of Solid State Physics, Chinese Academy of Sciences.

## Two-segment NT/NW heterostructures with Y-branched topology

By simply sequential electrodepositing metal NW (MNW) and chemical vapor depositing (CVD) Carbon NT (CNT) in different portions of Y-shaped nanochannels of anodic aluminum oxide (Y-AAO) template, the following four types of Y-branched two-segment CNT/MNW heterojunctions with different functionalities have been achieved: (i) Y-MNW/2CNTs, i.e. one Y-shaped MNW connects with two CNTs in the branches of the Y-shaped construct; (ii) MNW/Y-CNT, i.e. one MNW connects with a Y-shaped CNT; (iii) Y-CNT/2MNWs, i.e. one Y-shaped CNT connects with two MNWs in the Y-branches; (iv) CNT/Y-MNW, i.e. one CNT connects with a Y-shaped MNW.

### **Three-segment NT/NW/NT heterostructures with Y-branched topology**

Based on the above four types of two-segment CNT/MNW heterojunctions with Y-shaped topology, researchers tried to insert one more segment of NT on the other end of the NWs, to achieve complex three-segment NT/NW/NT hybrid nanostructures with Y-shaped topology. For this purpose, they utilized a combinatorial sequence of electrodeposition of MNWs, selectively etching part of the deposited NWs, and CVD growth of CNTs on both ends of the NWs inside the Y-shaped nanochannels. The resultant three types of three-segment CNT/NW/CNT heterojunctions with distinctive functionalities are as the following: (i) CNT/Y-MNW/2CNTs, i.e. one CNT connects with a Y-shaped MNW, and then with two CNTs in the Y branches; (ii) CNT/MNW/Y-CNT, i.e. one CNT connects with a MNW, and then with a Y-shaped CNT in sequence; (iii) Y-CNT/2MNWs/2CNTs, i.e. one Y-shaped CNT connects with two MNWs in the branches, and then with another two CNTs in the branches in sequence.

### **About the NW segment materials**

The NW segment in the above seven types of hybrid nanostructures with Y-shaped topology can consist of not only metals of magnetic (e.g. nickel) and nonmagnetic (e.g. aurum, copper), but also a wide range of other materials that can be achieved via electrodeposition, selectively etched and are stable in the growth of NTs as well. They have already constructed compound semiconductor CdS, magnetic alloys of CoPt and NiCo, as the NW segment in the hybrid structures. Even very stable noble metals (e.g. Au, very difficulty to etch) can also be built as the NW segments in the middle of the NT/NW/NT hybrid architectures via additional electrodepositing a sacrificial segment of metals (e.g. Co, easy to etch) before electrodepositing the desired noble metal Au NW segment in the fabrication process. Additionally, the NW segment itself in the hybrid nanostructures could also consist of two or more sub-segments of NWs consisting of different materials with distinct properties. For example, they have constructed two sub-nanowires consisting of magnetic metal Ni and nonmagnetic metal Ag as a whole NW segment in the hybrid structures of Y-CNT/2AgNWs/2NiNWs /2CNTs.

### **About the NT segment materials**

The NT segments in the hybrid architectures can consist of not only Carbon NTs, but also other materials that could be built into NTs inside the nanochannels of AAO via other techniques. For example, they have successfully replaced CNTs with semiconducting silicon NTs (SiNTs) and insulating SiO<sub>2</sub> NTs in the NT/NW and NT/NW/NT hybrid architectures. Additionally, the NTs on the two ends of the three-segment NT/NW/NT hybrid structures with Y-branched topology not only can consist of the same material of carbon, silicon and silica, but also can be constructed with different materials with distinct properties. They have built a hybrid architecture of Y-SiNT/2AuNWs/2CNTs, with one end consisting of a Y-shaped NT of silicon (Y-SiNT) and the other of two CNTs.

### **Heterostructures with more complex topology**

The Y-branched topology can be extended to multi-generation Y-branches and multi-branches from one stem if AAO template with corresponding shaped channels is used, as an example, they have built a three-segment hybrid nanostructure with three-branches: three-branched-CNT/3NiNWs/3CNTs, i.e. one three-branched-CNT connects with three NiNWs in the branches and then connects with three CNTs in the branches in sequence.

The above breakthrough has been published in *Angew. Chem. Int. Ed.* 48 (39), 7166-7170 (2009), and has been highlighted in the frontispiece at the beginning of the journal. Additionally, the breakthrough has been featured on *Nature China* after being published.

