Синтез нанокомпозитного материала Pd/PPy и его применения в органическом катализе

Воротынцев М.А., **Золотухина Е.В.**, **Магдесиева Т.В.**

Université de Bourgogne - CNRS, Dijon, France

МГУ, химфак, Москва

ИПХФ РАН, Черноголовка

РХТУ, Москва

Inorganic nanoparticles: new physical and chemical properties

Requirements:

- Uniform and controlled size of nanoparticles
- High density of particles in space
- Stability to aggregation (metals!)

Protective (solid / liquid / adsorption) layers

Strong effect on properties of particles

Need in "inert" stabilizing means

Composite materials

Polymer + incorporated inorganic nanoparticles
Transition metals, their oxides, salts…

Applications:

- Micro/nanoelectronic elements
- Sensors
- Nonlinear optics
- Catalysis
- Electrocatalysis (fuel cells…)

Nanocomposites: conjugated polymer-metal

Conjugated (conducting/electroactive) polymers:

Polypyrrole, polythiophene, polyaniline, polycarbazole

- Inexpensive materials
- Simple synthesis (chemical or electrochemical polymerization)
- High environmental stability
- Controllable morphology and physicochemical properties
- Electronic conductivity and redox activity
- High (nano)porosity
- Thermal stability

Synthesis of nanocomposite materials: metal/conducting polymer

Electrochemical method-1:

1) Electrodeposition of polymer film. 2) Electrochemical or chemical decomposition of metal precursor

Electrochemical method-2:

1) Synthesis of nanoparticles. 2) Solubilization. 3) Electropolymerization + incorporation

Chemical method:

1) Synthesis of nanoparticles. 2) Solubilization. 3) Chemical polymerization

Our goal:

To synthesize composites where monodisperse metal nanoparticles without a protective layer are uniformly distributed with high density inside conjugated polymer

One-step chemical synthesis

Redox reaction between a conjugated monomer (reductant) and a metal precursor (oxidizer)

Rapid sedimentation

Reaction medium: (micro)emulsion?

Particles with covered surface

One-phase medium + low concentrations?

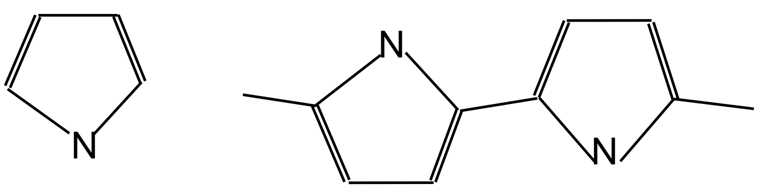
S. V. Vasilyeva, M. A. Vorotyntsev et al
J. Phys. Chem. C, 2008, **112**, 19878

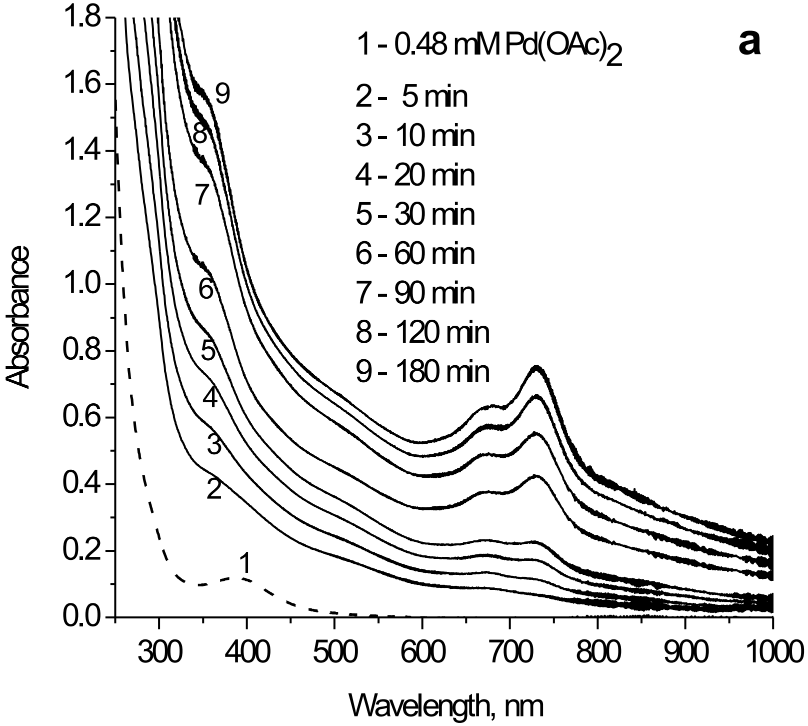
Composite polypyrrole - palladium

Reaction:

$Pd^{+2} + Py = Pd(0) + PPy + 2\ H^{+}$?

dilute $Pd(OAc)_2$ + excessive Py in AN





Colloid formation:
PPy globules

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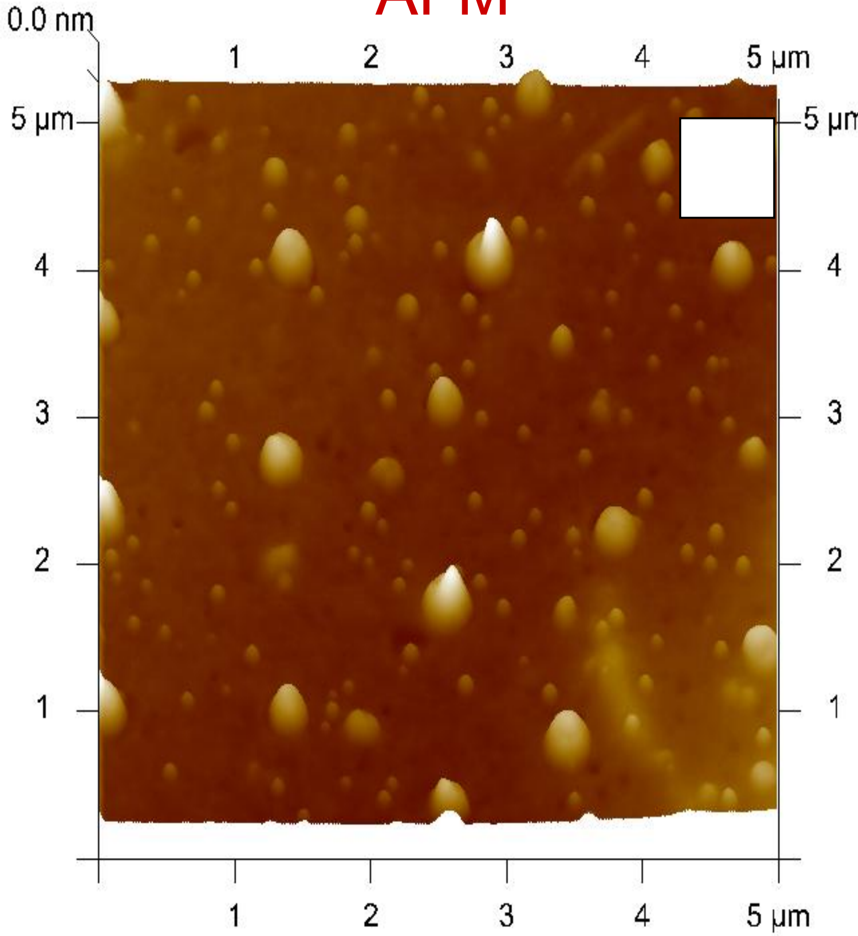
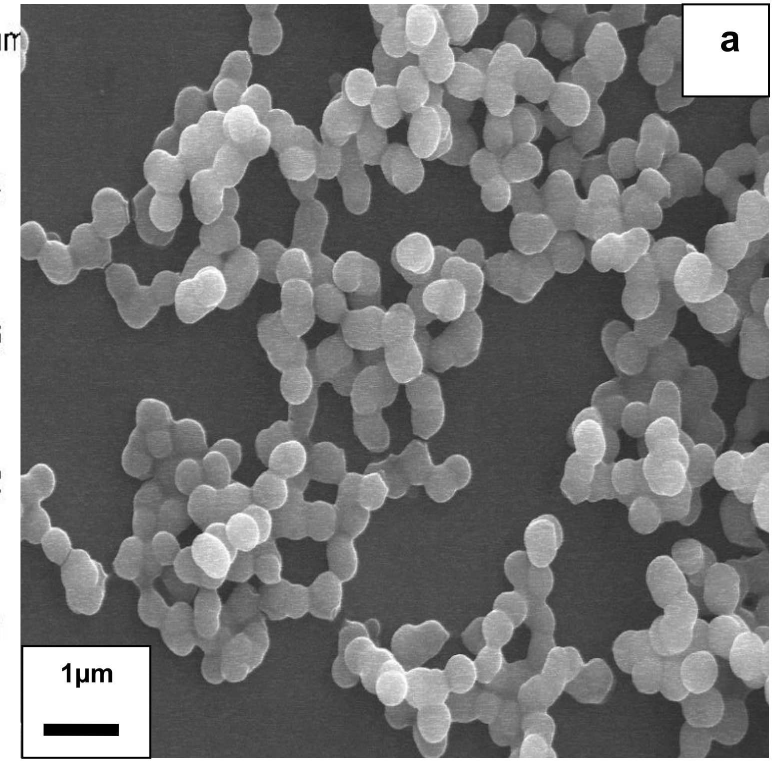
Composite polypyrrole - palladium

AFM



SEM



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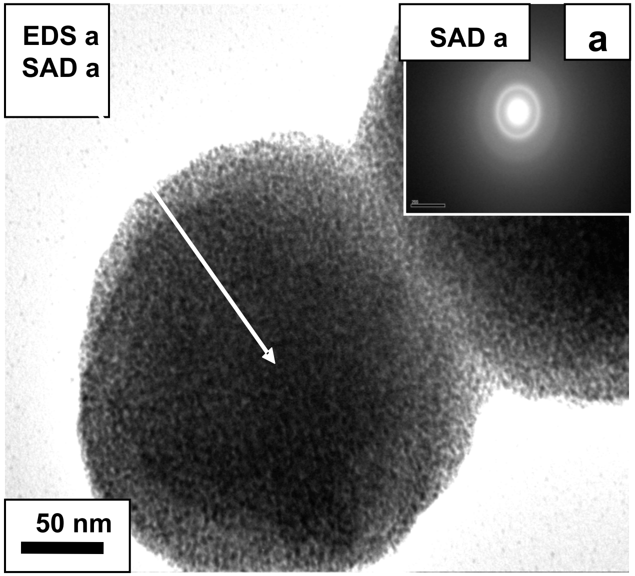
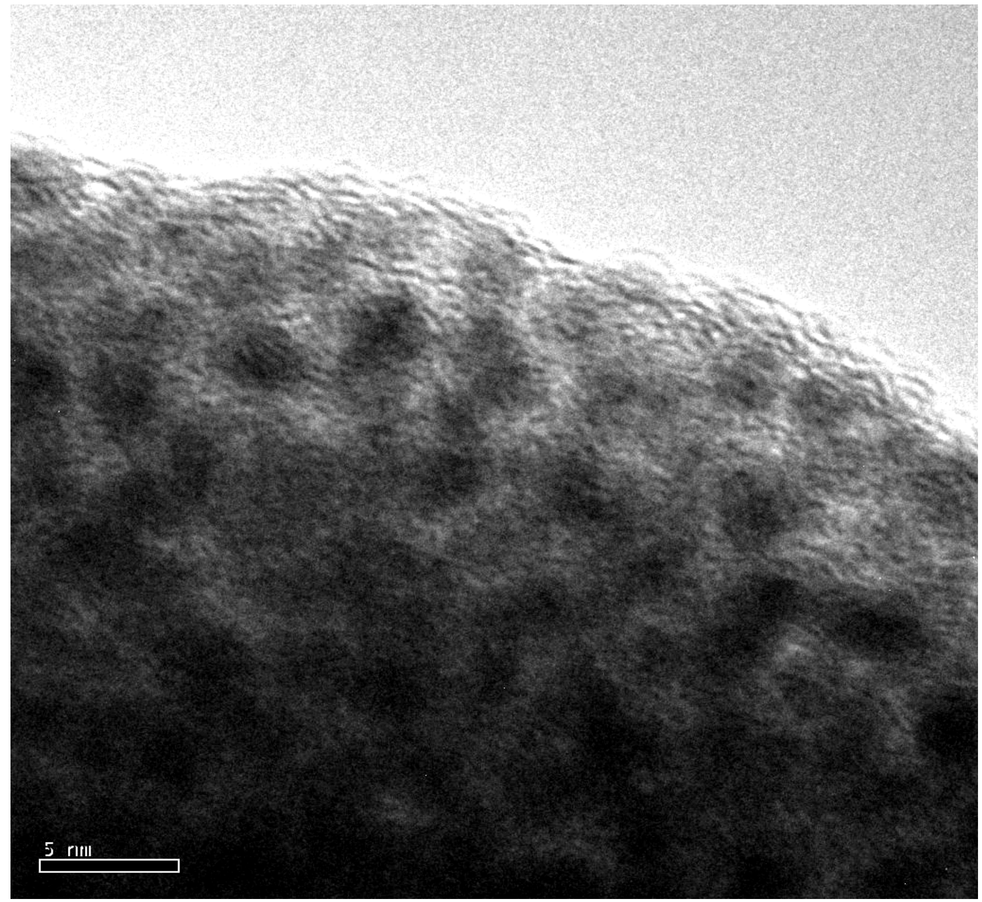
Composite polypyrrole - palladium



