Strategies to Stabilize Pd Nanoparticles by Polyamine based Hybrid materials for Catalytic Applications

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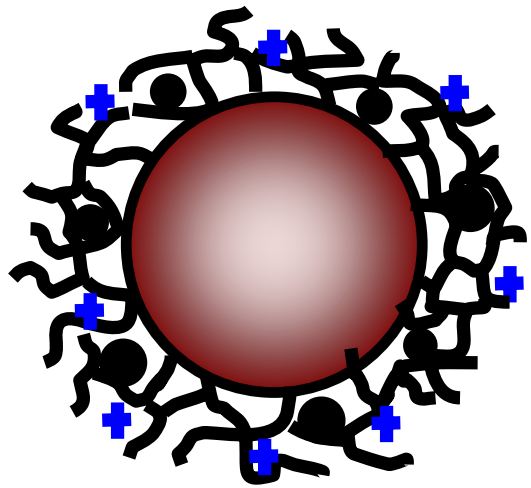
Strategies to Stabilize Pd Nanoparticles

Requirements:

- ❑ Catalytic activity
- ❑ Stability
- ❑ Easy separation of the catalyst
- ❑ Reusability
- ❑ Flexibility for multi-functionality



Stabilization of Pd Nanoparticles

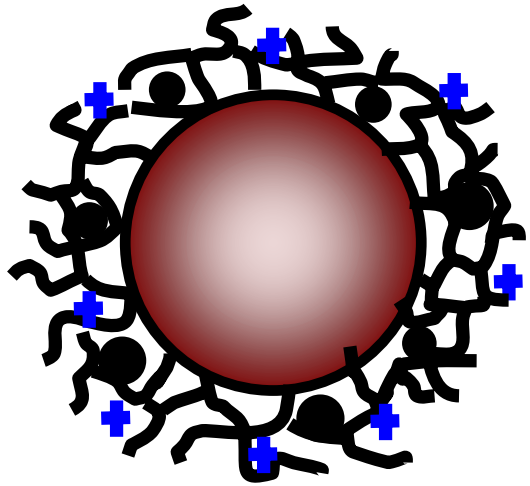
Organic/Inorganic Hybrid Materials

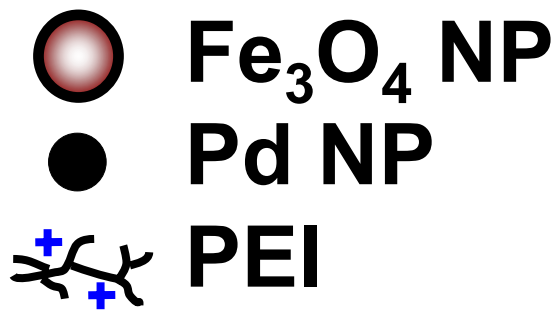
Polyethyleneimine(PEI):

- ❑ Catalytic activity
- ❑ Stability
- ❑ Reusability

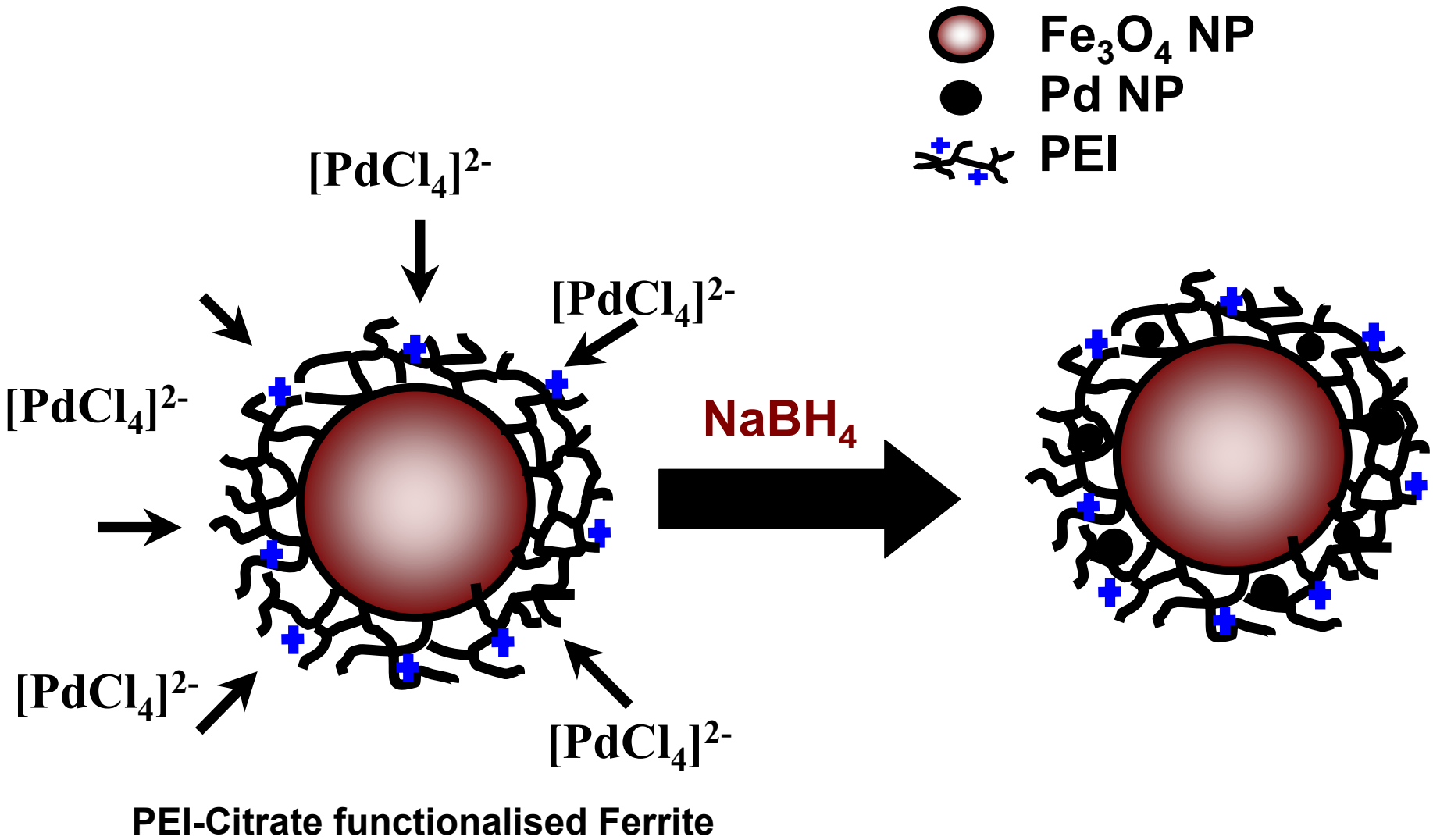
Magnetic NPs:

- ❑ Easy separation





Pd(0) stabilized on Fe_3O_4 NPs

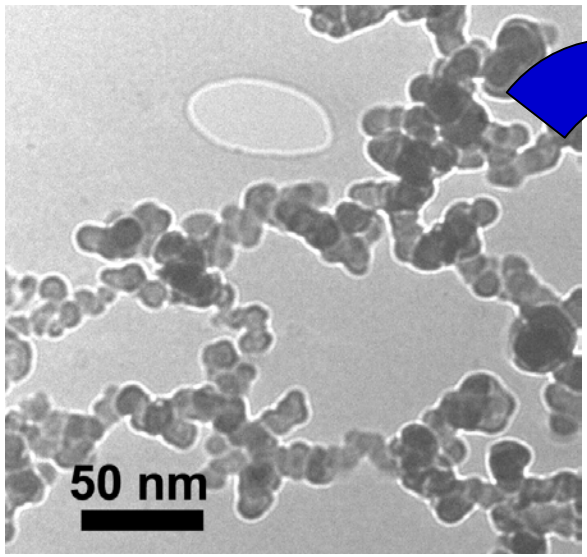


PEI-Citrate functionalised Ferrite

Amali and Rana, *Green Chem.*, 2009

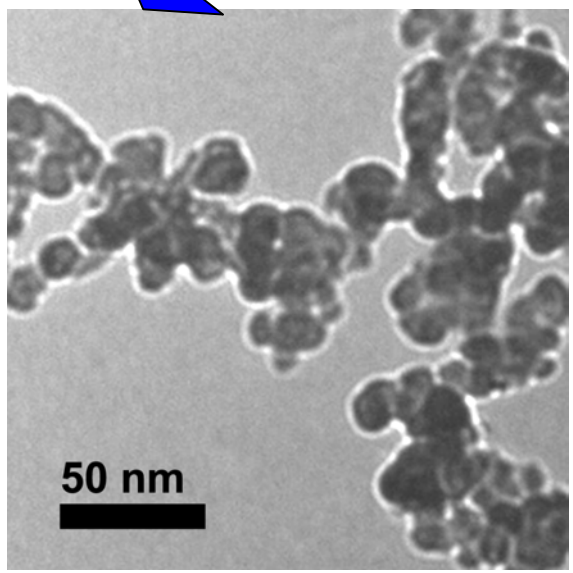
Pd(0) stabilized on Fe_3O_4 NPs

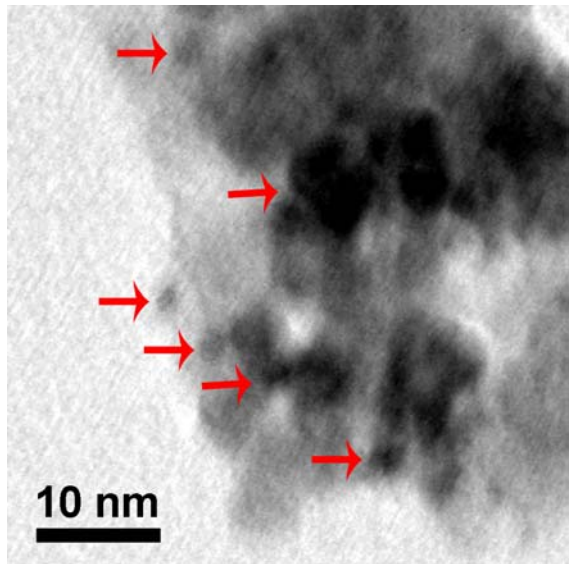
PEI-Citrate functionalised Fe_3O_4



particle size: ~10 nm

Pd(0) on PEI-Citrate functionalised Fe_3O_4

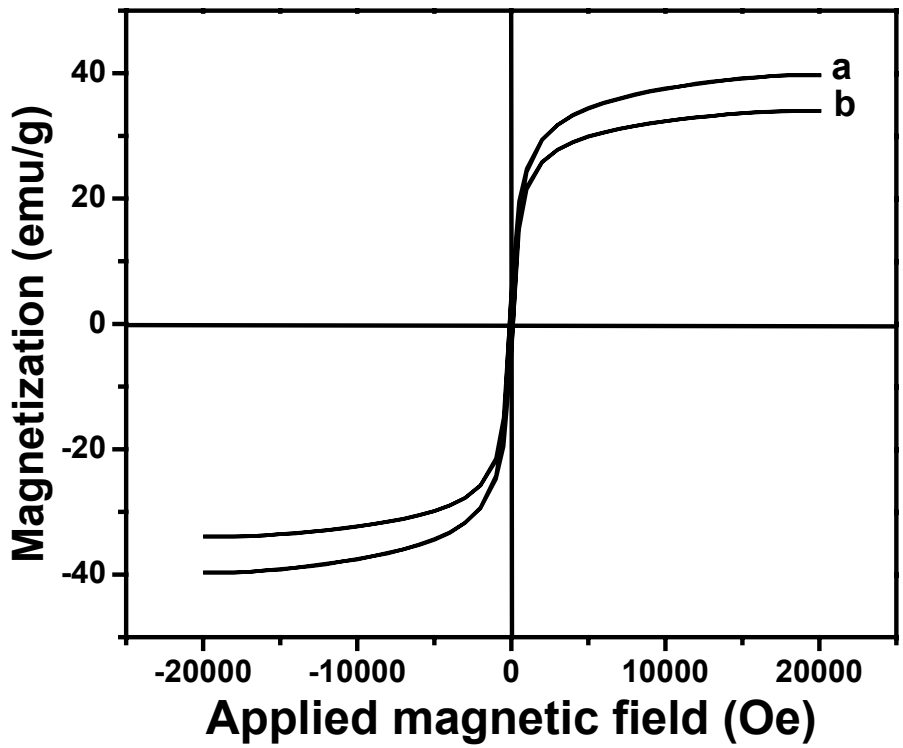




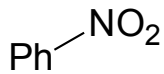
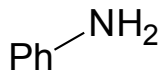
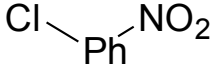
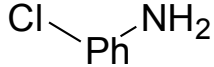
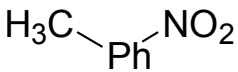
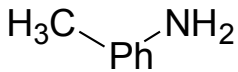
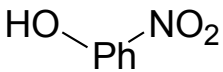
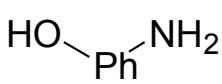
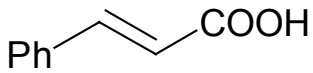
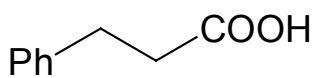
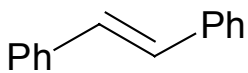
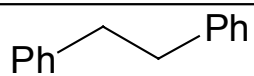
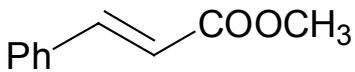
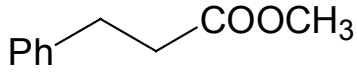
8.68 wt% Pd
Pd NP size: 2–6 nm

Magnetic Properties

Magnetisation curves of (a) PEI surface functionalised Fe_3O_4 (b) $Pd@Fe_3O_4$.

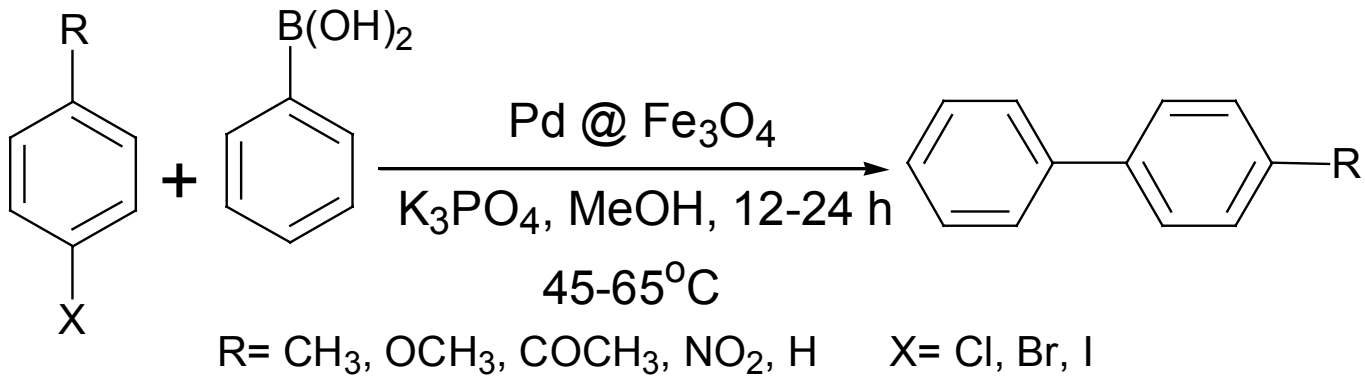


Hydrogenation using $Pd@Fe_3O_4$

Entry	Reactant	Product	Conversion (%)	Time (min)
1			>99 >99[b] >99[c]	60 60[b] 180[c]
2			>99	60
3			>99	60
4			>99	60
5			98	60
6			93	60
7			>99	60

a) Reaction conditions: catalyst - 50 mg (Pd, 0.203mol %); H_2 - 1atm; substrate - 2 mmol; solvent - ethanol; b) conversion after 10 runs; c) with Pd/C (Aldrich-10 wt% Pd)