This breakthrough work was supported by the National Science Fund for Distinguished Young Scholars (Grant No. 50525207), National Basic Research Program of China (Grant No. 2007CB936601) and CAS's talent program.

# **GABA Transporter-1 Activity Modulates Hippocampal Theta Oscillation and Theta Burst Stimulation-Induced Long-Term Potentiation**

On Dec 16, 2009, the Journal of Neuroscience published a full research article from Institute of Neuroscience, SIBS, CAS entitled "GABA Transporter-1 Activity Modulates Hippocampal Theta Oscillation and Theta Burst Stimulation-Induced Long-Term Potentiation". This work was carried out by postdoctoral fellow Dr. Neng Gong from the laboratory of Dr. Tian-Le Xu at ION, and collaborators.

The network oscillation and synaptic plasticity are known to be regulated by GABAergic inhibition, but how they are affected by changes in the GABA transporter activity remains unclear. Here we show that in the CA1 region of mouse hippocampus, pharmacological blockade or genetic deletion of GABA transporter-1 (GAT1) specifically impaired long-term potentiation (LTP) induced by theta burst stimulation (TBS), but had no effect on LTP induced by high-frequency stimulation (HFS) or long-term depression (LTD) induced by low-frequency stimulation (LFS). The extent of LTP impairment depended on the precise burst frequency, with significant impairment at 3 - 7 Hz that correlated with the time course of elevated GABAergic inhibition caused by GAT1 disruption. Furthermore, *in vivo* electrophysiological recordings showed that GAT1 gene deletion reduced the frequency of hippocampal theta oscillation. Moreover, behavioral studies showed that GAT1 knockout mice also exhibited impaired hippocampus-dependent learning and memory. Together, these results have highlighted the important link between GABAergic inhibition and hippocampal theta oscillation, both of which are critical for synaptic plasticity and learning behaviors.

This study was supported by grants from the National Natural Science Foundation of China (Nos. 30621062 and 30830035), the National Basic Research Program of China (No. 2006CB500803), and the Chinese Academy of Sciences (KSCX2-YW-R-35 and KSCX2-YW-R-100) to Dr. Tian-Le Xu. Dr. Neng Gong was supported by the China Postdoctoral Science Foundation, the Shanghai Postdoctoral Scientific Program and the Postdoctoral Research Program of Shanghai Institutes for Biological Sciences, Chinese Academy of Sciences.

## **Meta-analysis of Vitamin D, Calcium and the Prevention of Breast Cancer**

The journal *Breast Cancer Research and Treatment*, published online on October 23, 2009, reported a recent finding that vitamin D and calcium intake can prevent breast cancer. By a meta-analysis, PhD candidate Peizhan Chen and his supervising professor, Hui Wang, from the INS found that high intake of vitamin D and calcium could lead to significant decrease in breast cancer risk.

The investigators found that women with the highest quantile of vitamin D intake from diet and supplements had a 9% (RR = 0.91, 95% CI = 0.85-0.97) decrease in breast cancer risk compared to women with lowest quantile of vitamin D intake. The highest quantile of circulating 25(OH)D, the form of vitamin D stored in the body, was found to be associated with a 45% (OR = 0.55, 95% CI= 0.38-0.90) decrease in breast cancer when compared to the lowest quantile. No significant association for the circulating  $1\alpha,25(\text{OH})_2\text{D}$  level, which is the active form of vitamin D in the body, and breast cancer risk was found. For calcium, a 19% (RR = 0.81, 95% CI= 0.72-0.90) reduction in breast cancer was found for women with the highest quantile of calcium intake compared to those with the lowest quantile of intake. These findings indicate that vitamin D and calcium have chemo-preventive effects against breast cancer. Women can reduce their risk of developing breast cancer by increasing their dietary and/or supplemental intake of vitamin D and calcium. Modestly increasing exposure to sunlight, which will increase the vitamin D level in the body, may also be helpful.

This study was supported by research grants from the One Hundred Talents Program of the Chinese Academy of Sciences, the Knowledge Innovation Program Pilot Project of the INS, and the National Natural Science Foundation of China.