EDS-SAD

TEM



d(PPy): 200 nm;
d(Pd): 2-3 nm

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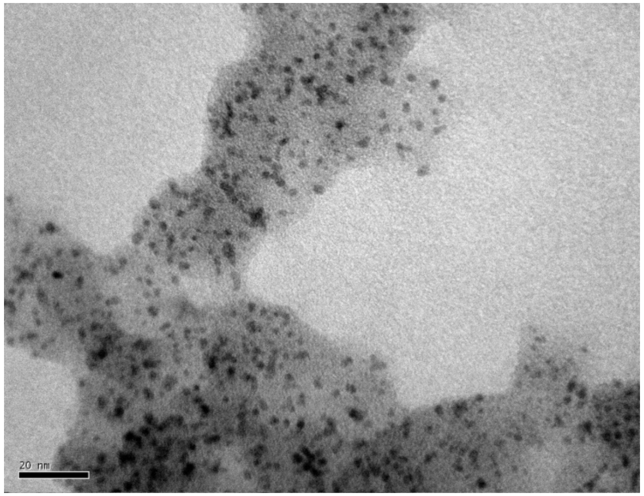
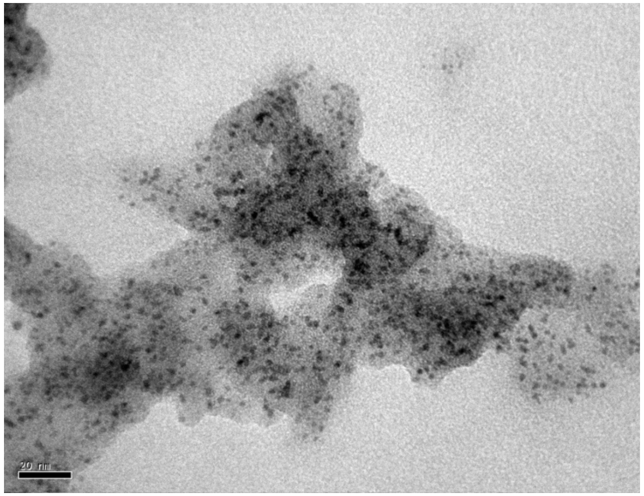
Composite polypyrrole - palladium

Reaction: dilute $Pd(OAc)_2$ + excessive Py in water

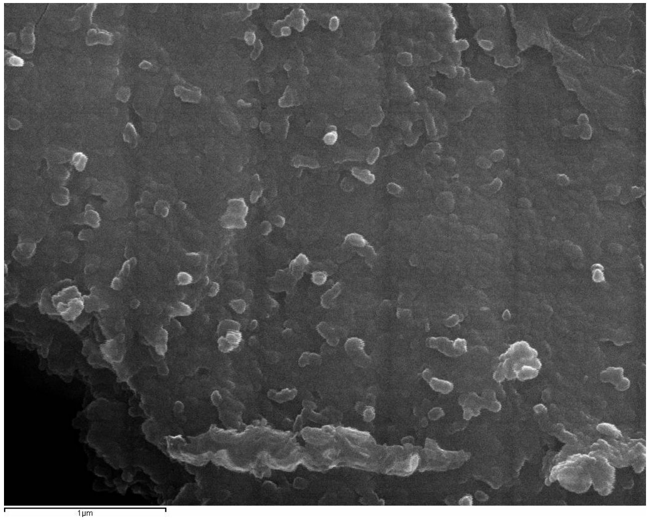
TEM





d(PPy): 20-150 nm;
d(Pd): 2-3 nm

SEM



XPS + ICP: 20-25 wt. % Pd

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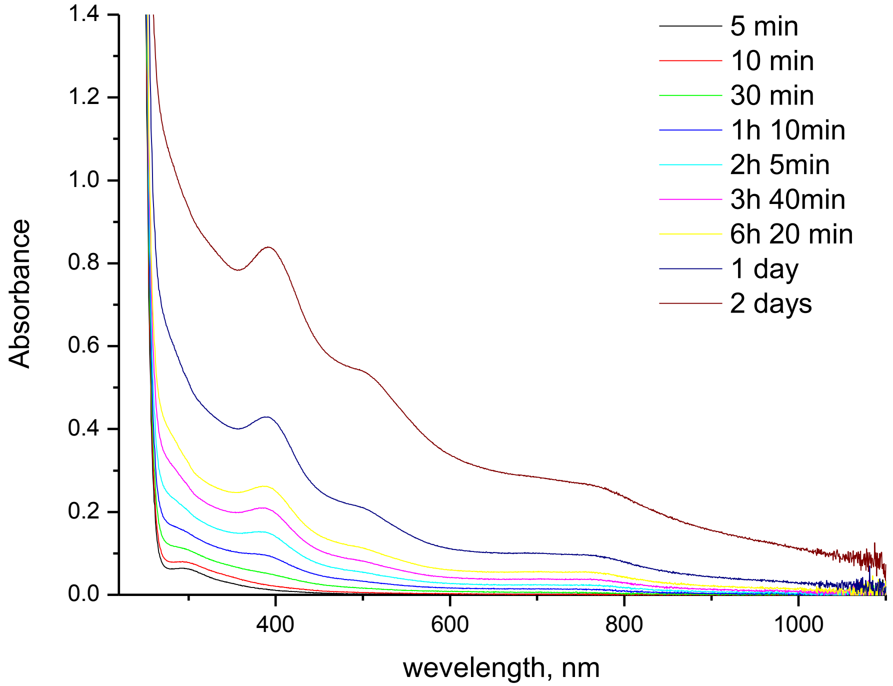
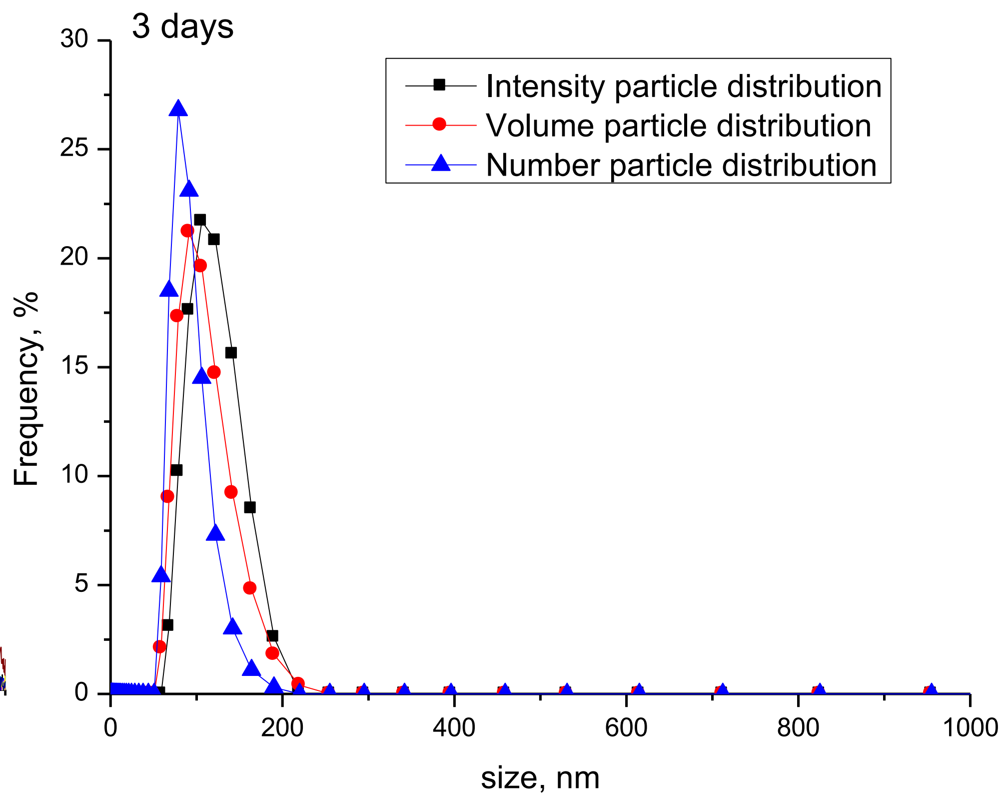
Adv. Funct. Mater., 2011, **21**, 1064

Composite polypyrrole - palladium

Reaction: dilute $Pd(NH_3)_4Cl_2$ + excessive Py in water





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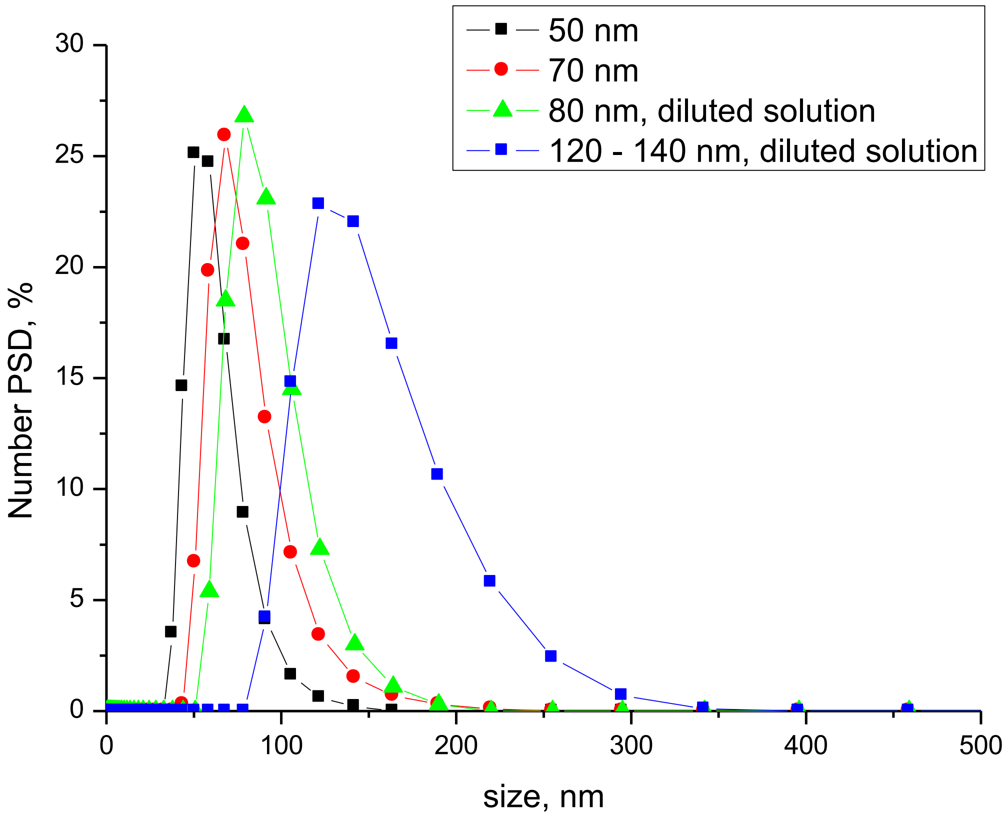