Suzuki -Miyaura Coupling Reactions



Reaction conditions:

catalyst - 50 mg (Pd, 0.816mol %);

aryl halide - 0.5 mmol; phenyl boric acid - 0.6 mmol; K_3PO_4 - 1.5 mmol;

solvent - methanol;

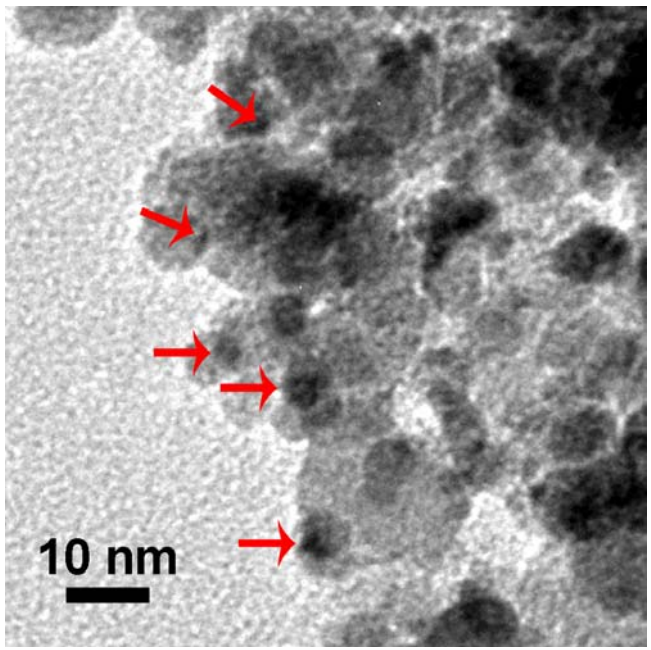
Suzuki -Miyaura Coupling Reactions

Entry	R	X	Yield (%)	TON $mol_{product}\ mol^{-1}_{Pd}$	TOF $mol_{product}\ mol^{-1}_{Pd}\ h^{-1}$	Time (h)
1	H	Cl	94	11.5	0.48	24
2	**NO_2**	**Cl**	**95 49***	**11.7 5.2***	**0.49 0.22***	**24 24**
3	CH_3	Cl	85	10.4	0.43	24
4	$COCH_3$	Cl	89	10.9	0.46	24
5	OCH_3	Cl	75	9.2	0.38	24
7	**NO_2**	**Br**	**96 60***	**11.8 6.4***	**0.65 0.35***	**18 18**
8	CH_3	Br	90	11.0	0.61	18
9	$COCH_3$	Br	92	11.3	0.63	18
10	OCH_3	Br	89	10.9	0.61	18
11	**NO_2**	**I**	**95 84***	**11.6 8.9***	**0.97 0.74***	**12 12**
12	CH_3	I	91	11.2	0.93	12
13	$COCH_3$	I	93	11.4	0.95	12
14	OCH_3	I	90	11.0	0.92	12

* with Pd/C (Aldrich-10 wt% Pd)

Reusability (After 5th run)

Run	R	X	Yield (%)	Accumulated TON $mol_{product}\ mol^{-1}_{Pd}$	Accumulated TOF $mol_{product}\ mol^{-1}_{Pd}\ h^{-1}$	Time (h)
1st 5th	H	Cl	94 92	11.5 57.0	0.48 0.48	24 24
1st 5th	H	Br	95 93	11.6 57.6	0.65 0.64	18 18



Pd @ PEI-Citrate functionalised Ferrite After 5th Run

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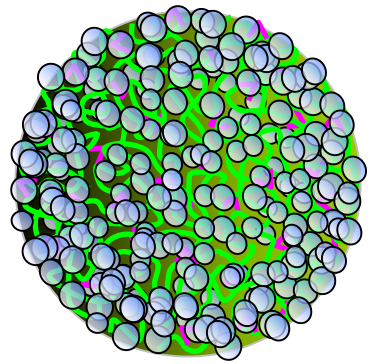
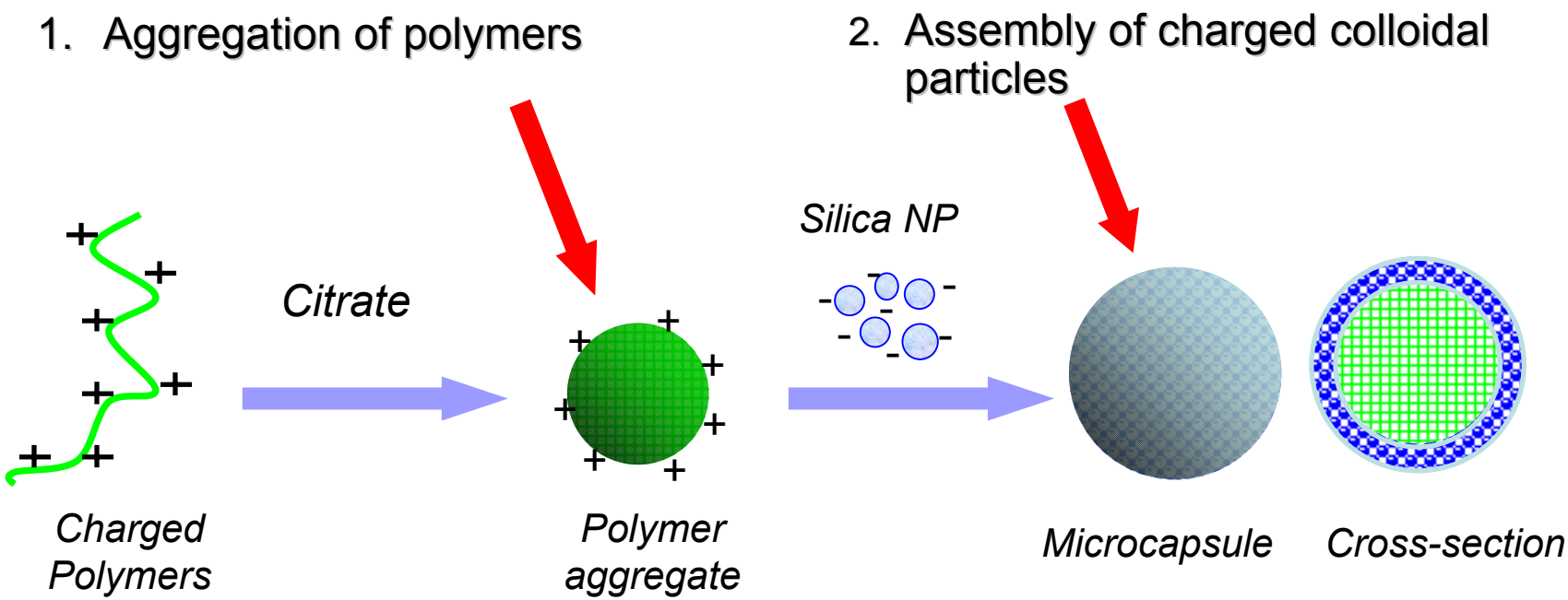