## **New findings on the origin of TrpRS**

On Nov. 26th, the well-renowned British journal *Nuclear Acid Research* published on line the latest research finding on TrpRS by the Structural Biology Group at the Institute of Biochemistry and Cell Biology (SIBCB), Shanghai Institutes for Biological Sciences (SIBS), Chinese Academy of Sciences. With structural and computational studies, PhD candidates Xianchi Dong and Minyun Zhou, and their mentor Prof. Jianping Ding show that TrpRS has an archaeal origin.

Aminoacyl-tRNA synthetases play an essential role in maintaining the fidelity of transferring the genetic information from mRNA to protein in protein synthesis. The Ding's group has published a series of papers on the mechanisms underlying the Trp activation and the subsequent transfer of the activated Trp to the cognate tRNA by human tryptophanyl- tRNA synthetase (TrpRS). As ancient and ubiquitous aminoacyl-tRNA synthetases constitute a valuable model system for studying early evolutionary events, and the evolutionary relationship of TrpRS and tyrosyl-tRNA synthetase (TyrRS) remains controversial, recently the Ding's group conducted the phylogenetic study of TrpRSs. They determined the first crystal structure of an archaeal TrpRS, the structure of *Pyrococcus horikoshii* TrpRS (pTrpRS) in complex with tryptophanyl-AMP (TrpAMP) and performed a more complete structure-based phylogenetic study of TrpRS and TyrRS, which for the first time includes representatives from all three domains of life. The results show that TrpRS originates from the archaeal branch of TyrRS, and the emergence of TrpRS and subsequent acquisition by Bacteria might have occurred at early stages of evolution. Due to the originality, significance and scientific excellence of the work, the article has been selected as a feature article of the issue.

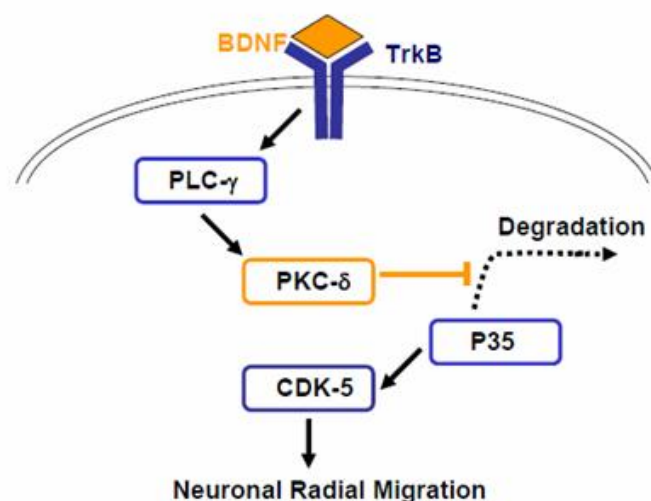
This research was supported by the Ministry of Science and Technology, National Natural Science Foundation of China, Shanghai Municipal Commission for Science and Technology, and Chinese Academy of Sciences. (IBCB)

## PKC $\delta$ Regulates Cortical Radial Migration by Stabilizing the Cdk5 Activator P35

On Nov 24, 2009, the *Proceedings of the National Academy of Sciences* published online a research article from ION entitled "PKC $\delta$  Regulates Cortical Radial Migration by Stabilizing the Cdk5 Activator P35". This work was carried out by graduate students Chun-tao Zhao, Kun Li, Wang Zheng, Jun-tao Li, Xun-jun Liang, An-qi Geng and Ning Li from the laboratory of Dr. Xiao-bing Yuan.

Cyclin-dependent kinase 5 (Cdk5) and its activator p35 are critical for radial migration and lamination of cortical neurons. However, how this kinase is regulated by extracellular and intracellular signals during cortical morphogenesis remains, a unclear novel PKC member. Chun-tao Zhao and colleagues found that PKC expressed in cortical neurons may promote cortical radial migration through maintaining proper level of p35 in newborn neurons. They found that PKC could stabilize p35 by direct phosphorylation and by its attenuating and in utero electroporation of specific down regulation of PKC $\delta$ degradation. Small interference RNA (siRNA) severely impaired the radial migration of newborn cortical neurons, similar to the migration defect caused by down regulation which could be activated by pro-migratory factor p35. Furthermore, PKC brain-derived neurotrophic factor (BDNF) was required for the activation of Cdk5 by BDNF. Both PKC and p35 were required for pro-migratory effect of BDNF on cultured newborn neurons. These results reveal a new mechanism for the regulation of cortical radial migration during development.

