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14. ABSTRACT The application of pulsed electron paramagnetic resonance (EPR) technique is used in quantum computing. Polarized electron spin created in the photo-excitation of organic molecules is used as the basis of quantum bit. The quantum coherence and superposition effects of the polarized electron spin at the level anti-crossing (LAC) region under the influence of an external magnetic field and microwave pulses is examined. Highly polarized state is present only during the preparation of quantum states in the photo-excitation. Future work should focus on nuclear polarization enhancement by optical pumping in the LAC region.					
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Progress Report for AFOSR on Taiwan – AFOSR Nanoscience Initiative

Project Titles: Applications of Nanotechnology in Biomimetics and Quantum Computing (2nd year)

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Introduction

Biocatalysis is referred to enzymatic catalysis. Biocatalysts are attractive because they provide unique products via stereoselectivity (enantioselectivity) and regioselectivity. Biocatalysis has become a very important application in chemical industries. However, it is known that most of native enzymes exhibit high reactivity and selectivity only under normal conditions. Under extreme conditions, such as high temperature or pH, enzymes are easily inactivated due to denaturalization, either by changes of conformation or other transformation of stereo chemical structure. Our effort is to apply nanosciences and nanotechnology to immobilize biocatalysts or biomimetic agents in active nanostructure, so that we can enhance their stability, and simplify the biocatalytic applications. The findings of biocatalytic research could be further developed into biosensing devices which can be applied to monitor bio terrorism which will be the topic of our 3rd period of research supported by AFOSR.

Another area of our 2nd year project is the application of pulsed electron paramagnetic resonance (EPR) technique in quantum computing. We utilize the polarized electron spin created in the photo-excitation of organic molecules as the basis of quantum bit (qubit). We have examined the quantum coherence and superposition effects of the polarized electron spin at the level anti-crossing region under the influence of an external magnetic field and microwave pulses. A brief description of our findings is given below:

(1) Effect of spin configuration on the reactivity of cytochrome c immobilized in mesoporous silica.

Cytochrome c (cytc), a heme protein with positive electric charge, is immobilized in the nanochannels of mesoporous silica (MPS) by either electrostatic force or covalent bonding. The electrostatic interaction between cytc and MPS arises from the introduction of aluminum into the framework of MPS to produce the negative charge on the porous surface (Al-MPS). The covalent bonding arises from the binding between heme iron center and the -SH group of the mercaptotriethoxysilane in the thiol-functionalized MPS (MPS-SH). The nanochannels of MPS provide the confining spaces that could prevent cytc from protein unfolding and preserve its activity. Cytc immobilized in Al-MPS exist in high spin state as inferred from ESR and UV-Vis studies. This is different from the native cytc, which shows primarily the low spin state. The high spin state arises from the replacement of Met-80 ligands of heme Fe (III) by water or silanol group on the silica surface, which could open up the heme groove for easy access of oxidants to iron center and facilitate the catalytic activity. MPS-SH-supported cytc could exist in both high and low spin states. The low spin state arises from the replacement of axial ligands of heme Fe (III) by the -SH group which could cause the poisoning of active site and decrease the catalytic activity toward the decomposition of H₂O₂. In ESR spin trapping experiments, we show that cytc catalyzes a homolytic cleavage of the O-O bond of hydro peroxide and generates a protein cation radical ($g = 2.00$). Possible mechanisms for MPS-cytc catalytic oxidation of hydro peroxide is proposed based on the spectroscopic characterizations of the systems.