Lab in a Particle

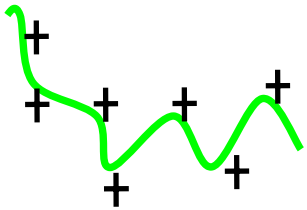
Self-assembly of Nanoparticles

- Bio-inspired Synthesis

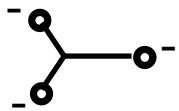


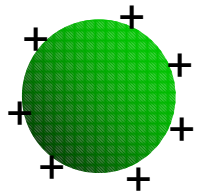
Two-step process of self assembly

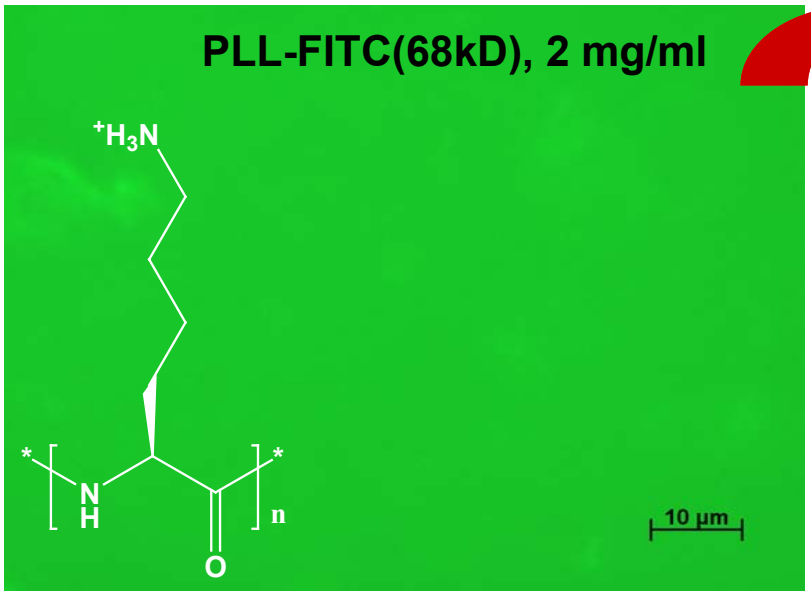
Step-1: Aggregation of polyamines

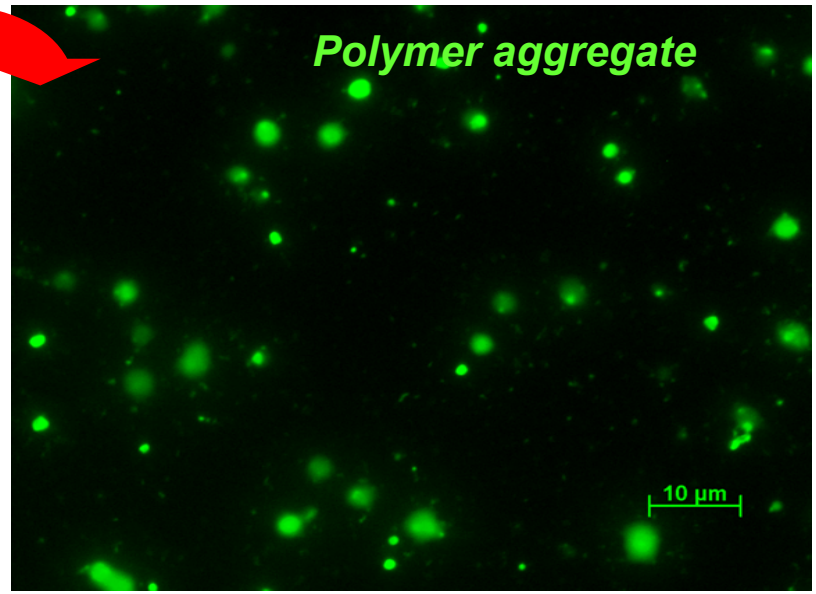


Citrate (4 mM)







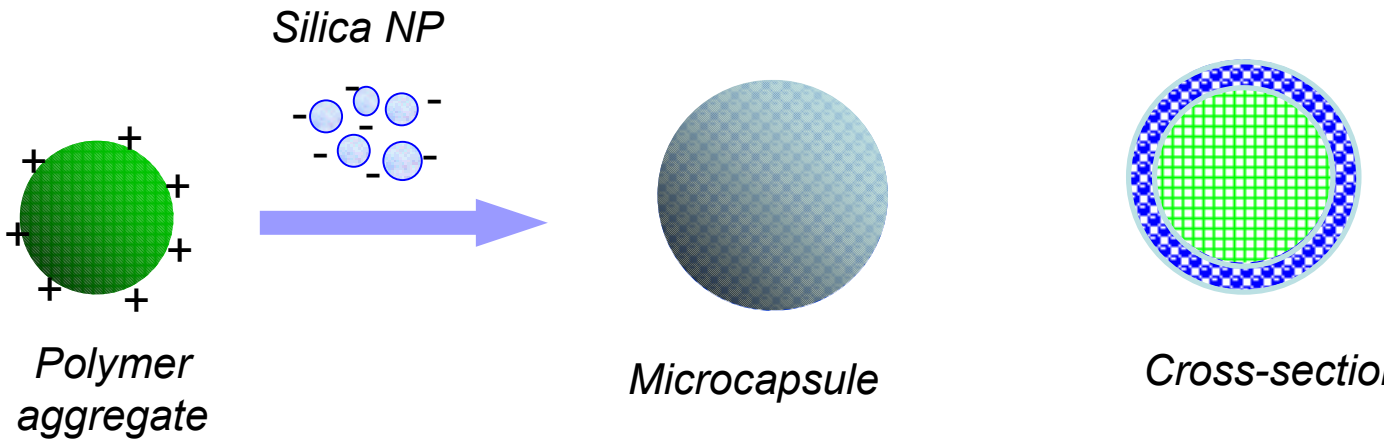


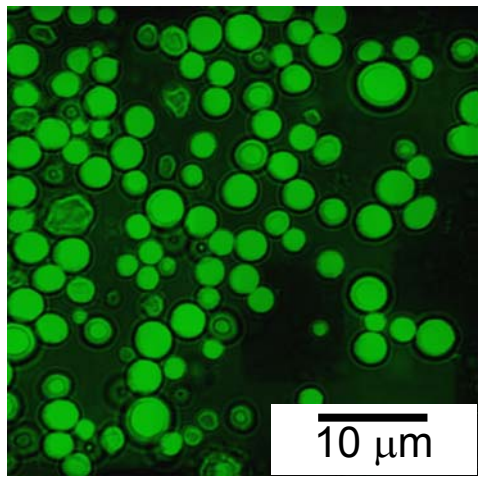
$$\text{Charge Ratio} = \frac{[anion] \times z^-}{[polymer] \times z^+} = 10$$

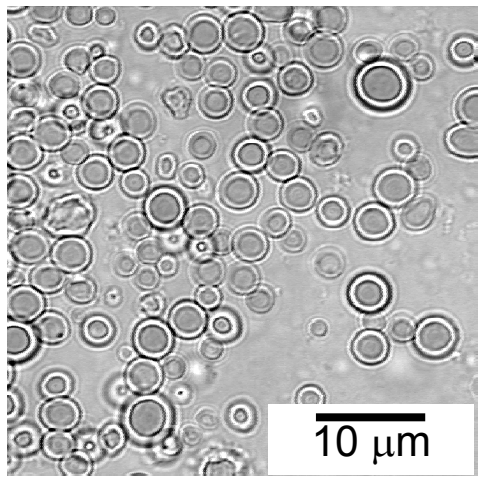
z^- : -ve charge per anion
z^+ : +ve charge per chain

- **Spherical aggregates form at *R* >1**
- **Various polyamines and salts can be used**

Step-2: Self-assembly of Nanoparticles



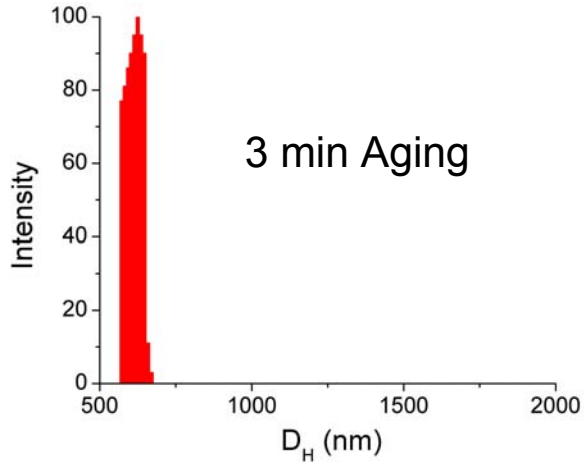




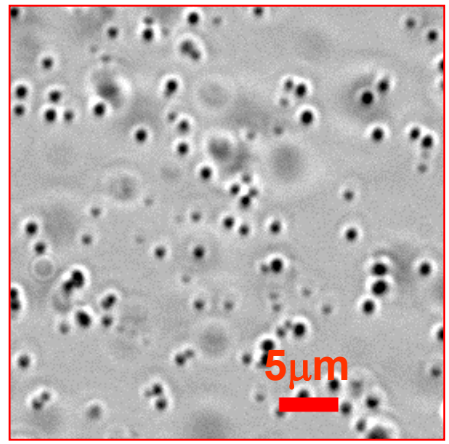
- Rapid formation (<1 min)
- Mild synthesis conditions