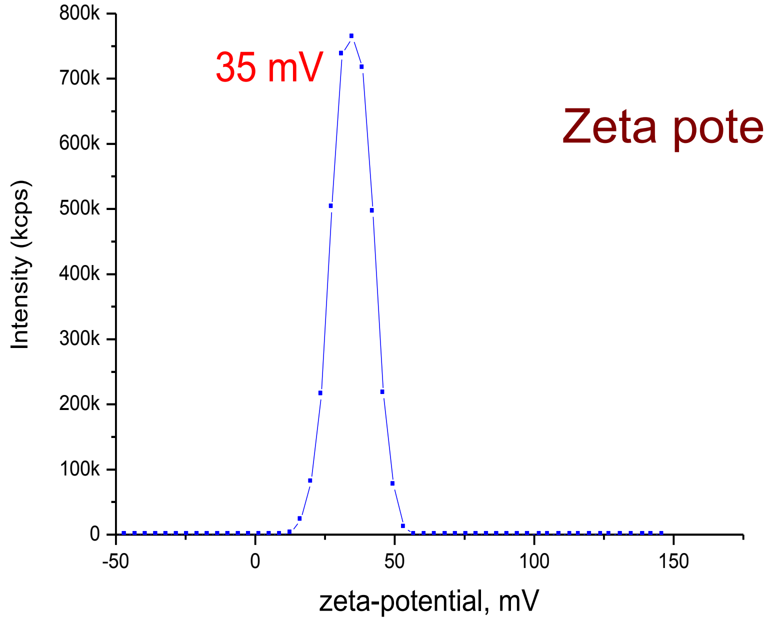

Zeta potential

Thanks to Dr. Chaumont for the help in measurements

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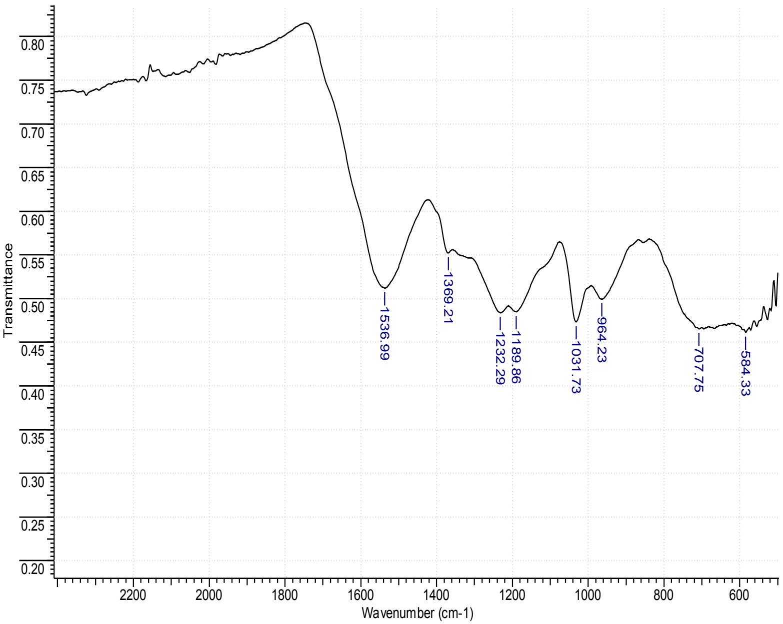
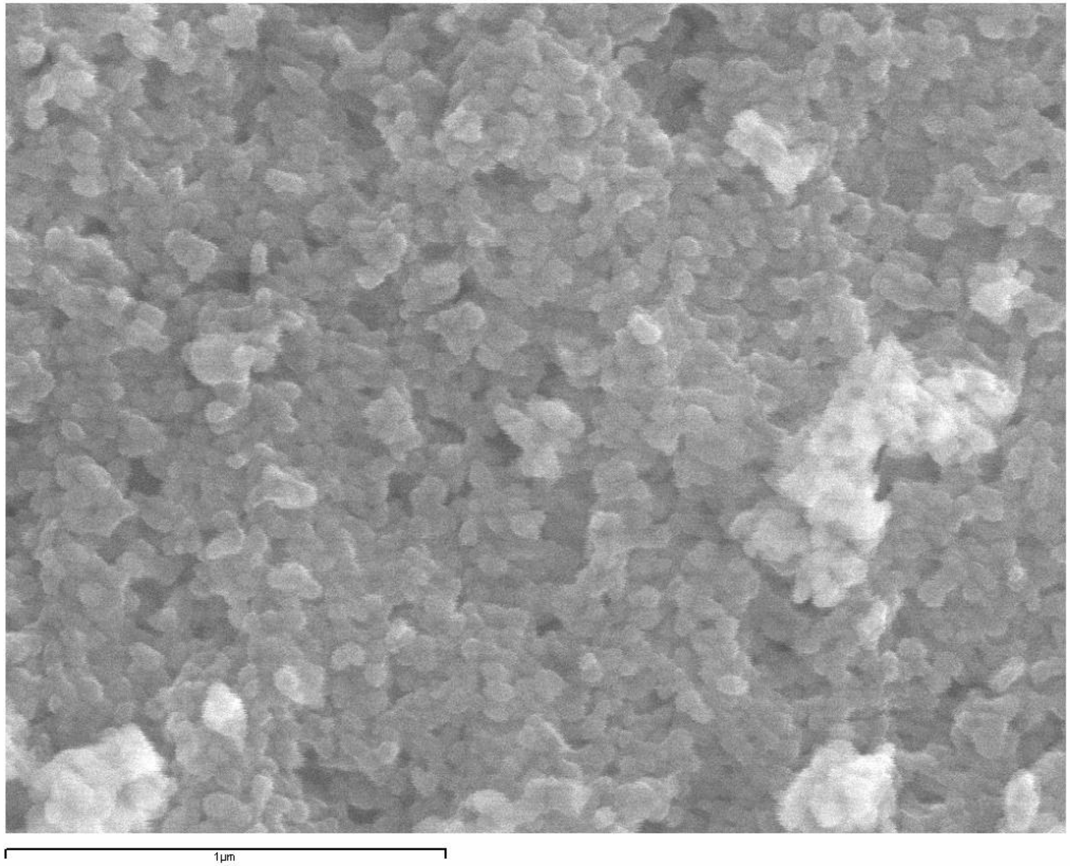
Composite polypyrrole - palladium

Reaction: dilute $Pd(NH_3)_4Cl_2$ + excessive Py in water

IR-ATR



SEM



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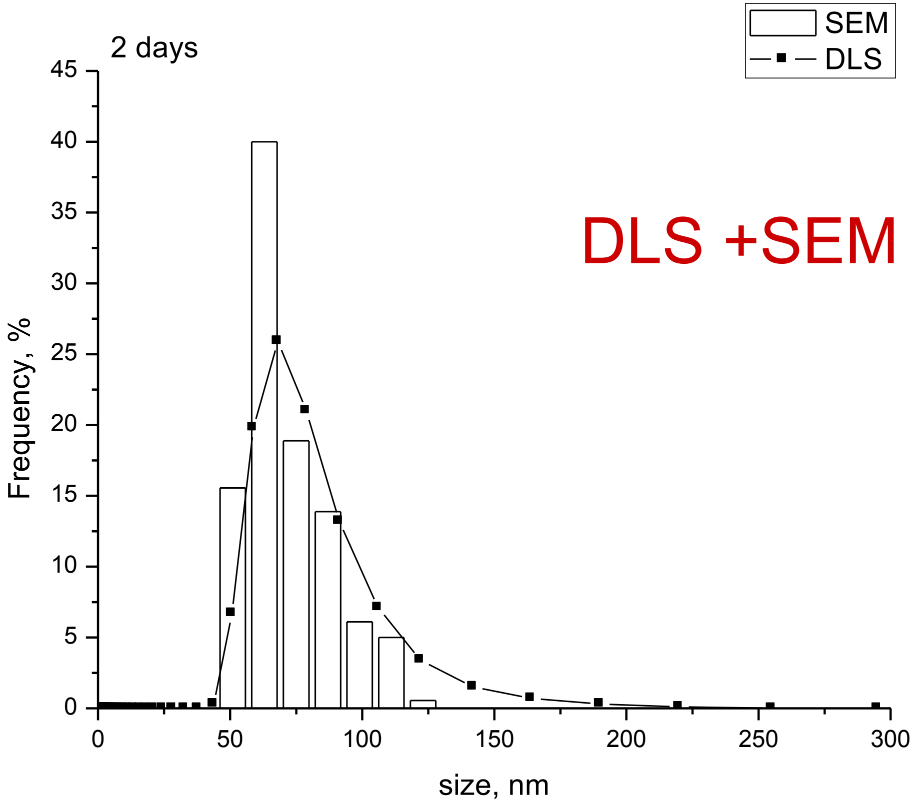

