Mn-based water oxidation catalyst as a functional model for the photosystem II

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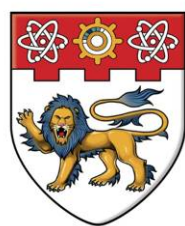
2008

https://hdl.handle.net/10356/95502

NANYANG TECHNOLOGICAL UNIVERSITY

URECA *Undergraduate Research Experience on CAmpus*

Category: 6
Project ID:SPMS07035

Introduction

Photosynthesis is one of the most important biochemical processes in nature. A key step for photosynthesis is the oxidation of water to oxygen catalyzed by a manganese tetramer, which is an essential co-factor in the enzyme Photosystem II (PS II). [1,2]

Understanding the mechanism for this step is essential for the future development of solar energy utilization.

Several catalytic models (mainly manganese terpyridine complexes (Mn-terpy) for the water oxidation process have been established so far including homogeneous and heterogeneous catalytic models.[3,4] However, they showed limited catalytic activity and poor reproducibility, which creates barriers to further study of PS II.

In our group, we integrate nanotechnology into this bioinorganic modeling study. It creates a semi-homogeneous catalytic system, preventing inter-catalyst interaction which is believed to be an important cause for the failure of the previous models. It is a good attempt to the birth of a new generation of water oxidation catalyst, with higher catalytic activity as well as better reproducibility.

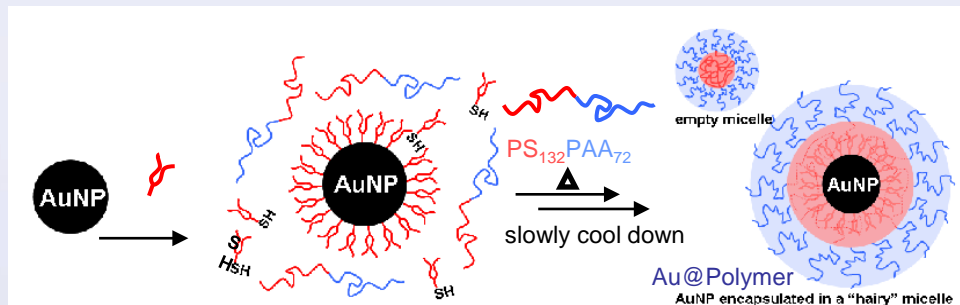## Methodology, results and discussion

1. Ligand Synthesis
Ligand 4'-p-aminophenyl-2,2':6',2"-terpyridine **(L)** will be synthesized based on the Kröhnke methdology.
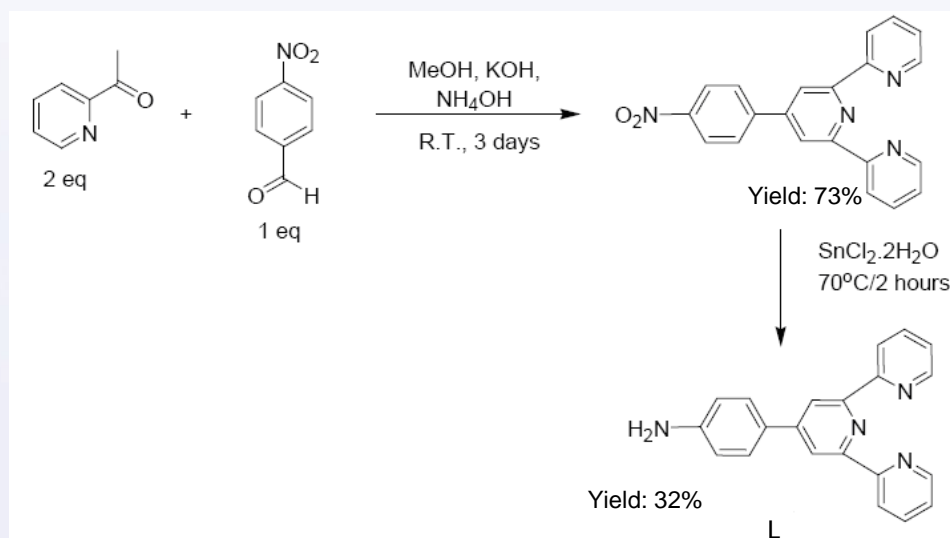
2. Encapsulation of gold nanoparticles (AuNPs)

The synthesized gold nanoparticles with controlled size is encapsulated with amphipathic block co-polymer (polystyrene-block-poly acrylic acid, $PS_{132}PAA_{72}$).
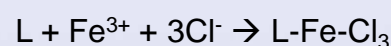

The AuNPs' size can be well controlled by changing reaction conditions. An appropriate size of AuNPs is beneficial for the further purification process.
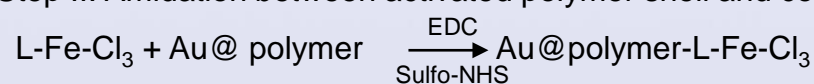
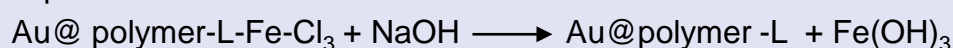*3. Conjugation of encapsulated AuNPs with terpy complex*

Method 1:

Step I: Formation of iron(III) complex:

$$L + Fe^{3+} + 3Cl^- \rightarrow L\text{-}Fe\text{-}Cl_3$$

Step II: Amidation between activated polymer shell and complex

$$L\text{-}Fe\text{-}Cl_3 + Au@ \text{ polymer} \xrightarrow[\text{Sulfo-NHS}]{\text{EDC}} Au@polymer\text{-}L\text{-}Fe\text{-}Cl_3$$