The results of these studies were presented at the 9th Spin Chemistry International Conference held at Oxford University, UK in September 2005. A manuscript based on this study acknowledging the support of Taiwan – AFOSR Nanoscience Initiative was published in *Molecular Physics*.¹

(2) Preparation and Characterization of Vanadium Oxide Species Supported on Mesoporous Silica for the Hydroxylation of Benzene

The homogenous liquid-phase direct catalytic oxidation of benzene to phenol was performed at 60° C in acetonitrile solvent using various catalysts of VO_x supported on aluminum substituted mesoporous silica (Al-MPS) and hydrogen peroxide as the oxidant. We employed the molecular designed dispersion (MDD) method to prepare the VO_x catalyst supported on Al-MPS. The deposit of monolayer VO(acac)₂

complexes could be achieved by hydrogen bonding or ligand exchange mechanism and subsequently decomposition of organic acetylacetonate (acac) ligands in an oxygen atmosphere at elevated temperature, yielding the six coordination of V^V center. The octahedral vanadium oxide samples possess much mobile ligands (i.e., H_2O or solvent) around the catalytic center that could be easily substituted by hydrogen peroxide and yielded the active peroxy intermediate for the hydroxylation of benzene. From the studies of powder X-ray diffraction (XRD), N_2 adsorption and desorption isotherms, diffuse reflectance UV-Vis, electron paramagnetic resonance (EPR), we show that highly dispersed isolated vanadium oxide catalyst center could be formed. Besides, we also prepared the tetrahedral vanadium oxide catalyst by the coordination of V^V center with mono-, di-, and tri-amine modified SiO_2 . The tetrahedral coordination of vanadium oxide catalysts lack mobile ligands for good leaving groups in the catalytic medium and yield a lower activity toward the hydroxylation of benzene.

The study is a stepping-stone to test some of the biomimetic modeling of vanadium containing proteins, such as insulin. The results of this study was published in Journal of Physical Chemistry-C acknowledging the support of Taiwan – AFOSR Nanoscience Initiative.²

(3) Superoxide dismutases (SOD) enzymes and model compounds to mimic CuZnSOD enzymes.

The role of SOD in biological systems is to convert superoxide anion radicals, O_2^- , to hydrogen peroxides. We employed the protocol shown in Fig. 1 to immobilize SOD proteins in MPS. There we applied Ni-NTA complex (NTA: N,N-bis(carboxymethyl)glycine) as the coupling bridge to the histidine tagged proteins and immobilized the complex in SBA-15 (pore 5 - 9 nm) solid supports. We examined the stability and their enzymatic activity in comparison with native enzyme and the corresponding biomimetics. Many model compounds have been synthesized and tested for their efficacies. Most recently, another model compound, imidazolato-bridged complex (Cu(II)-diethylenetriamino- μ -imidazolato-Zn(II)-tris(aminoethyle)amine perchlorate) has been also reported to mimic CuZnSOD.³ Follow the given protocols, we prepared the model complexes. We have successfully immobilize this model complex in the silica gel via hydrogen bonding which has shown good SOD activity, but not in zeolite or MCM-41. It has been indicated that the configuration of paramagnetic center Cu(II) and a weak spin-spin interaction are important to achieve high SOD activity. We plan to modify the mesoporous surface with either amine or other functional groups which should improve the binding with the model compounds and further improve the SOD activity. The modified surface of MPS should also provide the needed separation of paramagnetic centers which can be detected by EPR technique. Detailed studies are in progress.

In the future, we plan to immobilize SOD enzymes in MPS and the design of active mimicking model compounds in our future experiments. Specifically, we plan to pursue the following three steps: (1) Direct modify CuZnSOD mimic complexes to affect the encapsulation in MPS. Besides the usual covalent and electrostatic bonding, we plan to introduce active site ligands on CuZnSOD enzymes to enhance their affinity on MPS surface. (2) Investigate the activity and stability of CuZnSOD enzyme and mimic complexes in MPS. We expect the immobilization will widen the active range of temperature and pH of CuZnSOD enzyme and mimic complex in MPS materials. (3) Study the endocytosis pathway of immobilized CuZnSOD in mesoporous sphere nanoparticle (MSN). In our laboratory, we found MSN can enter into cells through endocytosis pathway. Thus, we would like to use MSN as a vector to transfer CuZnSOD enzyme and mimic complex into cell. Note that the enzymatic activity of SOD is to eliminate O_2^- species which can exert oxidative stress on tissues and expose living system to potential toxicity. The study may provide an essential defense against the potential toxicity of oxidative stress in vivo.

