One-step synthesis of Pd nanostructure for photocatalysis and SERS applications

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Introduction

The synthesis of controlled shapes of metallic nanoparticles (MNPs) has attracted attention because of their unique properties, including sensing and catalytic properties which mainly depend on the MNP morphology and surface characteristics. Therefore, considerable efforts have been devoted toward controlling the MNP shape. The investigation of metallic nano-cubic shapes such as Ag nano-cubes, Pd nano-cubes and Au nano-cubes, which has increased over the last decade, most often depend on the development of seed-mediated synthetic methods and electrochemical methods. A new approach for controlled shape nano-structures was innovated by means of metallic nanoparticles organized in a thin homopolymer film (PMMA) on a silicon. This method was previously used to synthetize Ag and Au pure-oxide nanoparticles with controllable morphology [1-4]. Control of size and shape until obtaining monodisperse cubic nanoparticles has been carried out by tailoring the concentration of the gold precursor. Substrates containing nano-particles synthesized by this technique have been introduced as SERS-active substrates. In this project we aim to extend this synthesis way to Pd nanomaterials due to the potential of Pd in photocatalysis, SERS and the difficulty to produce anisotropic Pd nanoparticles by simple synthesis methods [5,6]. To make it possible,

Materials and Methods

Pd nanoparticles synthesis

The fabrication procedure is illustrated in Figure 1. A reference mixture of Poly methyl methacrylate (PMMA)/Pd(NO3) salt was prepared by mixing a solution of Pd(NO3)-isopropanol/ethanol and a solution of PMMA-MIBK/Acetone. After the mixing, a phase separation takes place. Consequently, to eliminate this separation and to obtain a stable mixture, a co-solvent (acetone) was added in order to induce the miscibility of both mentioned solvents. The resulting mixture was then deposited by spin coating on silicon/Indium tin oxide glass substrates that allows the reduction of Pd^{2+} into Pd^{0}. We have investigated different synthesis parameters that influence nano-particle morphology and their optical properties

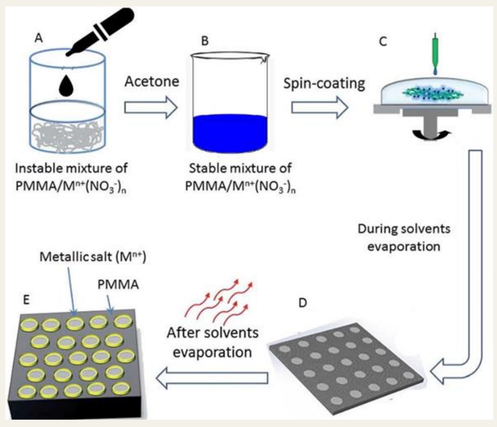


Fig1.Schematic representation of new approach to turn a wide variety of metallic salts into nano particle dispersed on a PMMA matrix. (A) Mixture of PMMA dissolved in toluene/acetone/MIBK and Mn+(NO3)n dissipated in isopropanol/ethanol (non-solvent of PMMA) shows phase separation. (B) The mixture becomes transparent after acetone addition (co-solvent). (C) Spin coating of the mixture on silicon substrate. (D) During solvents evaporation, vesicles are formed on the substrate surface and (E) will be exploded after complete solvents evaporation. Mentioned explosion forms nano-particles

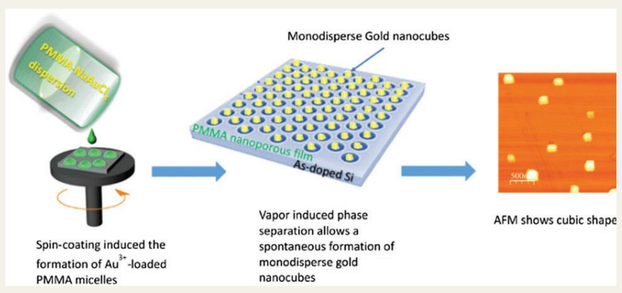


Figure 2. Schematic representation of the synthesis process of metallic nanoparticles and AFM image of an obtained sample showing the presence of gold nano-cubes.