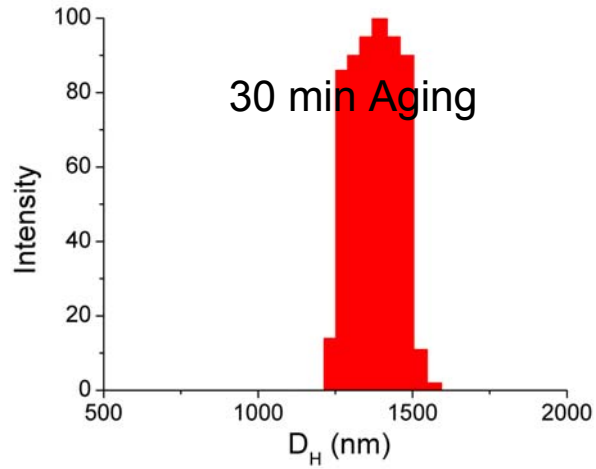
J. Phys. Chem. B 2006, 110, 25619

Effect of aging on microcapsule size

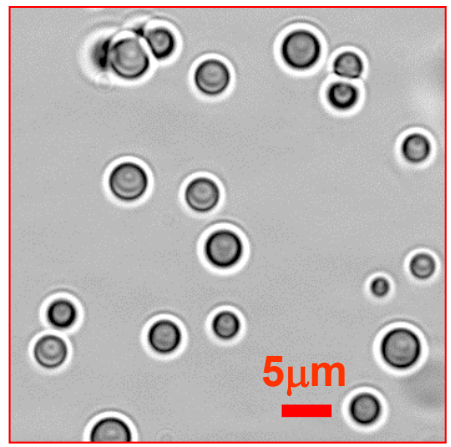


+ SiO_2 NPs





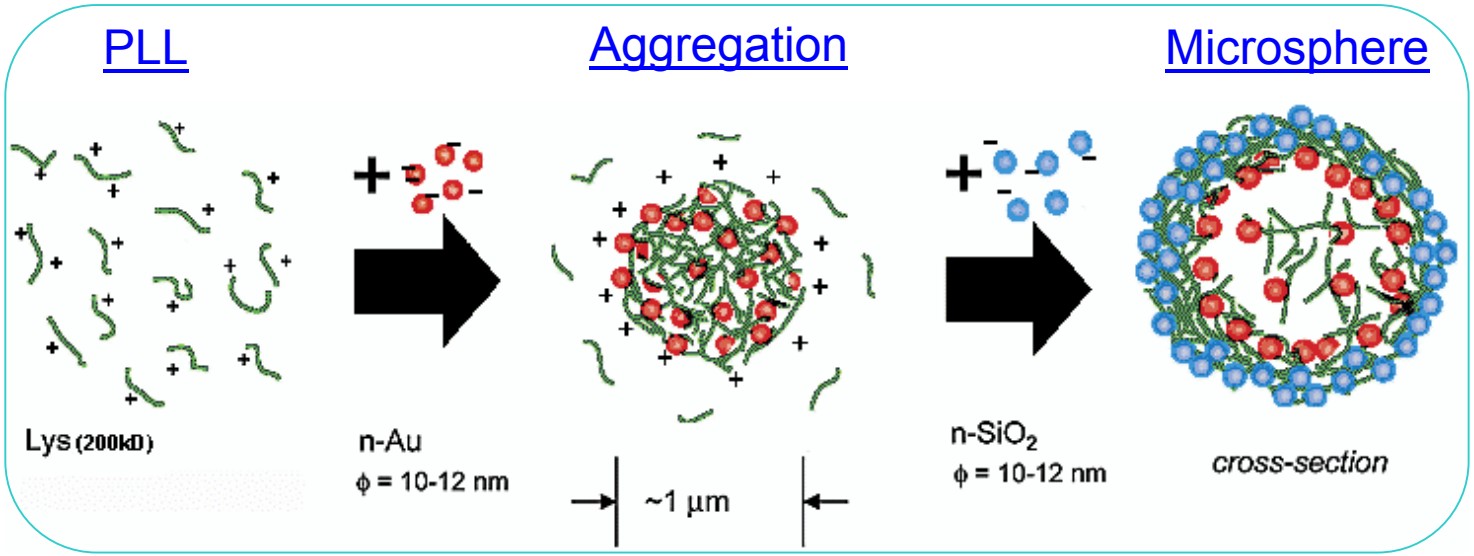
+ SiO_2 NPs



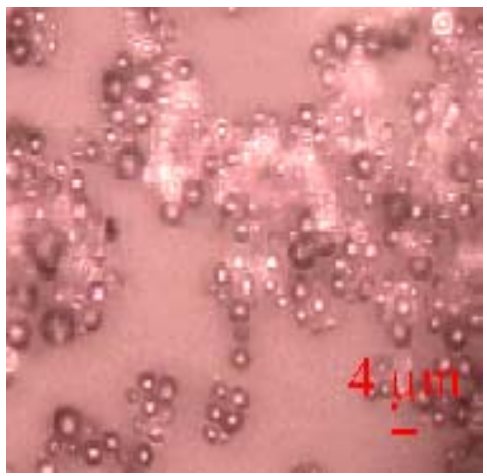
- **Microcapsule size can be controlled by aging of the PAH/salt suspension**