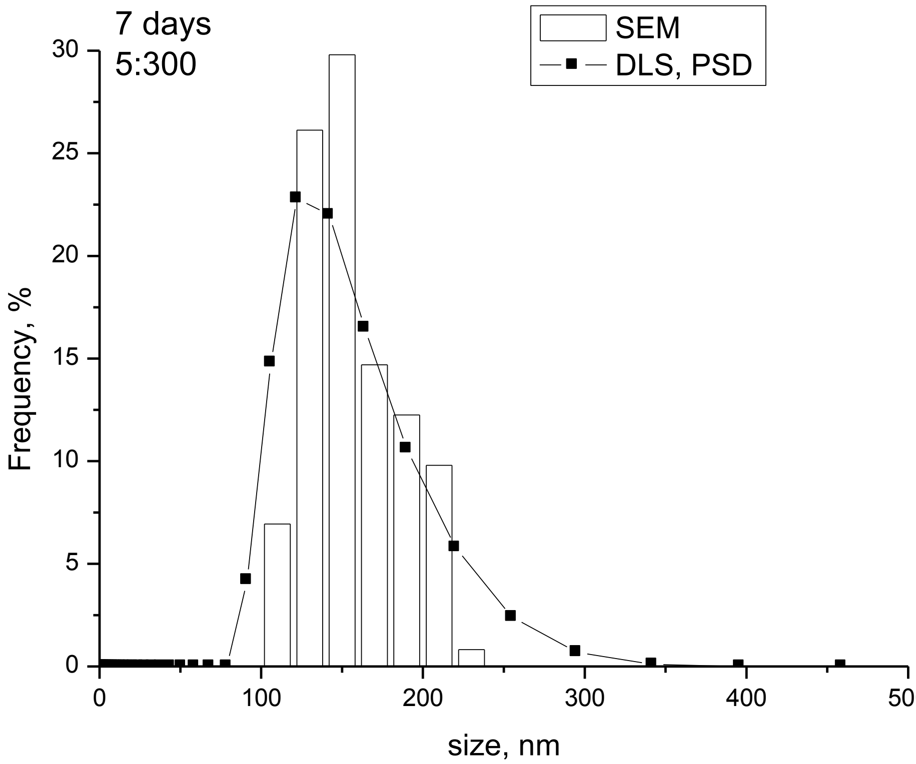

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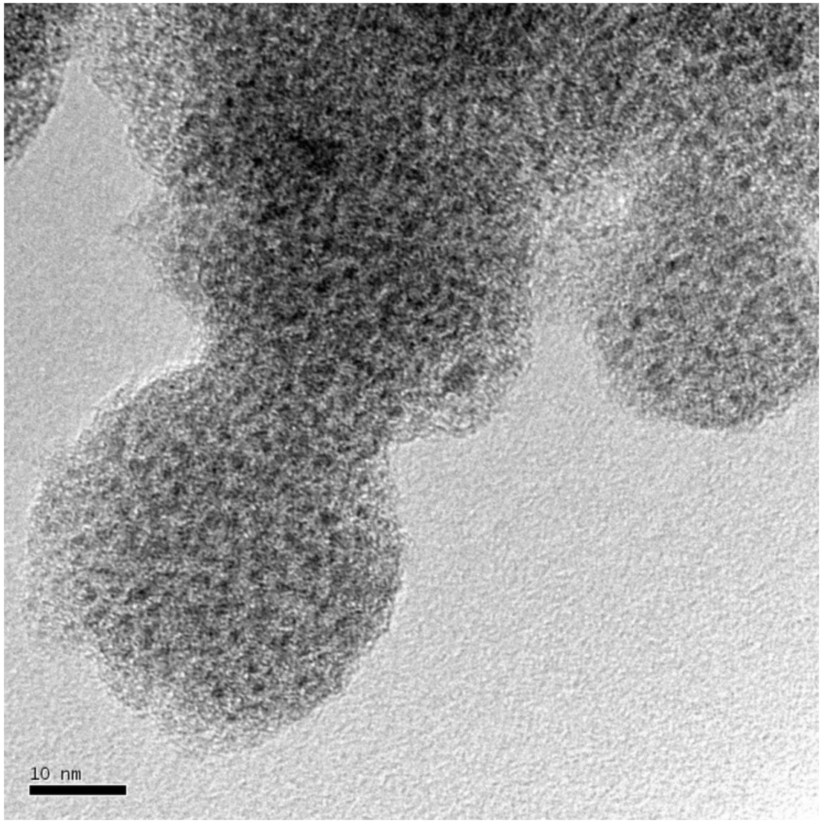
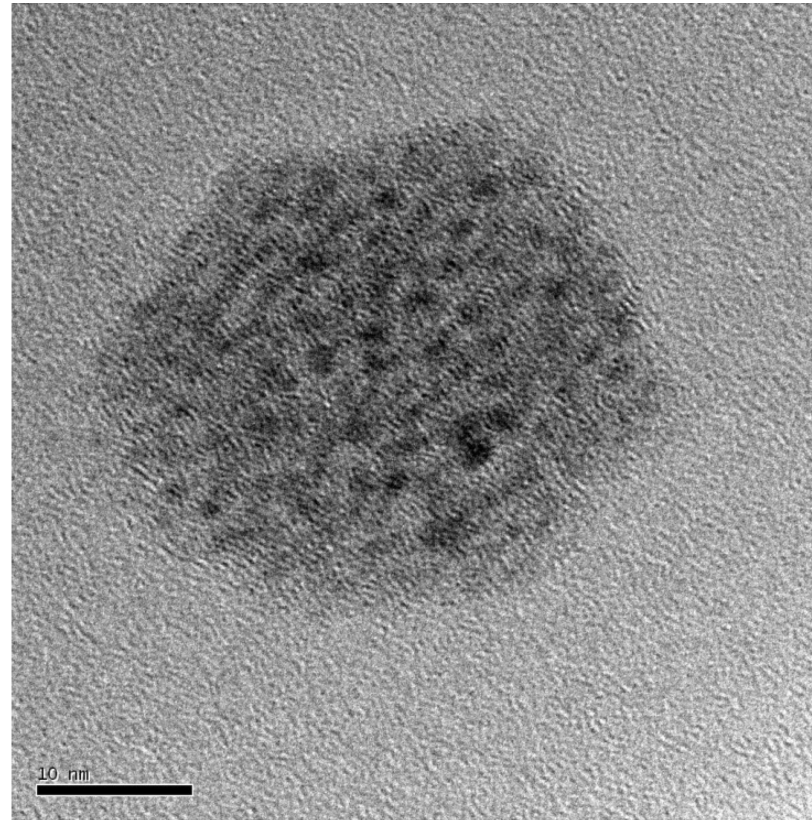


TEM



Polypyrrole particles : 30-150 nm

Nanoparticles of Pd : < 2 nm (constant!)

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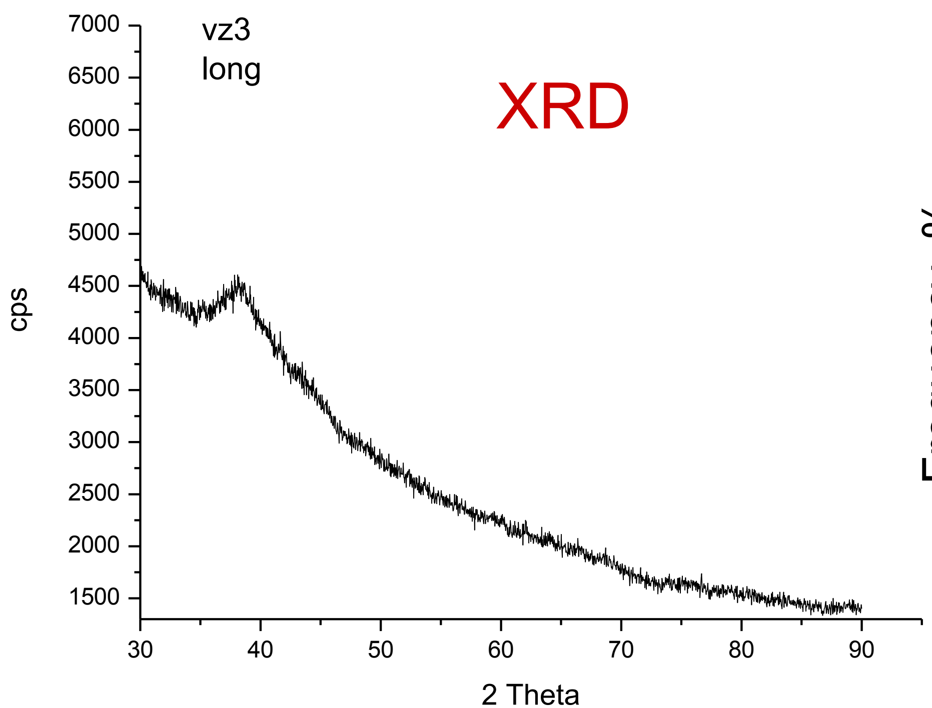
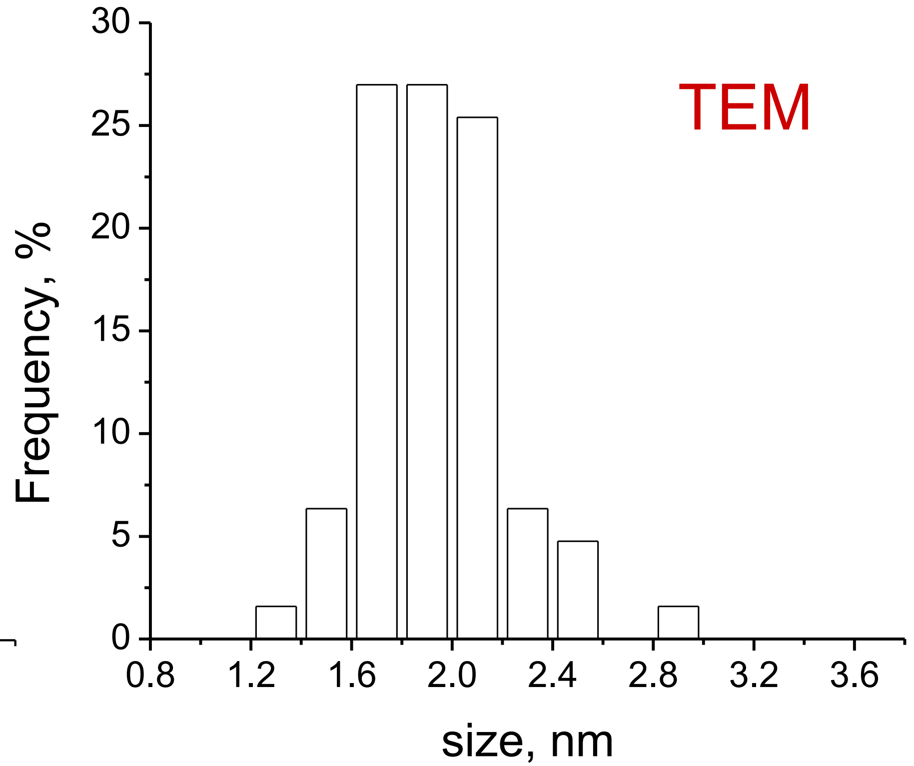
Adv. Funct. Mater., 2011, **21**, 1064

Composite polypyrrole - palladium

Reaction: dilute $Pd(NH_3)_4Cl_2$ + excessive Py in water





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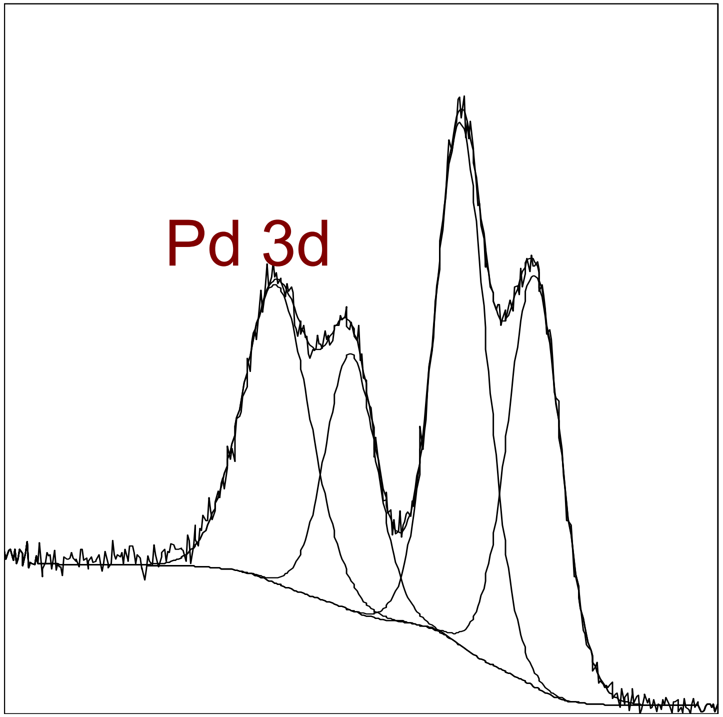
Composite polypyrrole - palladium

Reaction: dilute $Pd(NH_3)_4Cl_2$ + excessive Py in water

XPS



Chemical composition:
XPS, EDX, ICP, CHNS
Pd: 35-40 wt.%

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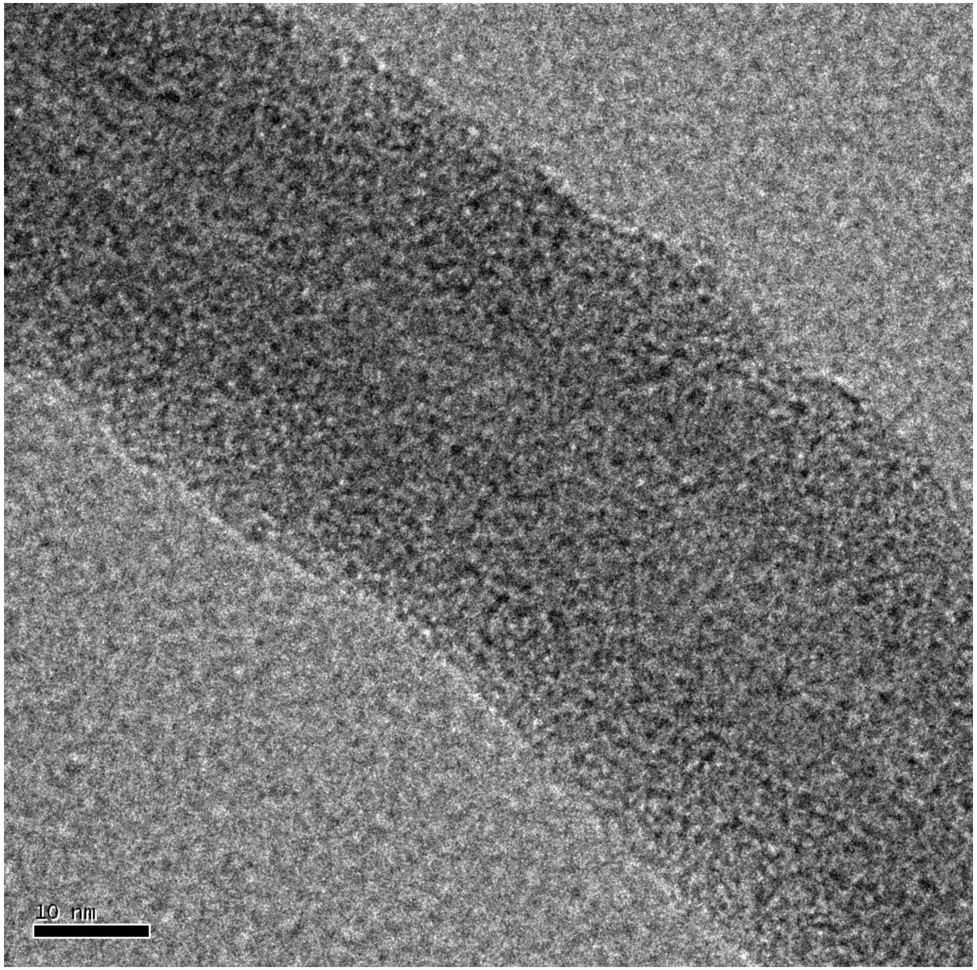
Composite Pd/PPy/CNT:
polypyrrole – palladium - carbon nanotubes



Conclusions

Simple, inexpensive and well-reproducible method towards nanocomposite materials with conjugated polymer matrix via one pot and one step procedure.