This work was supported by 973 projects (2006CB806600, 2006CB943903), National Natural Science Foundation of China (30625023, 30721004), and Chinese Academy of Sciences (KSCX2-YW-R-103).





## **PKU Research Team Publishes Papers on Inhalation Exposure to Pollutant and Cancer Risk**

A research team from the College of Urban and Environmental Sciences of Peking University published papers on the analysis of a pollutant in China that brings cancer risks on Dec 14.

One of the research findings of the "Tao Shu Team," led by PKU Professor Tao Shu, is recently published in Proceedings of the National Academy of Sciences (PNAS), entitled "Inhalation exposure to ambient polycyclic aromatic hydrocarbons and lung cancer risk of Chinese population". It is one of the accomplishments of the team on the emission, transportation and exposure risks of the hydrocarbons, under financial support from National Natural Science Foundation and "Major Project of Chinese National Programs for Fundamental Research and Development" (973 Program) of the Ministry of Science and Technology of China.

Polycyclic aromatic hydrocarbons (PAHs) are included in the Convention on Long-Range Transboundary Air Pollution Protocol on Persistent Organic Pollutants, and the cancerogen is among the most toxic organic pollutants of concern in China.

The team, using the CanMETOP (Canadian Model for Environmental Transport of Organochlorine Pesticides) model based on a high-resolution emission inventory and meteorological data, predicts the atmospheric transport of PAHs for the reference year of 2003.

The model framework applied in research is a combination of three models including an atmospheric transport model, a population exposure model and a lung cancer risk assessment model.

The uncertainty and variability of the predicted exposure risk are evaluated through the analysis of the rectified calculations.

Because of the population and energy structure, China's PAH emission is more intensive than that of developed countries. Open straw burning, biomass burning and small-scale coke production are main sources of PAH pollution in the environment, while the traffic gas combustion accounts for the major one in urban areas, according to the research.

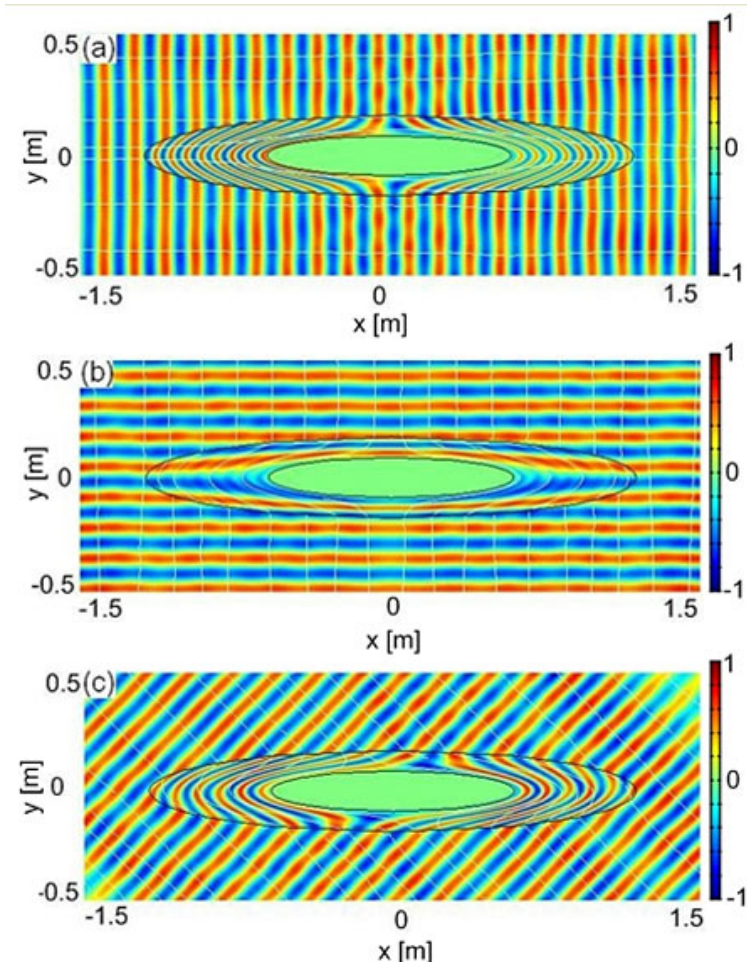
Although the spatial variability is high, lung cancer risk in eastern China is higher than in western inland regions, and populations in major cities have a higher risk of lung cancer than rural areas.