Characterization of Pd nanoparticles

The characterization of Pd nanoparticles was carried out to study the structural and optical features of the Pd nano particles.

SEM micrographs were obtained by using a Hitachi SU8030 operating in secondary electron imaging mode with an accelerating voltage of 15 and 20 kV and 8 mm working distance.

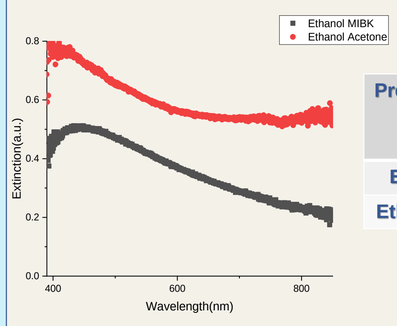
Extinction test has been carried out by using Horita Dilor-108N –SPEX Machine.

Results

In order to investigate the ability of above mentioned synthesis method, impact of different synthesis parameters including: precursor/PMMA solvents, precursor concentration on nano particle morphology, optical properties have been investigated as follow. At the end some simulations in order to morphology influence on optical properties will be demonstrated.

Impact of Precursor Solvent-non solvent

Fig. 3 shows the influence of PMMA –Precursor solvents on extinction peak position. As can be seen in Fig.4 acetone favors the formation of smaller nano particles among the sponged structure PMMA but for MIBK there is no sponged structure.



Precursor-PMMA solvents	Wavelength (nm)	Extinction (a.u.)
Ethanol-MIBK	450	0.494
Ethanol-Acetone	423	0.78

Figure 3. Extinction spectra showing the influence of Precursor/PMMA solvent on surface plasmonic resonance. All samples have been obtained by deposition of 60mM precursor solution on silicon substrate and 5000 rpm spin coating.

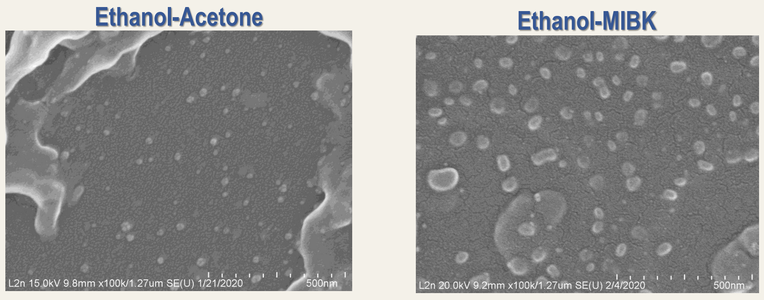


Figure 4. SEM micrograph of obtained Pd nano-particles by different precursor/PMMA solvents: Ethanol-Acetone and ETHANOL-MIBK. All samples have been obtained by deposition of 60mM precursor solution on silicon substrate and 5000 rpm spin coating.

Impact of Precursor concentration

the role of the precursor concentration was investigated in order to achieve shape control because for bottom up synthesis, the precursor amount is generally adjusted to tune the NP size. Fig 5 shows SEM images of Pd NPs obtained with different [Pd]. There is a noticeable increase in the number of Pd NPs on the surface with increasing [Pd]. Increasing of NPs size is also observed in these images by increasing the concentration. According to Fig 6 redshift of extinction peak can be observed. The redshift of extinction peak can be attributed to mentioned size increase.