Broad range of materials: dispersed elements of transition metals (Pd), salts (Prussian Blue, CuI)…

Formation of great number of Pd nanoparticles uniformly dispersed inside PPy matrix.

No protective layers around Pd particles.

Sizes of both polypyrrole spheres (30–150 nm) and Pd particles (1.2–3 nm): controlled by reaction conditions.

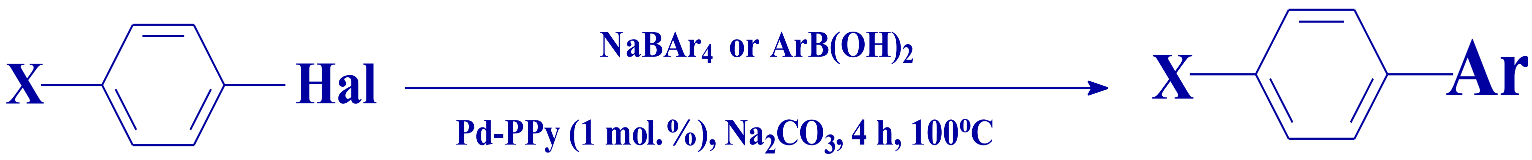
II

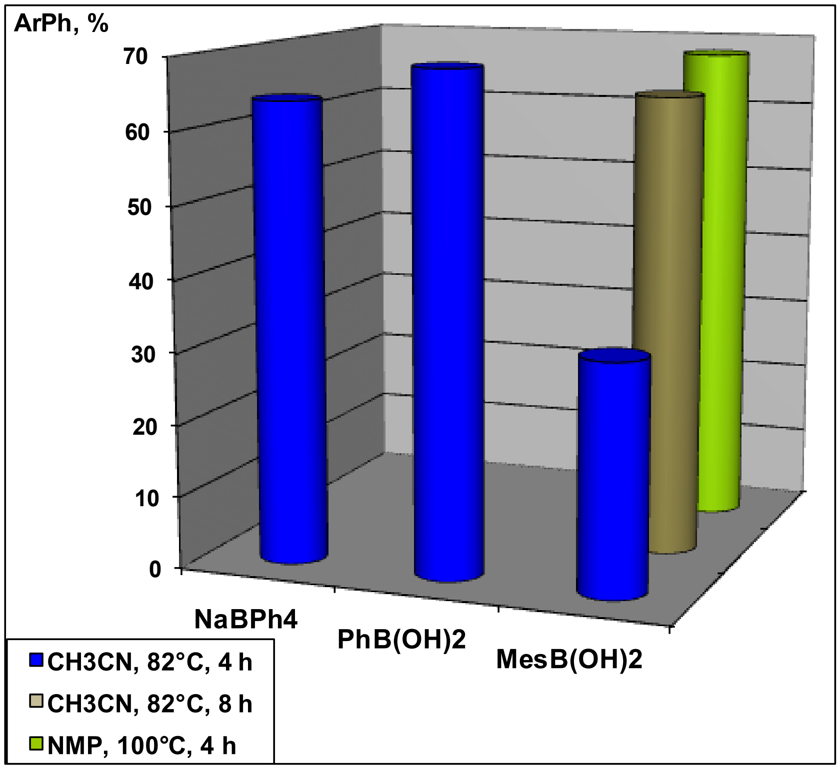
Pd-полипиррольный нанокомпозит как катализатор образования С-С связи

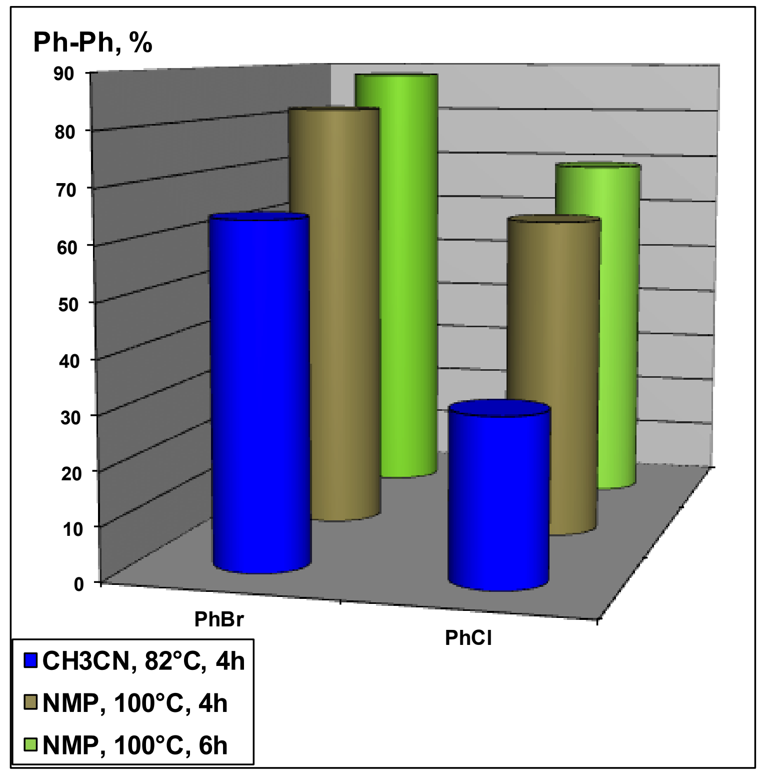
Преимущества Pd/PPy нанокомпозита:

- Каталитическая поверхность, свободная от адсорбатов
- Система вариабельна в плане геометрических параметров частиц (***d PPy глобул (28 и 93 нм), d частиц Pd (1.2 – 1.4 нм), содержание Pd в глобулах (34 и 42 масс. %)***)
- Отсутствие токсичных лигандов
- Композит устойчив в водном растворе

Test-reaction - Suzuki coupling

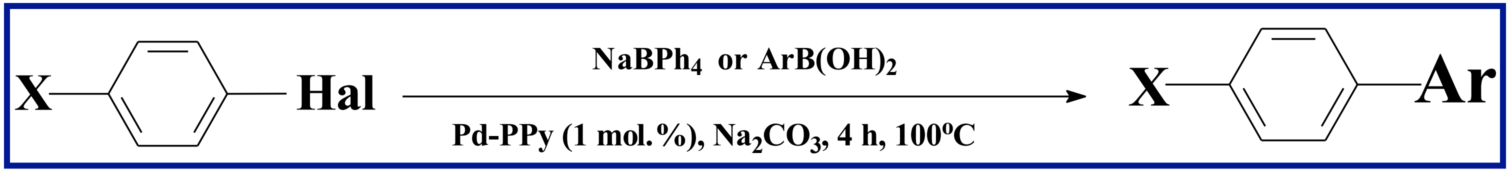


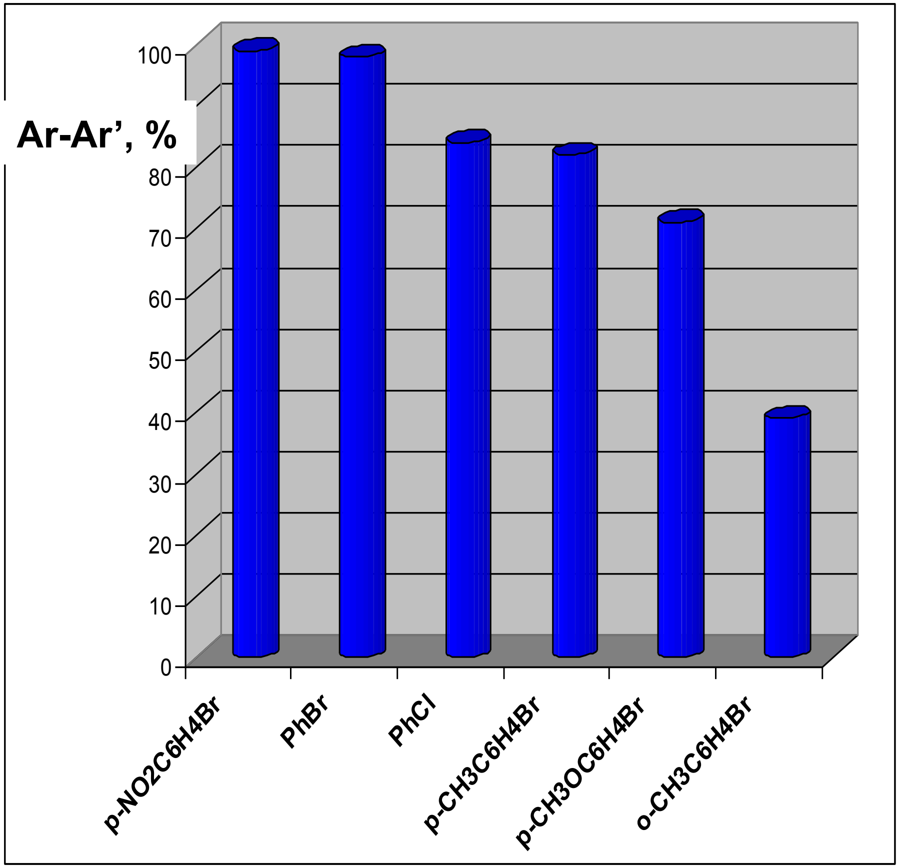




PPy spheres: 93 nm, Pd nanoparticles: 1.3 nm,
Pd content in the globule : 34 wt.%