Step II: Dissociation of iron:

$$Au@ \text{ polymer-L-Fe-Cl}_3 + NaOH \longrightarrow Au@polymer\text{ -L }+ Fe(OH)_3$$

Objective: make the hydrophobic ligand more hydrophilic, beneficial for conjugation.
Iron: labile metal, easy for ligand dissociation, beneficial for further steps.
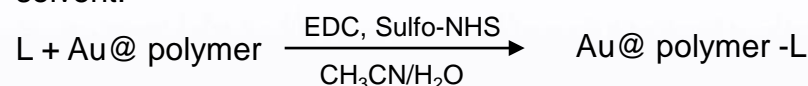Results: AuNPs aggregation during purification (centrifugation).
Discussion: Aggregation may occur when the particles merging to each other.
Solution: Introduce purification techniques without contraction of AuNPs. (To be developed)

Method 2:

Conjugation of L and AuNPs@ polymer in presence of organic solvent:

$$L + Au@ \text{ polymer} \xrightarrow[\text{CH}_3\text{CN/H}_2\text{O}]{\text{EDC, Sulfo-NHS}} Au@ \text{ polymer -L}$$

Objective: a mixture of water and acetonitrile increases solubility of L, which is beneficial to the conjugation reaction.
Results: Aggregation of AuNPs observed.
Discussion: the presence of acetonitrile may destroy the polymer shell.
Solution: adjust the solvent system, which can dissolve the ligand with no effect on the polymer shell. (To be developed)
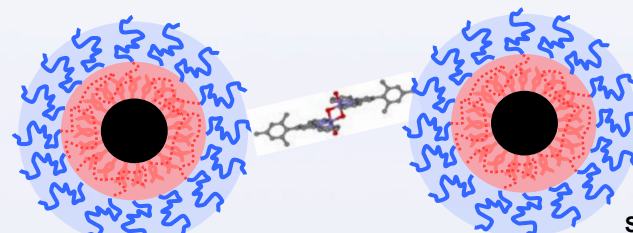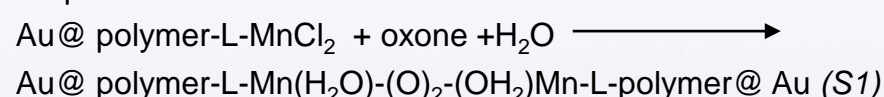
4. Synthesis of the water oxidation catalystr (To be developed)
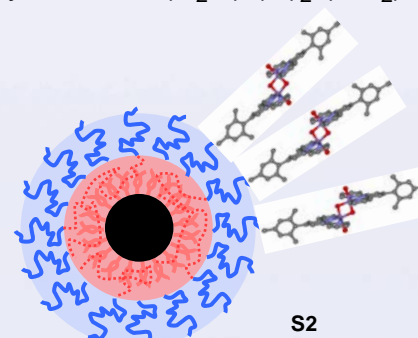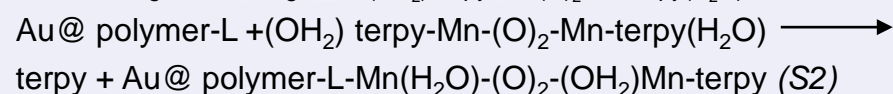
Method 1:

Step I: Formation of Mn(II) complex
$$Au@ \text{ polymer-L} + MnCl_2 \longrightarrow Au@ \text{ polymer-L-MnCl}_2$$

Step II: Oxidation:
$$Au@ \text{ polymer-L-MnCl}_2 + \text{oxone} + H_2O \longrightarrow$$
$$Au@ \text{ polymer-L-Mn(H}_2O)\text{-(O)}_2\text{-(OH}_2)\text{Mn-L-polymer@ Au } (S1)$$

Method 2: Ligand exchange with (OH_2) terpy-Mn-$(O)_2$-Mn-terpy(H_2O)
$$Au@ \text{ polymer-L} +(OH_2) \text{ terpy-Mn-(O)}_2\text{-Mn-terpy(H}_2O) \longrightarrow$$
$$\text{terpy} + Au@ \text{ polymer-L-Mn(H}_2O)\text{-(O)}_2\text{-(OH}_2)\text{Mn-terpy } (S2)$$

5. Study of water oxidation catalytic activity (To be developed)

$$H_2O \xrightarrow[\text{Oxidant}]{S1(S2)} O_2$$
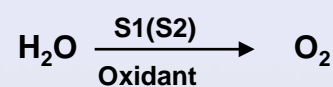
Oxidant= oxone, Ce(IV)
The reaction's rate constant (k) and turnover number (TON) will be determined.

Conclusions

The integration of nanotechnology into water oxidation catalyst creates a unique semi-homogeneous catalytic environment. Self-destruction of the catalyst may be minimized. Thus this catalytic model may provide higher catalytic efficiency as well as better reproducibility. This work may lead to the birth of a new generation of water oxidation catalyst.

References

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2. Loll, B.; Kern, J.; Saenger, W.; Zouni, A.; Biesiadka, J., *Nature*, **2005**, 438, 1040-1044.
3. Limburg, J.; Vrettos, J. S.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H.; Brudvig, G. W., *Science*, **1999**, 283, 1524-1527.
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School of Physical and Mathematical Sciences
Project Title: Mn-based Water Oxidation Catalyst as a Functional Model for the Photosystem II
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