The scaling effect in the atmospheric transport model is rectified by interpolating the calculated concentrations based on the emission inventory. The research also builds the genetic susceptibility for lung cancer risk, which is associated with the polymorphism of genes related to metabolism of carcinogens and DNA repair. Based on these relationships, the variability in respiration rate and susceptibility is taken into account in a population-level exposure risk assessment.

The trend of China's PAH emission is analyzed with potential controlling strategies. Major measures to control the PAH emission and to reduce the exposure risk include the closure of small-scale coke ovens according to the law, the promotion of natural gas stoves and centralized heating facilities, and improvement of rural biomass burning stoves in efficiency.

Other achievements of the research team have been published in journals including PNAS, ES&T and AE.

# Progress of the Research on Arbitrarily Elliptical Invisibility Cloaks



The research group led by Professor Tie Jun Cui, the State Key Laboratory of Millimeter Waves, Southeast University, has made an important progress in invisibility cloaks. “EuroPhysics News” reported their result as a Research Highlight in the June issue (EuroPhysics News, Vol. 39, no. 3, p24). The group designed elliptical-cylindrical invisibility cloaks with arbitrarily axis ratio using the theory of optical transformation. The corresponding paper was published on March 20, 2008 in Journal of Physics D: Applied Physics.

Due to the exciting property of invisibility, electromagnetic cloaks have attracted more and more attention. In earlier times, many theoretical and numerical works had been devoted to the circularly-cylindrical cloak, which is very restricted in practical applications. Prof. Cui and his group designed elliptical-cylindrical invisibility cloaks with arbitrarily axis ratio by using the techniques of optical transformation, which is based on the form-invariance of Maxwell's equations. They presented the expression of electromagnetic parameters for such invisibility materials and provided validation by finite-element simulations. The simulation results showed that the designed elliptical cylindrical cloaks have very good performance of invisibility. They also showed that the material parameters in elliptical cloaking are singular at only two points, instead of on the whole inner boundary for circular cloaking. Such invisibility cloaks can be realized by artificial meta-materials.

This work was supported by the National Natural Science Foundation of China and the National Basic Research Program of China.

# An Advance in Complete Oxidation of Formaldehyde at Low Temperatures

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**Editor's comments:** *Formaldehyde (HCHO) emitted from chemical manufacturing plants including methanol-gasoline/diesel fuel vehicles and the construction and decoration materials is one of the major air pollutions, which induces photochemical pollution and hazards human health. Great efforts have been made for the reduction or control of the emission of HCHO to satisfy the stringent environmental regulations. Now, a new study supported by the National Natural Science Foundation of China reports mesoporous manganese oxide with novel nanostructures for the decomposition of HCHO. The obtained manganese oxide nanomaterials showed high catalytic activities for oxidative decomposition of HCHO at low temperatures. Complete conversion of HCHO to CO<sub>2</sub> and H<sub>2</sub>O were achieved, and no harmful byproducts were detected in effluent gases. The catalytic activities of these nanomaterials are significantly higher than those of previously reported manganese oxide octahedral molecular sieve (OMS-2) nanorods, MnO<sub>x</sub> powders, and alumina-supported manganese-palladium oxide catalysts. These results provide a new route for the removal of HCHO and other air pollutions.*

**Key words:** Manganese oxide, honeycomb nanosphere, hollow nanosphere, formaldehyde, oxidation

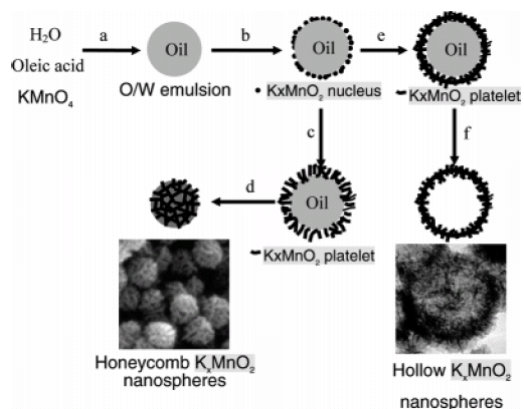
The indoor environment plays an important role in human health, because people generally spend more than 80 % of their time in indoors, which contributes a higher risk from inhalation of pollutants than outdoors. Formaldehyde (HCHO) emitted from the construction and decoration materials is one of the most dominant volatile organic compounds (VOCs) in the indoor environment. Previous research indicated that serious health problems including nasal tumors, irritation of the mucous membranes of the eyes and respiratory tract, and even lethal diseases such as nasal cancer can be caused if people are exposed to an indoor environment polluted with elevated HCHO levels for an extended length of time.<sup>1-3</sup>