Various aryl halides in Suzuki coupling with $NaBPh_4$



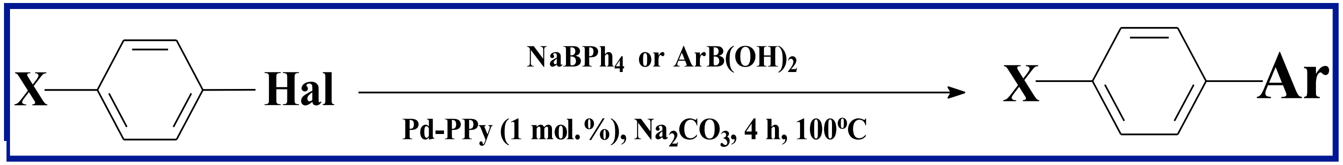


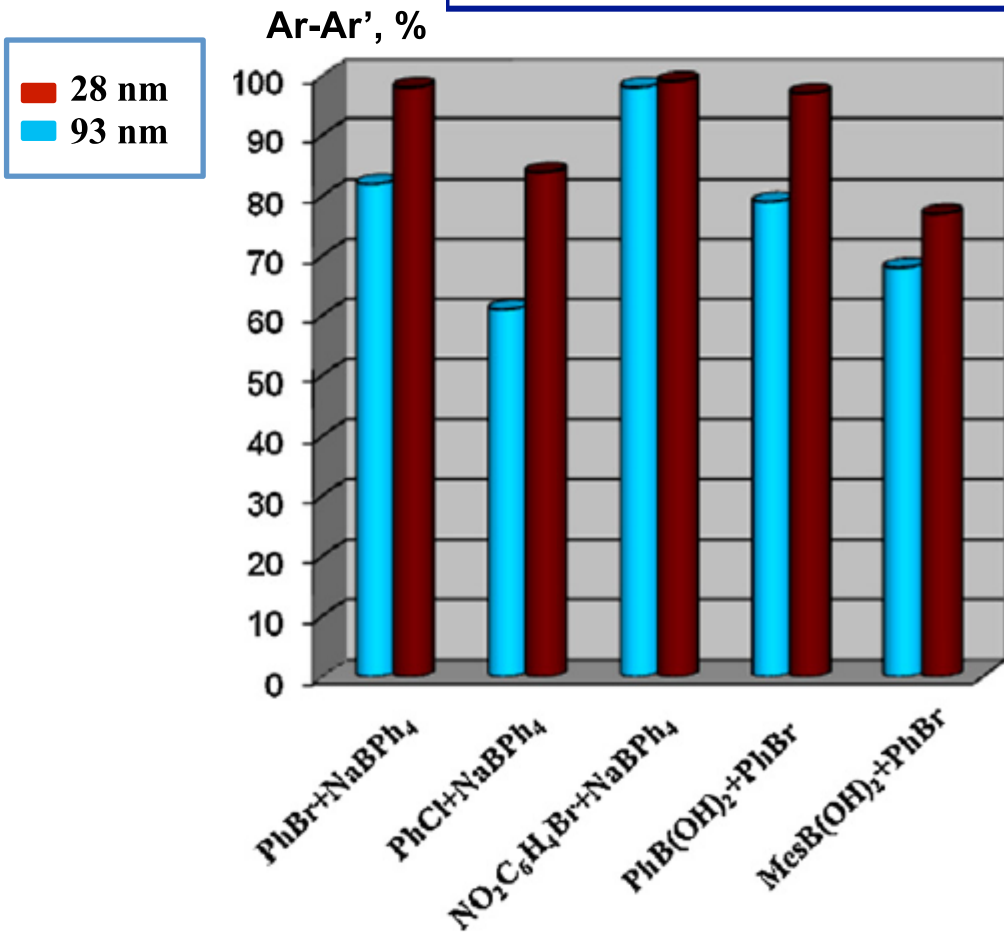
Pd/PPy dispersion in NMP

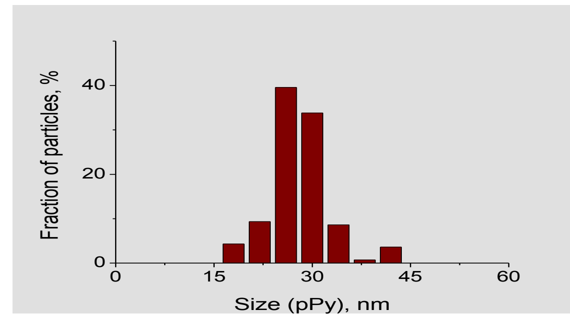
d of PPy spheres: 28 nm,
d of Pd nanoparticles: 1.3 nm,
Pd content in the globule: 34 wt.%

T. Magdesieva, O.Nikitin, M.Vorotyntsev, et al. / J. Molecular Cat. A: Chemical 353/354 (2012) 50

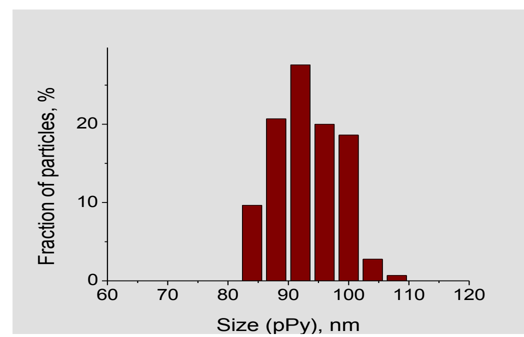
Comparison of Pd/PPy globules: 93 or 28 nm ?







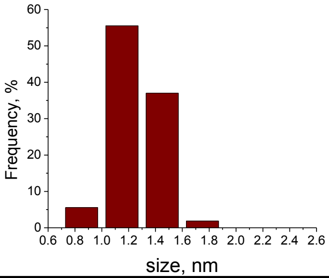
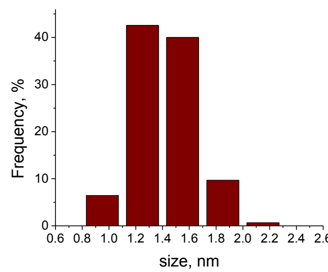
28±1 nm



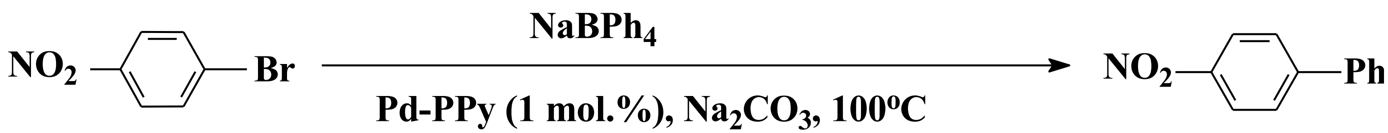
93±2 nm

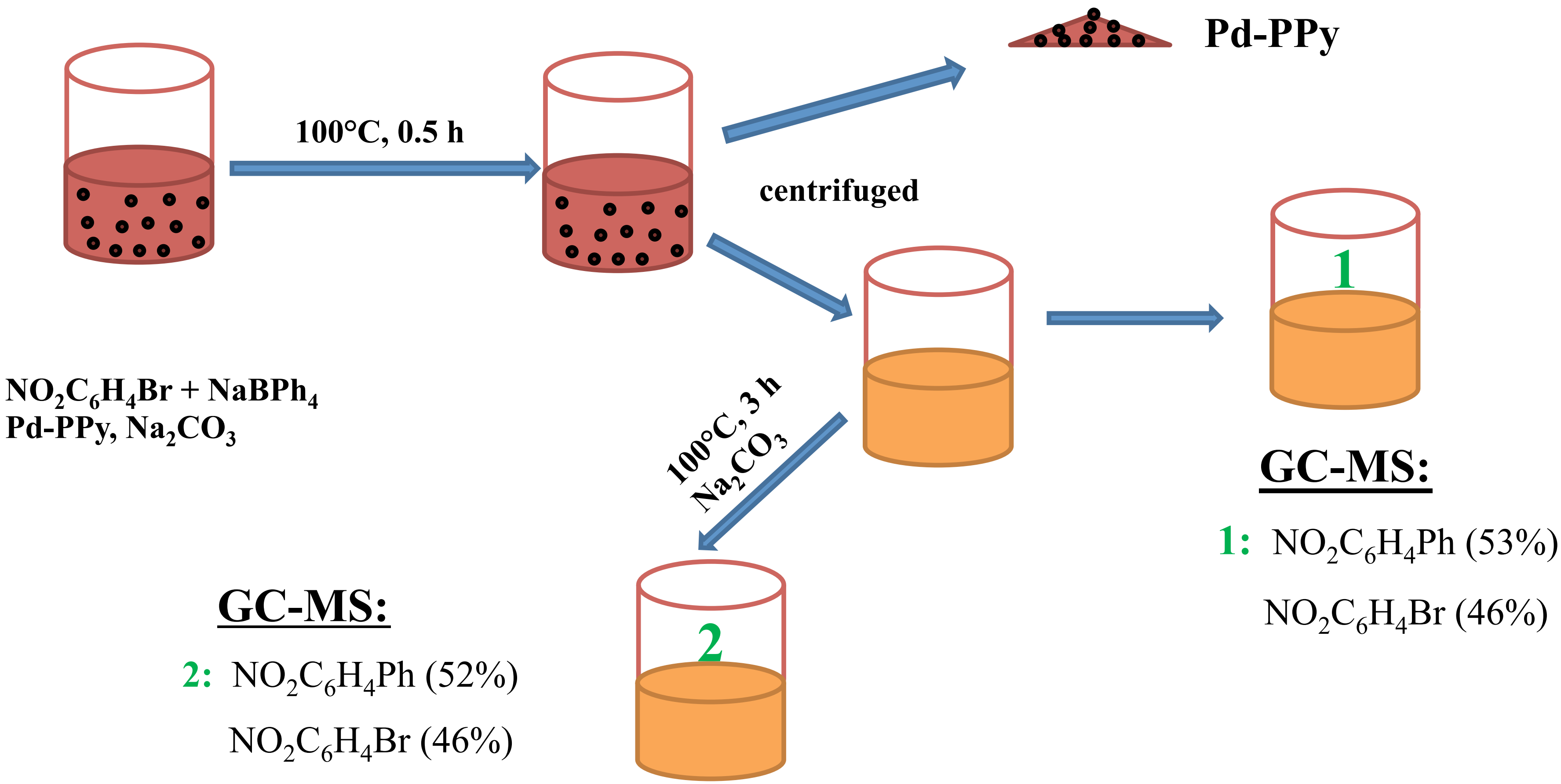
Pd nanoparticles: 1.3 nm, Pd content in the globule : 34 wt.% 100^{0}C, 4 h, NMP

Comparison of Pd/PPy with different Pd content

diameter of PPy spheres	28 nm	28 nm
Pd nanoparticles size distribution:		
Pd content in the PPy globule:	**34 %**	**42%**
Pd mol% respectively to PhBr:	1 mol %	1 mol %
The yield of biaryl in p-$CH_3C_6H_4Br$ + $NaBPh_4$ coupling (NMP, 100^{o}C, 4 h):	84%	83%
The yield of biaryl in PhBr + $NaBPh_4$ coupling (NMP, 100^{o}C, 4 h):	96 %	95 %

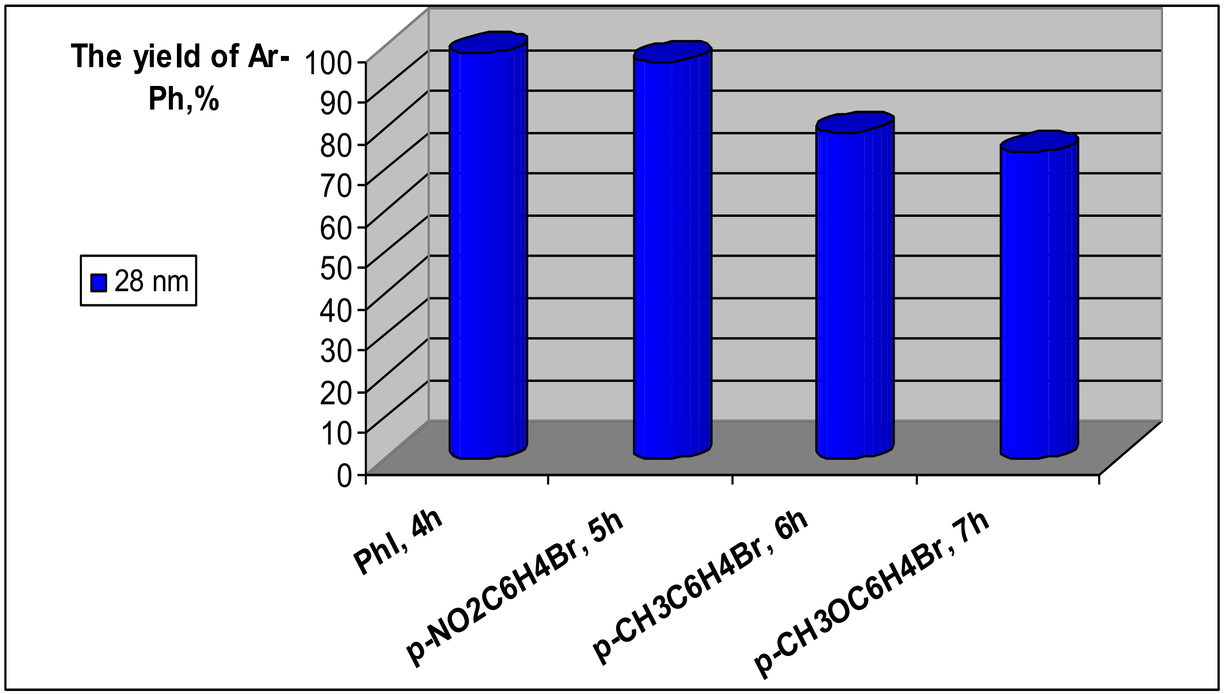
Leaching tests





Suzuki coupling in water

Pd/PPy (≈ 0.1 mol % of Pd as calculated to PhBr),
d of PPy spheres: 28 nm, d of Pd nanoparticles: 1.3 nm,
Pd content in the globule : 34 wt.%