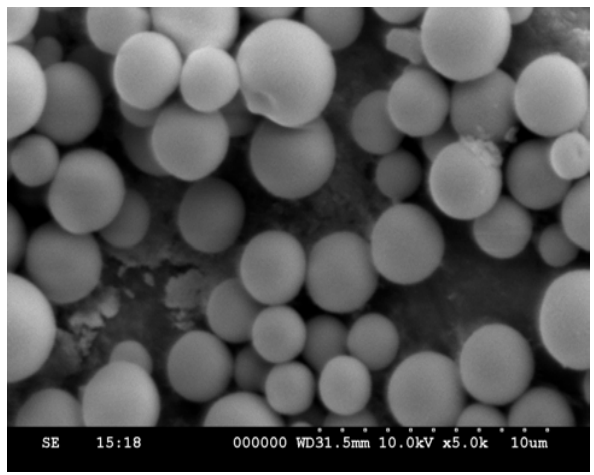
Encapsulation of Nanometals

Two-Step Microshell Formation

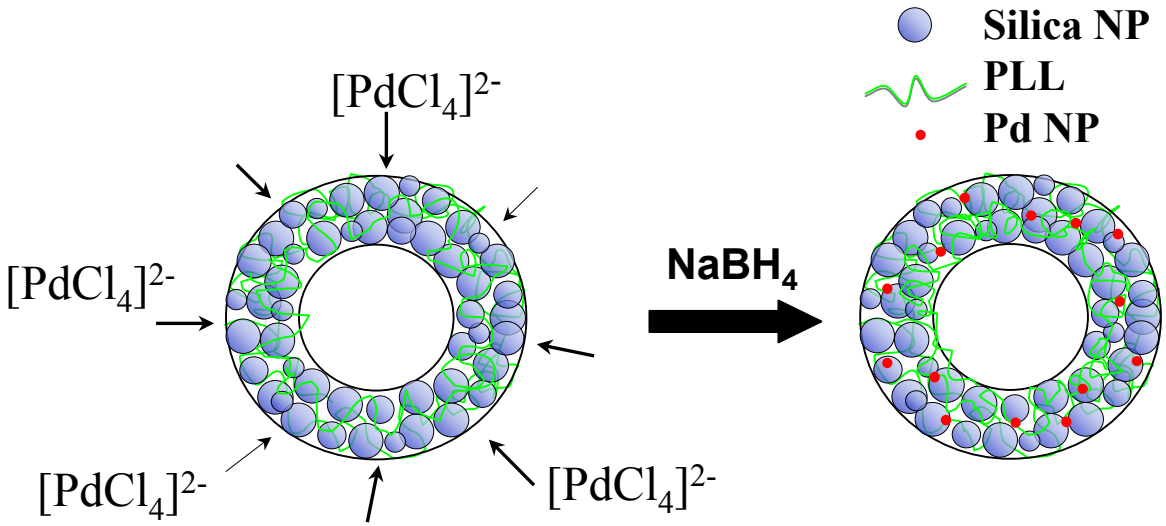


Microcapsules encapsulating Gold nanoparticles

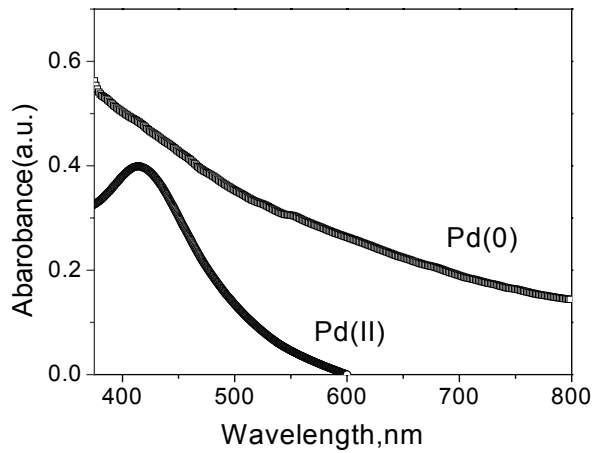




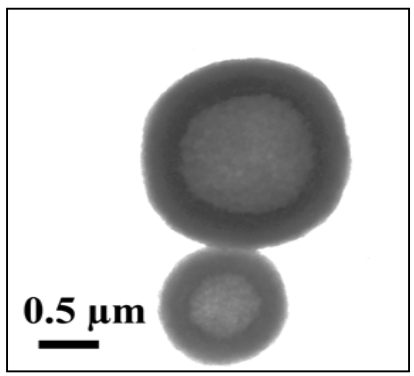
Encapsulation of Nanometals (Pd@MC)

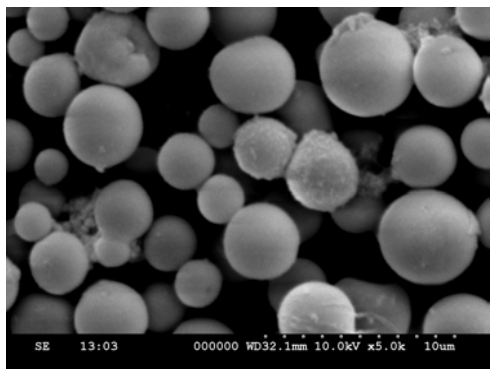


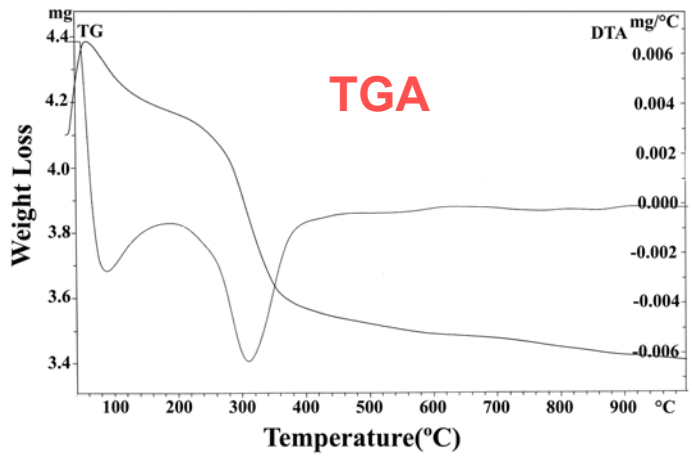
UV-Vis spectra



AAS: Pd content 4.31%





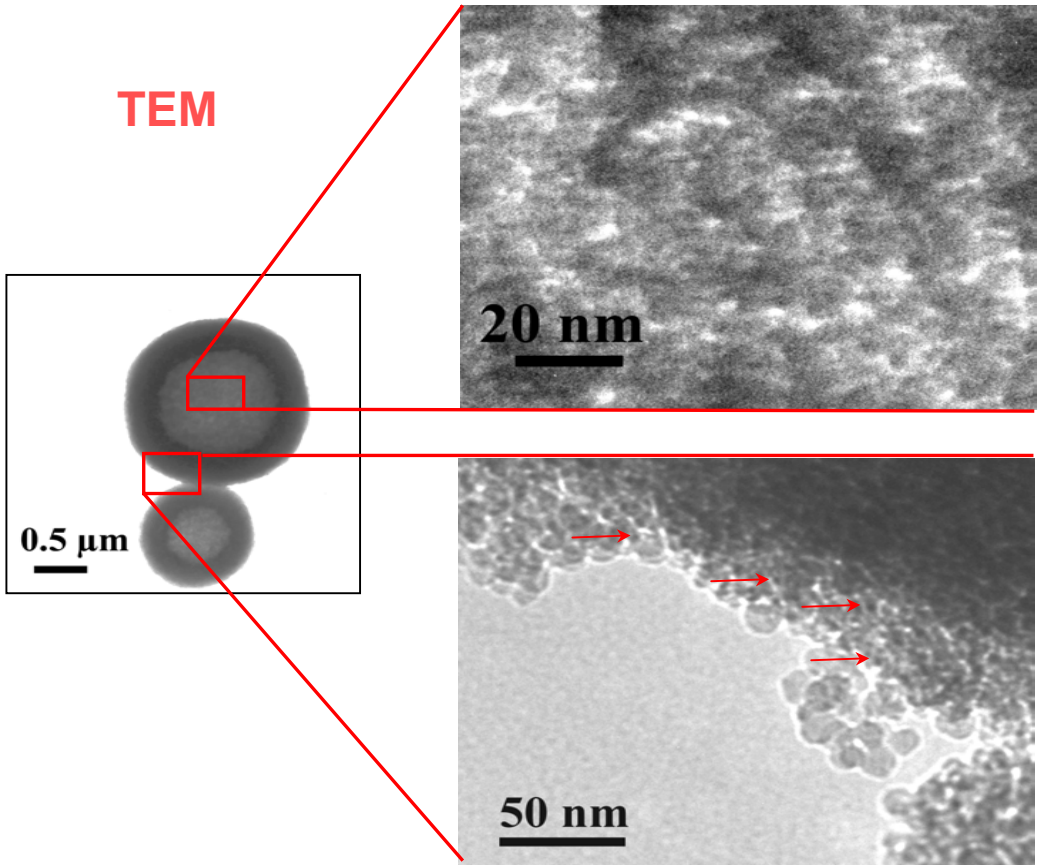


- ***in situ* reduction method**

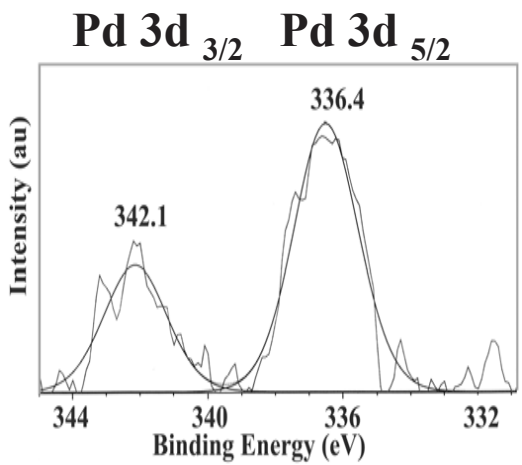
Amali and Rana, *Chemical Communications*, 2008, *4165*