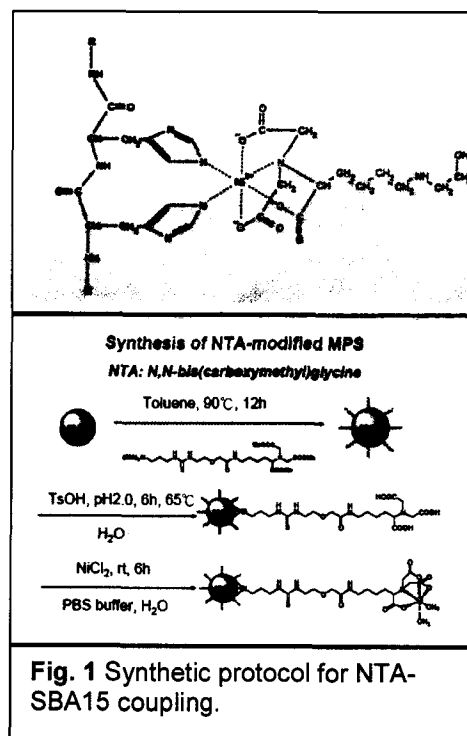


Fig. 1 Synthetic protocol for NTA-SBA15 coupling.

(4) Pulsed EPR and quantum computing

Previously, we reported the feasibility of utilizing the polarized electron spin created by the laser-excitation of the pentacene molecule as the bases of quantum bit (qubit).⁴ We found that the highly polarized electron spin could increase the detectable signal and eliminate the intrinsic limiting factor of thermally populated nuclear spin states in quantum computer (QC) - NMR techniques.

In the EPR approach, the couplings between the electron spin and nuclear spins (HFI) constitute the basic qubits for the superposition and entanglement of spin states. This is especially important in the level anti-crossing (LAC) region where a strong HFI exists, and the polarization can easily transfer from electron spin to proton spins.⁵ The coupling strength at a particular molecular site is proportional to the spin density at that site, which is different from the NMR experiments in which each atom interacts only with a few of its nearest neighbors. In the case of the pentacene molecule, 14 protons can be divided into 4 inequivalent groups because of molecular symmetry. The coupling of the electron spin with four distinct protons will be good for a 4-qubit-QC. However, the molecular symmetry can be lowered in a partially deuterated sample or in a nitrogen-containing pentacene. Then, in principle, we can build up to 14-qubit-QC system using a pentacene-like triplet molecule. The synthesis of functionalized pentacene-like molecules has recently been reported.⁶

In the preliminary studies, we utilized diluted mixed crystals of *p*-terphenyl doped with pentacene molecules. The diluted probe molecule (possibly single-molecule, single-spin) could avoid the strong dephasing - relaxation problem. We utilized the following special features of the pulsed EPR experiments in the quantum computer experiments: (1) reduce the intermolecular interaction and the decoherence interference and improve the operation cycles, (2) establish the stability of the organic molecule in mixed crystals or imbedded in the channel wall of mesoporous silicas, and (3) preserve the optical integrity allowing the host materials and the channel wall to be transparent to the laser. Furthermore, by working with the excited state of a molecule will lift the high purity requirement, unless the impurity affects the optical properties of the system, such as a trapping impurity. The highly spin-polarized state is present only during the preparation of quantum states in the photo-excitation.

In the future, we plan to perform nuclear polarization enhancement by optical pumping in the LAC region. The enhanced NMR signal and the associated superposition and entanglement of spin states will facilitate the detection of quantum states, qubits, and phase coherence in such a simple system. We plan to perform the proposed quantum computing experiments with both NMR and EPR techniques.

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