$2 \cdot 10^{-4}$ mol ArHal, $0.5 \cdot 10^{-4}$ mol $NaBPh_4$, 10^{-3} mol Na_2CO_3, 100°C

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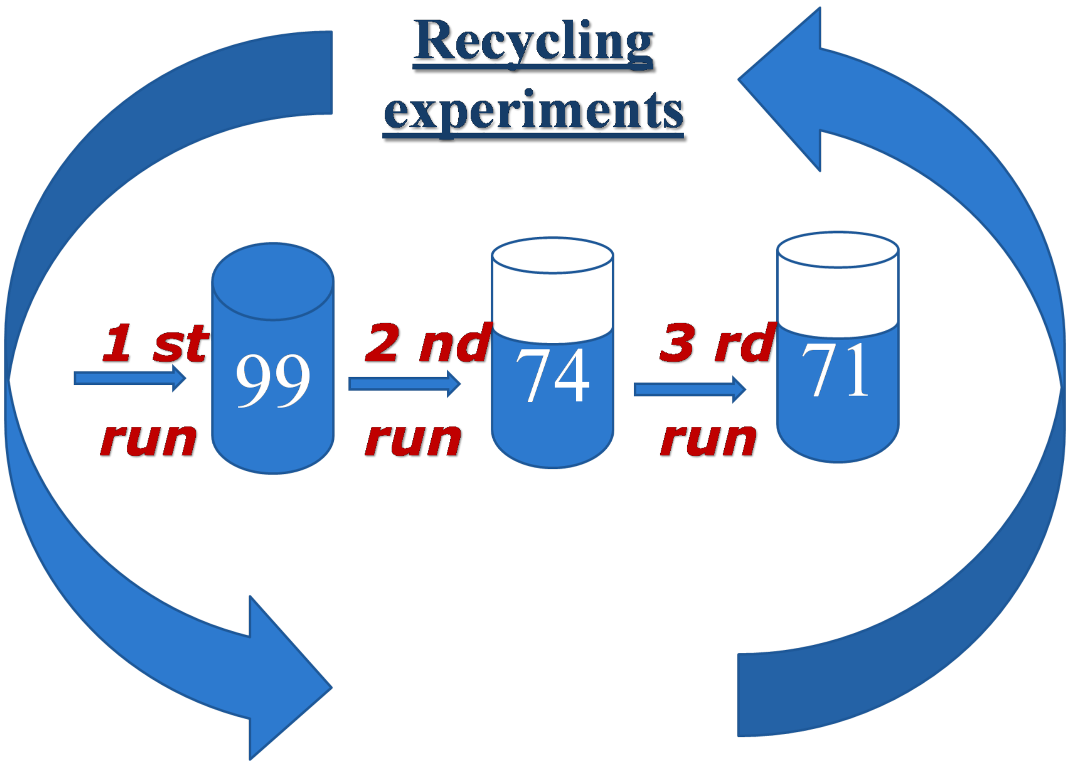
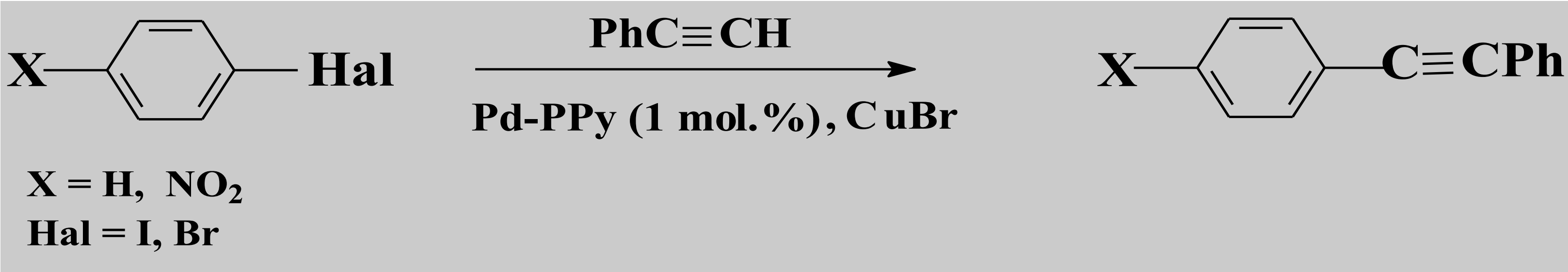
Possibility of recycling:

Pd/PPy (☒ 0.1 mol % of Pd as calculated vs. PhBr),
d of PPy spheres: 28 nm, d of Pd nanoparticles: 1.3 nm,
Pd content in the globule : 34 wt.%



$2 \cdot 10^{-4}$ mol PhBr, $0.5 \cdot 10^{-4}$ mol $NaBPh_4$, 10^{-3} mol Na_2CO_3

Pd/Ppy– Catalyzed Sonogashira Coupling



ArHal	PhI	PhBr	PhBr*	*p*-$NO_2C_6H_4Br$	*p*-$NO_2C_6H_4I$
PhC≡CPh, %	70	66	76	78	86
ArHal, %	31	32	22	19	16

* 6 h

PhC≡CH (0.3·mmol) , ArHal (0.2 mmol), Na_2CO_3 (1 mmol), Pd/PPy (1 mol. %), CuBr (2 mol. %), NMP, 100°C, 4 h.

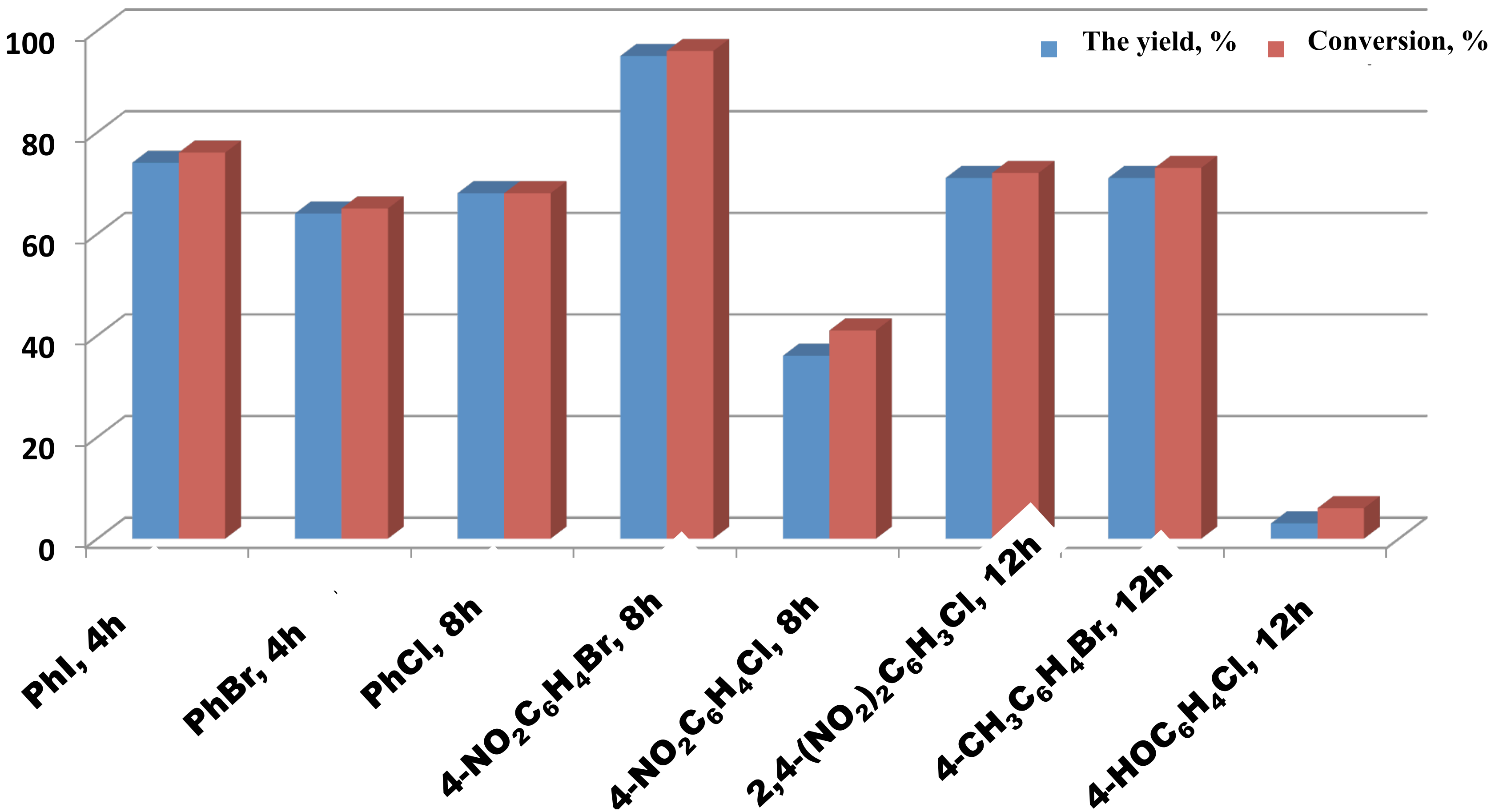
T. Magdesieva, O.Nikitin, M.Vorotyntsev, et al., *Mend. Commun*., 2013, v. 22, p. 305

Pd/PPy catalyzed aryl halides cyanation with $K_4Fe(CN)_6$

$$\text{ArHal} \xrightarrow[\text{NMP, 100}^{o}\text{C , Na}_2\text{CO}_3]{\text{K}_4\text{Fe(CN)}_6\ \ [\text{Pd}]\ \text{1 mol \%}} \text{ArCN}$$