Pd@MC

TEM

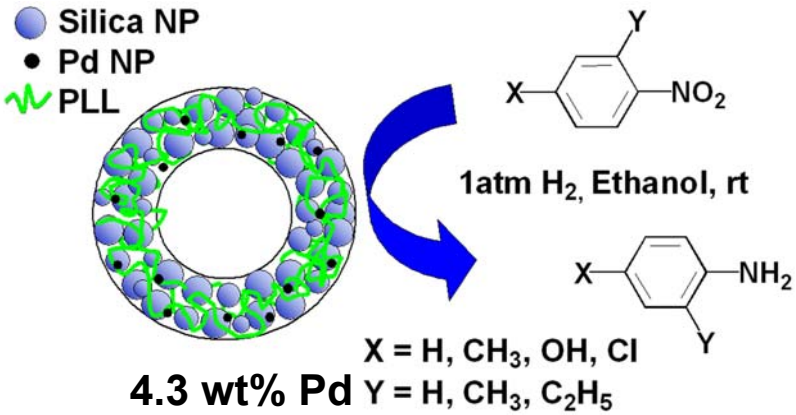


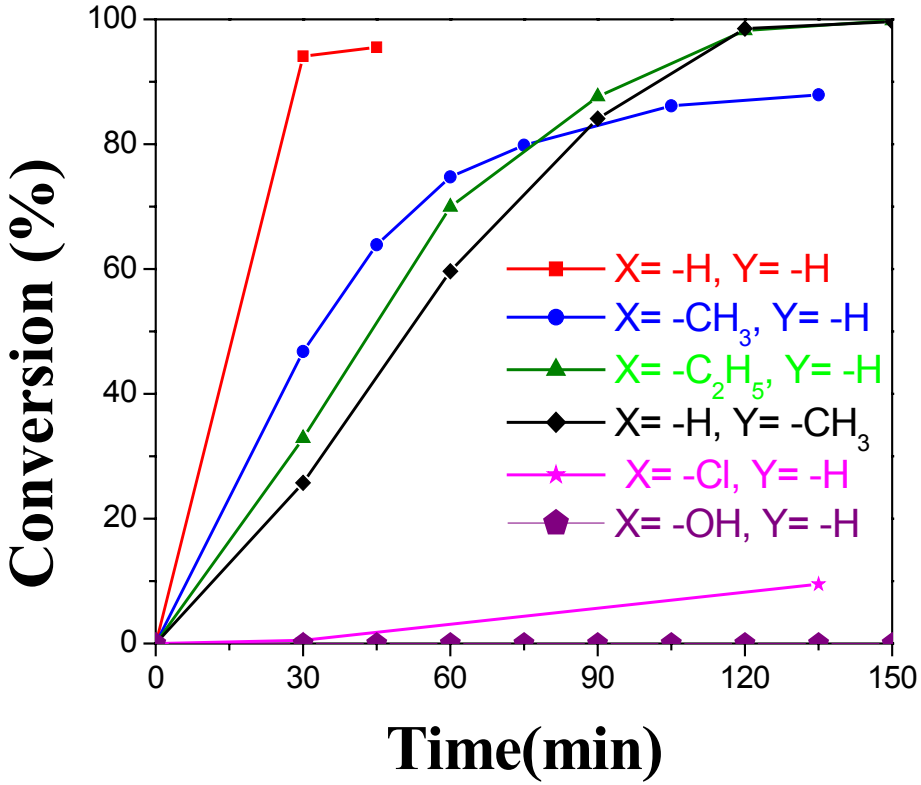
XPS



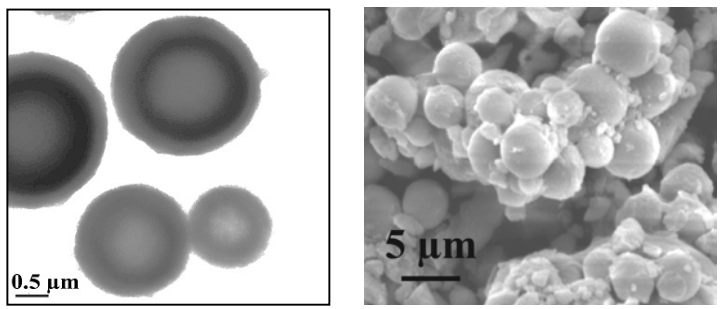
- **Pd is in metallic state and are entrapped in the Microspheres**

Pd@MC in liquid phase organic reactions





Microcapsules after the reaction



- **The catalyst morphology is stable with no change in Pd content**

Catalysts for liquid phase organic reactions

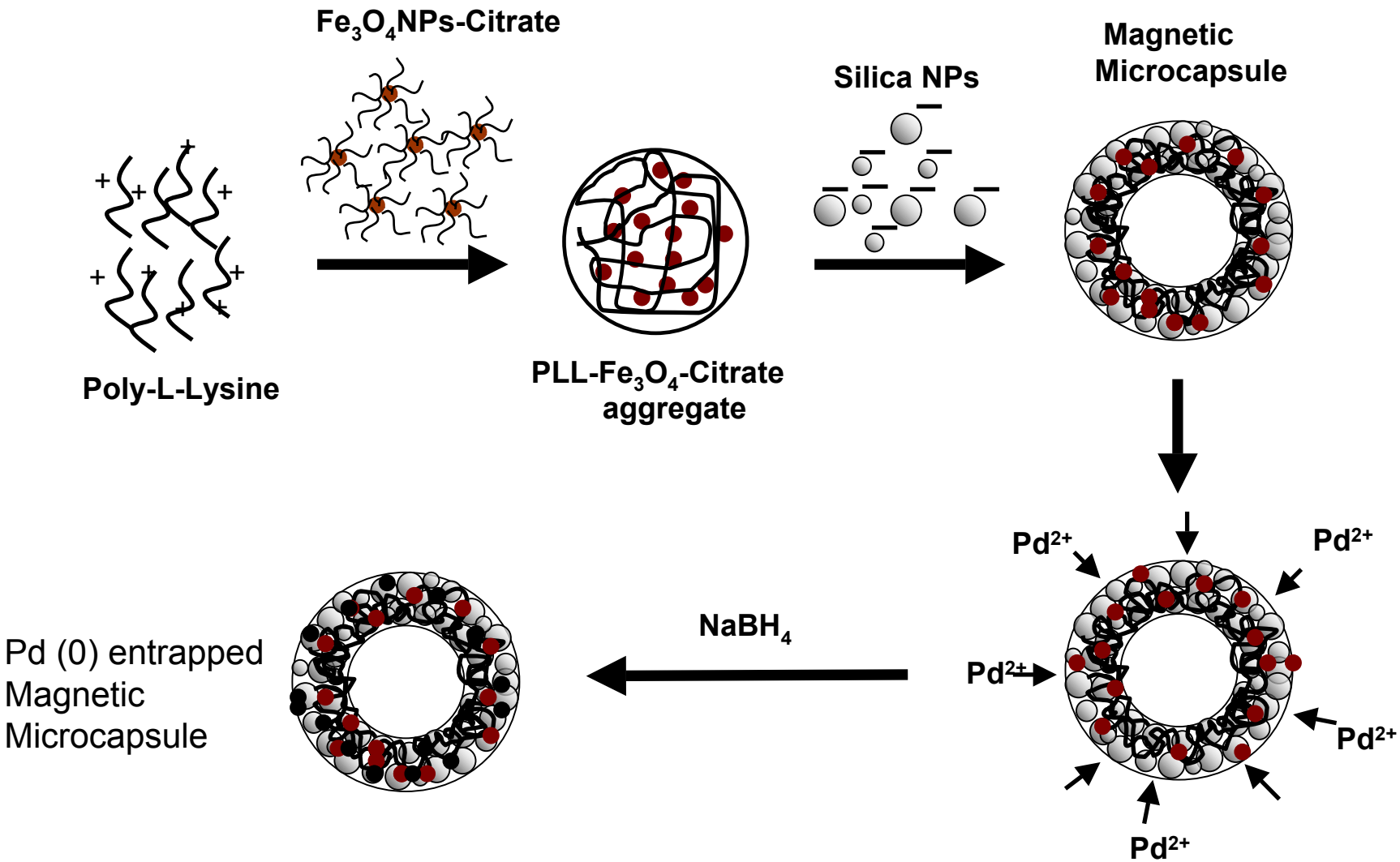
Pd-PLL catalyzed Conversion of nitroarenes