Currently effective removal of HCHO is attracting much attention. The catalytic decomposition of HCHO has been achieved in the temperature range 90~500 °C. Facile decomposition of HCHO at low temperature, however, is still a challenge though there are increasing concerns on HCHO in the indoor environment. Catalytic oxidation is a promising approach as HCHO can be oxidized to CO<sub>2</sub> over catalysts at lower temperatures than thermal oxidation.<sup>4,5</sup> MnO<sub>x</sub> powders, MnO<sub>2</sub> octahedral molecular sieve (OMS-2) nanorods, and alumina-supported manganese-palladium oxides (Mn-Pd/Al<sub>2</sub>O<sub>3</sub>) were used as catalysts for decomposition of HCHO, and the latter two catalysts showed high activities at low temperatures.<sup>6,7</sup> Very recently, Sinha A. *et al.*<sup>8</sup> reported that mesostructured 2.8 wt % Au/γ-MnO<sub>2</sub> nanoparticle composites could be used for extensive air purification.

Control over the size, shape, and structure of inorganic nanomaterials to search for new properties has become one of the major objectives of nanoscale science and technology, because of their structure, size and shape-dependent characteristics and novel chemical properties.<sup>9,10</sup> Different MnO<sub>2</sub> morphologies have so far been prepared, including rods, wires, tubes, urchin-like microstructures, etc. However, few works were reported on nanostructures of layered MnO<sub>2</sub>, such as birnessite-type MnO<sub>2</sub> (A<sub>x</sub>MnO<sub>2</sub>, where A = H<sup>+</sup> or metal cation). A<sub>x</sub>MnO<sub>2</sub> is a layered structure consisting of edge-sharing MnO<sub>6</sub> octahedra with an interlayer spacing of ca. 0.7 nm.<sup>11</sup> Recently, Our group prepared novel mesoporous nanospheres of layered manganese oxide (K<sub>x</sub>MnO<sub>2</sub>) with honeycomb and hollow nanostructures

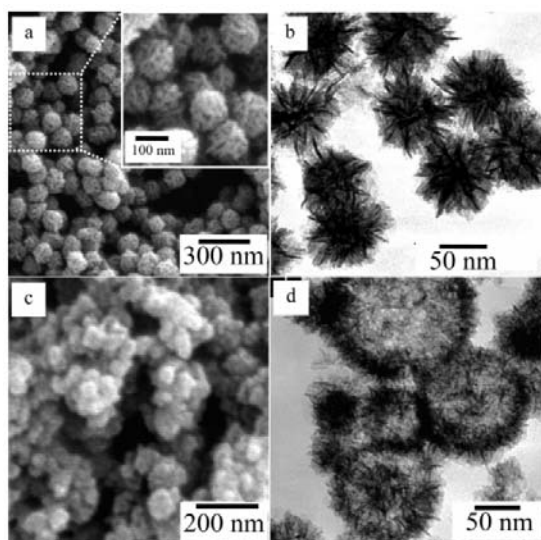
via a facile approach at room temperature.<sup>12</sup> The catalytic activities of these manganese oxide nanostructures showed a 100 % conversion of HCHO to CO<sub>2</sub> + H<sub>2</sub>O at 80 °C. It was the first report of catalytic decomposition of HCHO by mesoporous layered K<sub>x</sub>MnO<sub>2</sub> nanomaterials at such low temperatures.