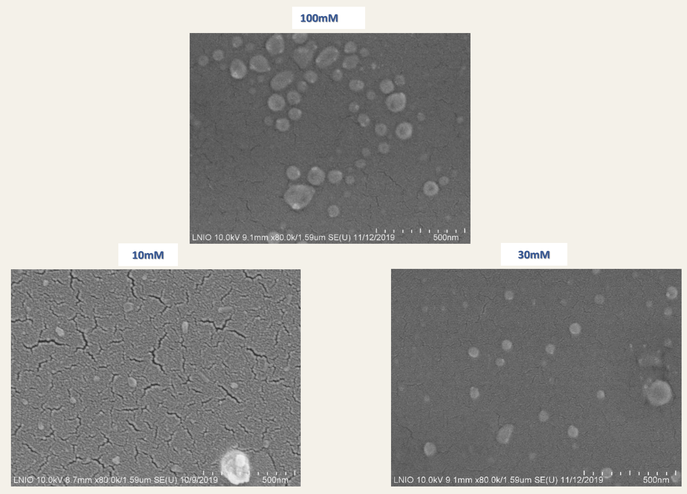
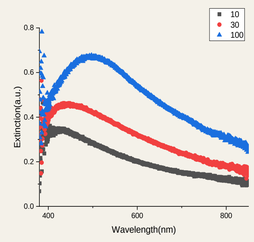


Figure5. SEM images showing the impact of increasing the concentration of Pd(NO3) from 10mM into 100 mM for Ethanol-MIBK solvents. Samples have been prepared on Silicon substrate and spin coated at 3000 rpm.



Concentration(mM)	Wavelength(nm)	Extinction peak
10	428	0.349
30	438	0.459
100	492	0.675

Figure6. Extinction peaks of Pd nano-particles obtained with different Pd precursor concentrations (10 , 30 and 100mM) for Ethanol-MIBK solvents. Samples have been prepared on silicon substrate and spin coated at 3000rpm

Simulation

Different plasmonic resonance wavelength as a function of Pd NPs size for spherical and cubic shape can be seen in Figures 7 and 8. These results were obtained using FDTD Solutions software from lumerical Solutions.

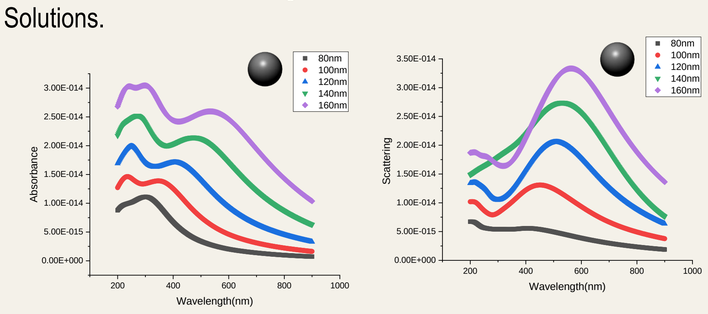


Figure 7. Absorbance and Scattering peaks as a function of spherical Pd NP obtained by FDTD Solutions software from lumerical Solutions. These NPs are surrounded by air as they have been formed in PMMA holes.

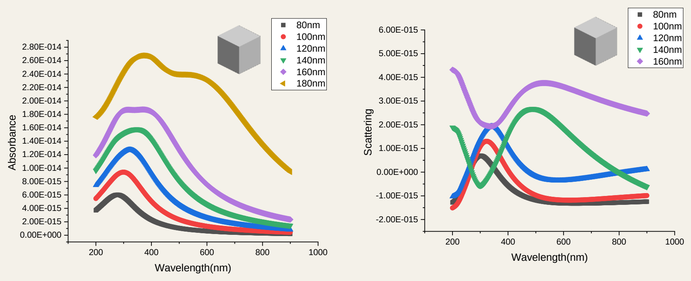


Figure 8. Absorbance and Scattering peaks as a function of cubic Pd NP obtained by FDTD Solutions software from lumerical Solutions. These NPs are surrounded by air as they have been formed in PMMA holes.

Conclusion

- In conclusion, we have presented a facile, fast and cheap method which is based on phase separation that could vary the morphology and dimension of the Pd NPs in a controlled manner by adjusting the synthetic parameters.
- For PMMA solvents, It has been found that Acetone induces sponged structure with very small nano particles and MIBK provokes non spherical structure.
- For ethanol-MIBK as precursor/PMMA solvents, increasing concentration of Pd precursor favors the formation of non spherical structure and larger particle.
- Increasing of precursor concentration lead to red shift of plasmon resonance.
- All experimental data are in agreement with simulation results for influence of Pd NP size/shape on resonance wavelength position.

References

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