Substrate	Time (min)	Conversion (%)
nitrobenzene	60	>99
p-chloro nitrobenzene	60	> 99
p-nitro phenol	60	> 99

Reusability of the Pd@MC catalyst

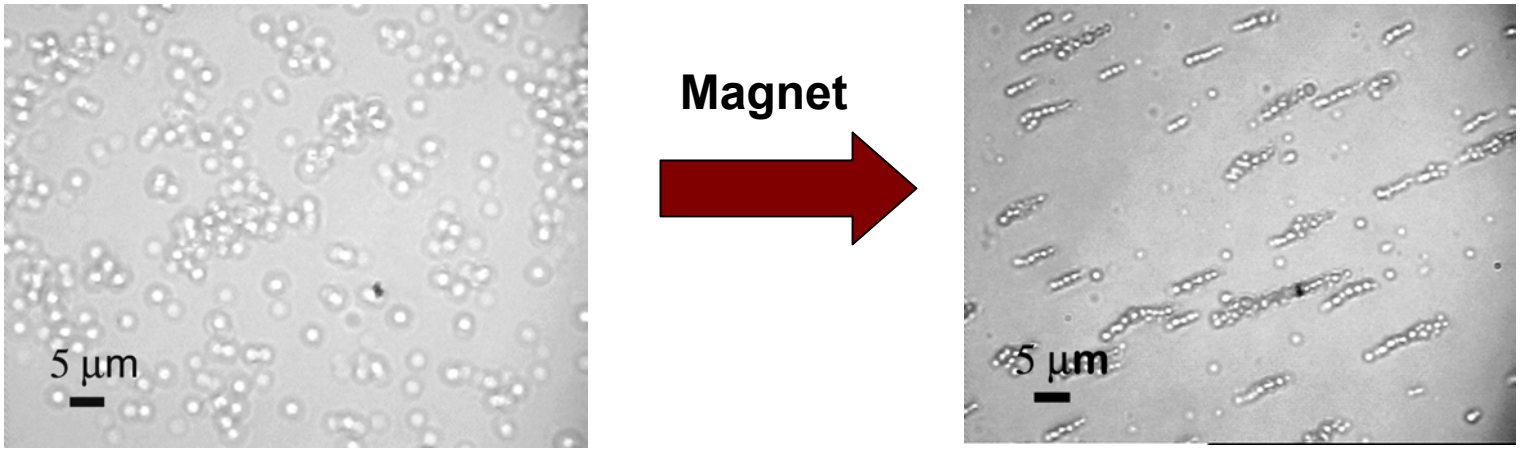
Run number	Conversion(%)
1	> 99
2	> 99
3	> 99
4	> 99
5	> 99

Magnetically separable Pd@MMC

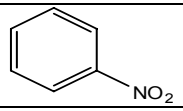
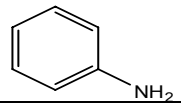
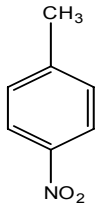
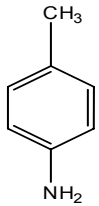
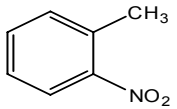
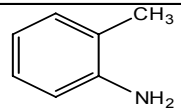
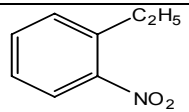
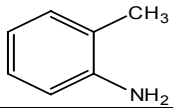
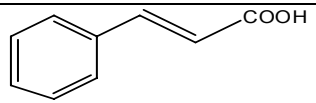
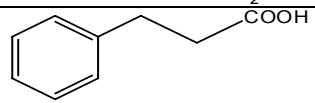
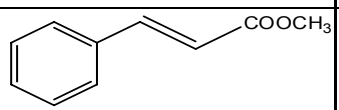
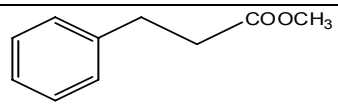
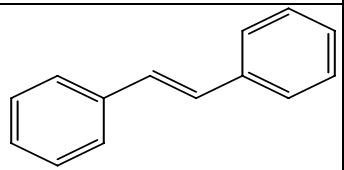
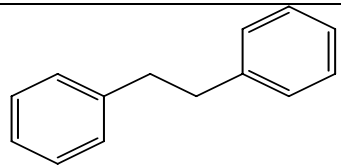
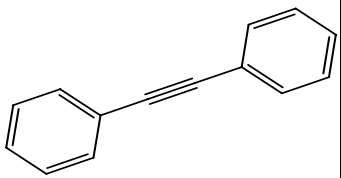
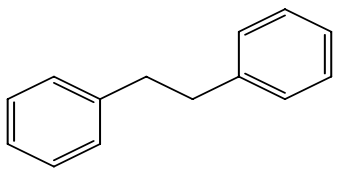


Schematic illustration of the Magnetic Microcapsule formation encapsulating Pd (0) Nanoparticles.

Magnetically separable Pd@MMC



Magnetically separable Pd@MMC

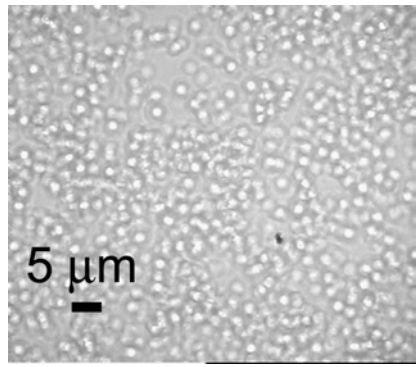
Entry	Reactant	Product	Conversion (%)	Time (min)
1			>99 97[c]	30
2			>99 38[b] >99[b]	30 180
3			>99	30
4			>99	30
5			>99	30
6			>99	30
7			>99	30
8			>99	30

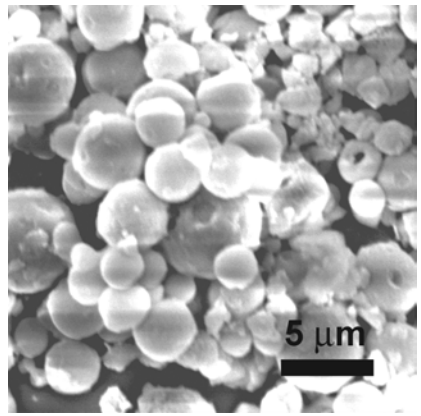
Pd-2.98 wt% (AAS)

Reaction Condition: 0.050 gm Pd@MMC, 0.5mM reactant, 5 ml EtOH,H_2 1atm

b- Pd/C 10wt%; c- Conversion in 5th cycle

Pd@MMC-After 5 runs

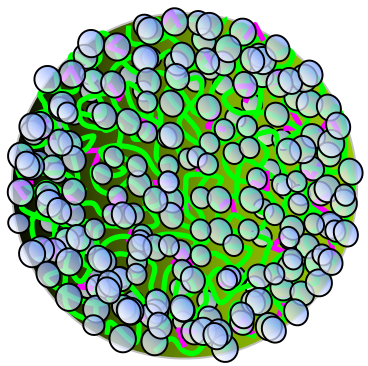




Summary

- Polyamines are used to anchor Pd NPs on to Fe_3O_4 NPs
  - » Exhibited good catalytic activity for hydrogenation reactions
  - » Magnetically separable catalyst
  - » Good reusability
- Microcapsules assembled using Polyamine and SiO_2 NPs
  - » Encapsulation of metallic NPs
  - » Encapsulation of citrate functionalized Fe_3O_4 NPs
  - » Easily separable and recyclable catalyst
  - » Selectivity

Lab in a Particle



- Multi-catalytic sites
- Morphology & Porosity
- Surface functionality
- Selectivity
- Enzyme encapsulation

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Ms. Arlin Jose Amali

Mr. Joydeb Manna

Prof. B. Viswanathan

Thank You