We used oleic acid (OA) as reducing agent of potassium permanganate (KMnO<sub>4</sub>). In the reaction system, oleic acid formed a stable O/W emulsion (Scheme 1), in which the “Baeyer test for unsaturation” reaction<sup>13</sup> quickly occurred between KMnO<sub>4</sub> and oleic acid at the O/W interface and produced K<sub>x</sub>MnO<sub>2</sub> nuclei there. At low KMnO<sub>4</sub> concentration, an unstable shell of loosely packed platelets formed (process c). Removal of oleic acid and formed

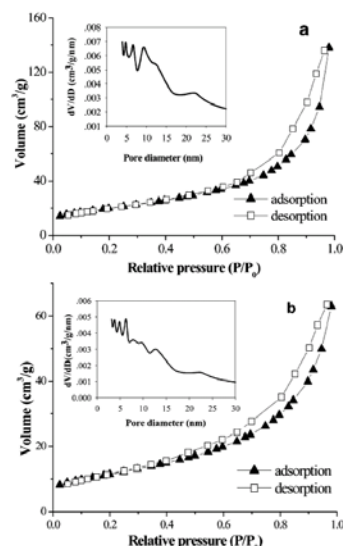


**Scheme 1: Plausible formation mechanism of honeycomb and hollow K<sub>x</sub>MnO<sub>2</sub> nanospheres.**

cis- diol by ethanol resulted in collapse of the shell, giving honeycomb nanospheres. At high KMnO<sub>4</sub> concentration, large amounts of lamellar platelets were produced, and a robust shell of densely packed platelets formed (process e). After removal of oleic acid and formed cis-diol, hollow nanospheres were produced. The morphology and mesoporous character of the as-prepared nanomaterials are shown in Fig. 1 and Fig. 2, respectively.



**Fig. 1. SEM (a) and TEM (b) images of honeycomb K<sub>x</sub>MnO<sub>2</sub> nanospheres (KMnO<sub>4</sub>/OA=1:5) and SEM (c) and TEM (d) images of hollow K<sub>x</sub>MnO<sub>2</sub> nanospheres (KMnO<sub>4</sub>/OA=1:1).**



**Fig. 2. Nitrogen sorption isotherms and pore size distributions (inset) of honeycomb (a) and hollow (b) K<sub>x</sub>MnO<sub>2</sub> nanospheres.**

These new nanomaterials had robust nanostructures and showed morphology-dependent catalytic activities for decomposition of formaldehyde. The HCHO conversion by the hollow K<sub>x</sub>MnO<sub>2</sub> nanospheres (50 mg) increased to 100 % when the temperature increased to 80 °C, and that by the honeycomb nanospheres (70 mg), however, needed 85 °C to reach a 100 % conversion, as shown in Fig. 3.

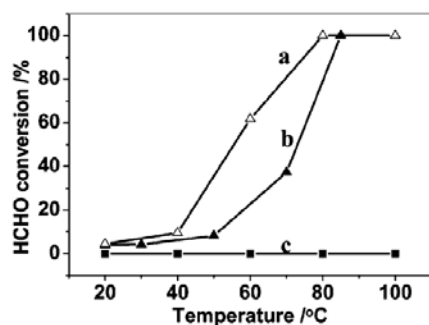


Fig. 3. HCHO conversion on control (■), honeycomb  $K_xMnO_2$  nanospheres (70 mg) (▲), and hollow  $K_xMnO_2$  nanospheres (50 mg) (△), respectively.

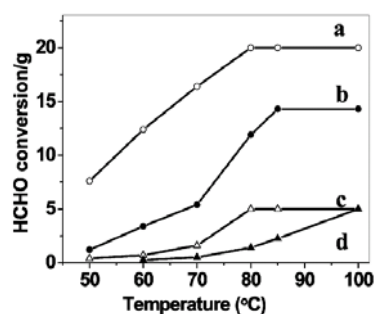


Fig. 4. HCHO conversion per gram of samples on  $MnO_x$  powder (▲), OMS-2 nanorods (△), honeycomb  $K_xMnO_2$  nanospheres (●) and hollow (○)  $K_xMnO_2$  nanospheres, respectively.

These decomposition temperatures are much lower than those achieved by using similar manganese oxide materials. We compared the catalytic activities of the current as-prepared  $K_xMnO_2$  nanomaterials with previously reported materials. It was found that the catalytic activities of honeycomb and hollow  $K_xMnO_2$  are much higher than those of  $MnO_x$  powder, OMS-2 nanorods, and even  $Mn-Pd/Al_2O_3$  catalysts (Fig. 4). Therefore, these mesoporous  $K_xMnO_2$  nanospheres with large surface area and high dispersity are convenient and effective catalysts, and may provide a promising approach for oxidation decomposition of indoor pollutants and other VOCs in environment. Future research efforts will be necessary to offer significant improvement over this approach. In fact, with the support of the National Natural Science Foundation of China, we are currently investigating more convenient methods to synthesize the catalysts.<sup>14</sup>

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