Hal = I, Br, Cl

T. Schareina, et al, Chem.Commun. (2004) 1388



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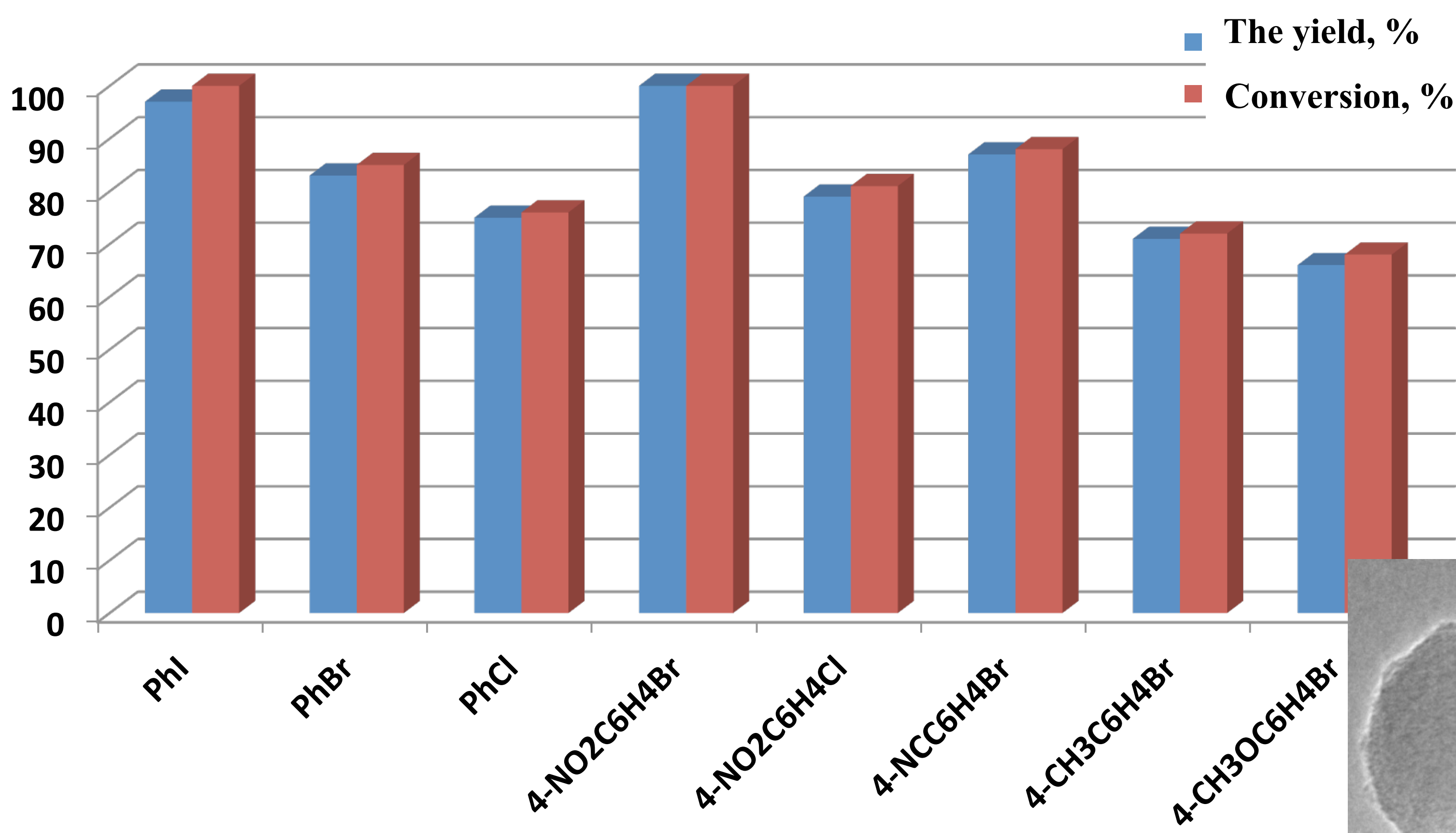
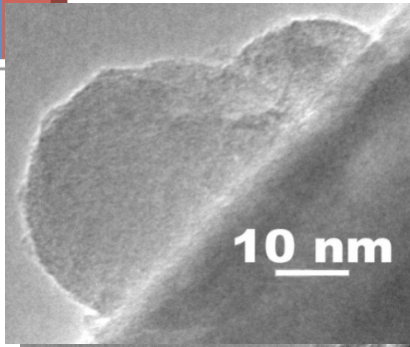
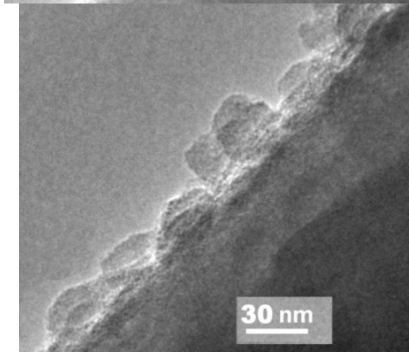
Cyanation of aryl halides in water

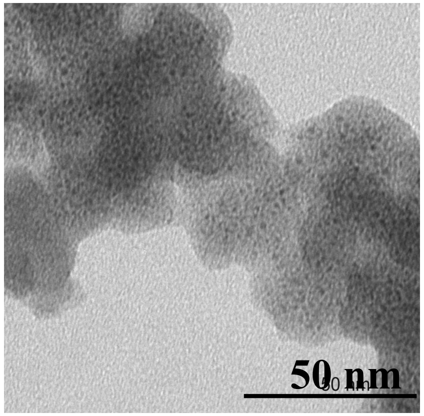


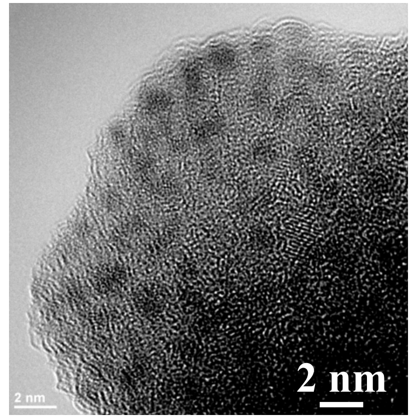


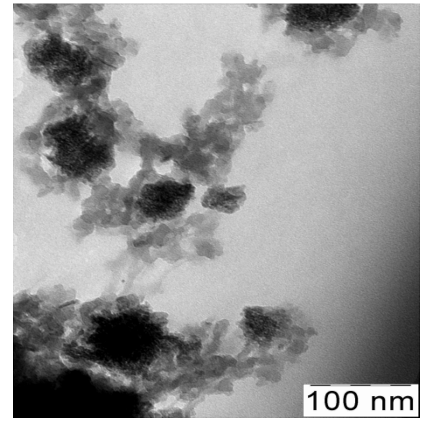


ArHal (0.2 mmol), $K_4Fe(CN)_6$ (0.035 mmol),
Pd/pPy (28 nm, 35 % wt. Pd), immobilized on carbon felt
0.2 mol% Pd, Na_2CO_3 (1 mmol), 100^{o}C

Morphology of the catalyst and yields of nitriles

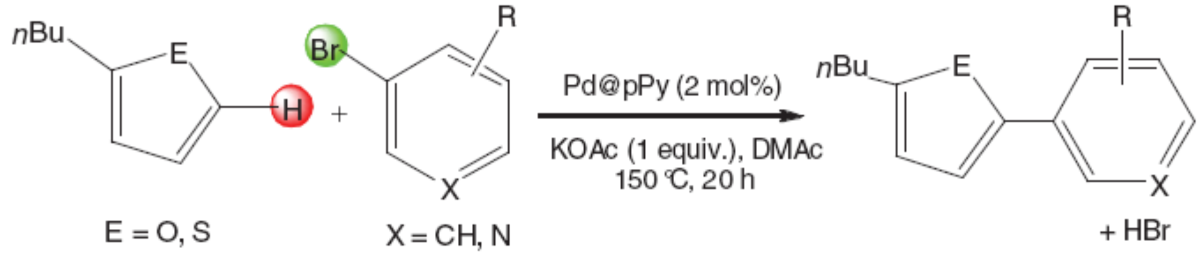


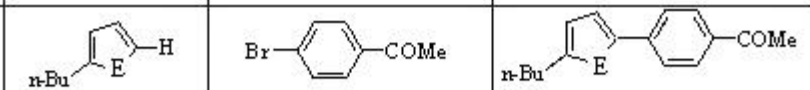
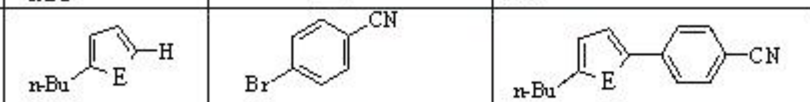
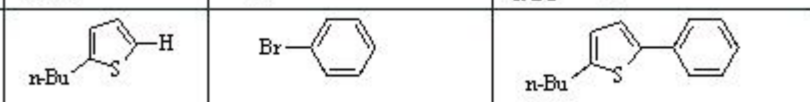
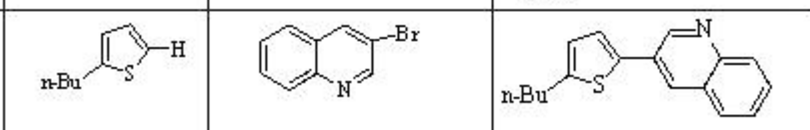
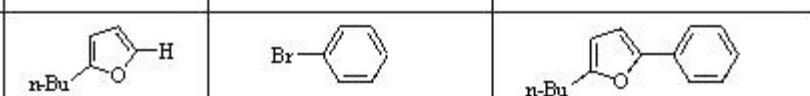
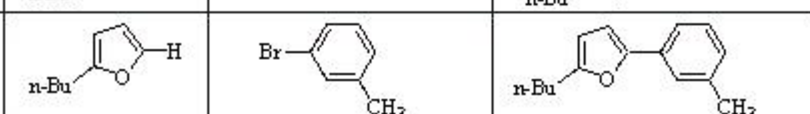
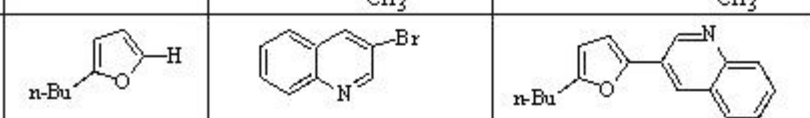




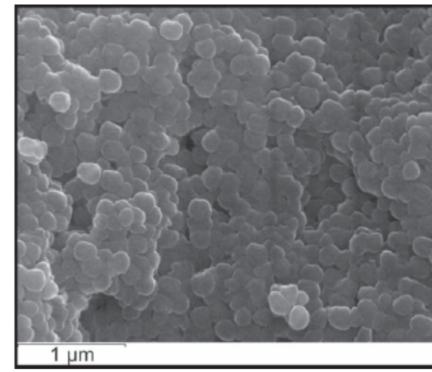
Conditions		d(Pd), nm
Initial value after composite synthesis		1.25±0.15
Extracted after catalysis of cyanation of $4\text{-}NO_2C_6H_4Br$, Na_2CO_3,	87% yield	1.08±0.08 No change of the size or morphology
Extracted after catalysis of cyanation of $4\text{-}NO_2C_6H_4Cl$, Na_2CO_3 base,	36 % yield	Pd nanoparticles are mainly located outside PPy globules and form agglomerates of 30 nm in diameter
Extracted after catalysis of cyanation of $4\text{-}NO_2C_6H_4Br$, K_3PO_4 base,	34% yield	2.24±0.27 Significant number of enlarged Pd particles

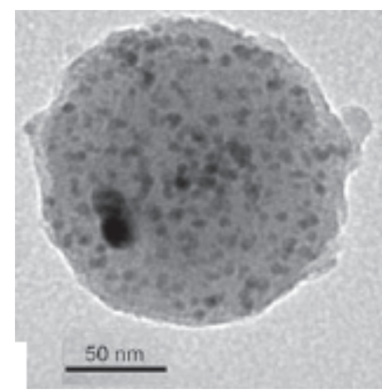
Pd/PPy for catalytic arylation of heteroaromatics



N°	Heteroaryl / Aryl/ Heteroaryl bromide / Product	Conversion (GC-MS)
1		100* %
2		100 %
3		90** %
4		100*** %
5		90** %
6		50 %
7		100 %

E = O, S





V. Zinovyeva, M. Vorotyntsev, J.-C. Hierso Adv. Funct. Mater., 2011, **21**, 1064

Выводы:

- Pd/PPy нанокомпозит –**экологичная**, синтетически доступная **альтернатива гомогенным Pd катализаторам** с фосфиновыми лигандами;

- Pd/PPy проявляет высокую **каталитическую активность** в реакциях образования связей **C(sp^2)-C(sp^2)** и **C(sp^2)-C(sp)** :

➢ **Сузуки-Миаура:** для арилиодидов, бромидов и хлоридов, как в органических растворителях, так и в воде;

➢ **Соногашира;**

➢ **Экологичное цианирование** нетоксичным $K_4Fe(CN)_6$ в воде (для арилиодидов, бромидов и хлоридов,

➢ **Кросс-сочетание арилбромидов с гетаренами**.

Выводы:

- **Каталитическая активность зависит от морфологии катализатора**; оптимальный вариант: PPy сферы диаметром около 30 nm, содержащие наночастицы Pd диаметром около 1.2 nm;
- **Морфологию композита можно настраивать** путем варьирования условий синтеза: соотношение мономер/окислитель; время полимеризации, концентрация реагентов ;
- **Содержание Pd** внутри PPy глобул не влияет на каталитическую активность, если общее количество Pd постоянно;
- «Вымывания» **Pd из PPy глобул в** ходе каталитичского цикла не происходит ; **возможно повторное использование катализатора**

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Thank You for your attention !

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