Structural assessment of silica and amino-functionalized silica nanoparticles by FTIR and Raman Spectroscopy

[1]I. Petreanu [*], [1]V. Niculescu, [1]S. Enache, [1]C. Iacob, [2]M. Teodorescu

[1] National Research and Development Institute for Cryogenic and Isotopic Technologies, ICSI Rm. Valcea, 4th Uzinei Street, 240050, Ramnicu Valcea, Valcea, Romania

[2] The University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu Street/132 Calea Grivitei Street, Bucharest, Romania

E-mail: irina.petreanu@icsi.ro

Abstract

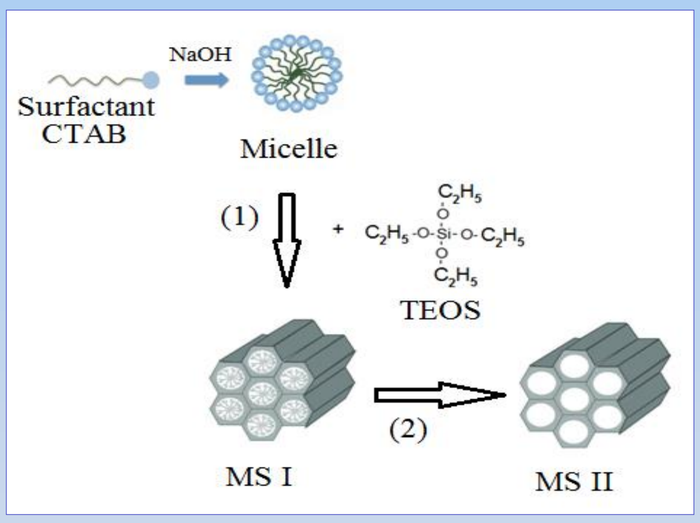
Mesoporous silica nanoparticles were synthesised by sol-gel method using cetyltrimethylamonium bromide (CTAB) micelles as template and used the same method for amino-silica nanoparticles synthesis. Compositional and structural analysis of materials involved FTIR and Raman spectroscopic study. A comparative study of the spectra revealed the distinctive pattern for the observed samples, such as a strong peak at 1030-1050 cm^{-1} in the FTIR spectra, characteristic for Si-O-Si stretching vibration or the specific pattern of silica between 900-500 cm^{-1} and 2880-2980 cm^{-1}, in the Raman spectra. A point of interest in this study was the control of CTAB removal during the second stage of synthesis. This was highlighted in the FTIR spectra by decreasing in intensity or disappearance of the peaks 2850 and 2930 cm^{-1} due to absorption of -CH_2- groups. The presence of –NH_2- in the amino-silica was highlighted by the changes in the region 1000-1500 cm^{-1} in the Raman spectra. The two spectroscopic methods offer valuable information for structural characterization of silica nanoparticles.

Materials and methods

Synthesis of mesoporous silica nanoparticles (MS) proceeds through two stages:

(1) the build up of silica nanoparticles , as silica network around of surfactant micelles (**MS I**);

(2) extraction of surfactant by refluxing into acidic dioxane solution , results mesoporous silica nanoparticles (**MS II**).



Scheme 1. Synthesis of the mesoporous silica nanoparticles (MS II)

Materials:

Silicon sources:

- tetraethylortosilicate (TEOS);
- aminopropyletryethoxysilane (APTES, just for amino-silica).

Surfactant: cetyltrimethylamonium bromide (CTAB);

Others: Sodium hydroxide (NaOH); Dioxane; Hydrochloric acid (HCl); distiled water.

Results

Threee samples including intermediate compound (MS I), mesoporous silica (MS II) and amino-functionalised silica (MS-NH_2) were analysed by ATR-FTIR and Raman Spectroscopy, and the resulted spectra (Fig. 2 and 3) were compared in order to confirm chemical structure and composition .

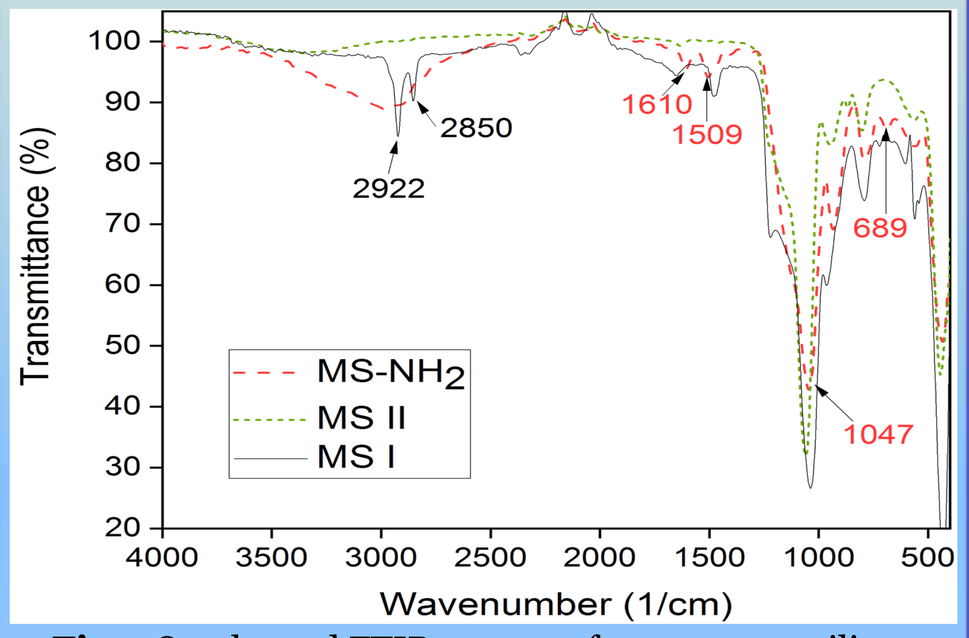


Fig.2 Overlapped FTIR spectra of mesoporous silica : (MS I), (MS II) and amino-silica (MS-NH_2)

Table 1: Specific peaks in the FTIR spectra

Sample	Peaks (wavenumber/cm^{-1}) and attribution
MS I	- Peaks from 2922, 2850 cm^{-1}- stretching vibration of C-H from CH_2 (CTAB); -1090-1020 cm^{-1}, Si-O-Si stretching; - Broad band 3700-3200 cm^{-1} and peak between 955-835 cm^{-1}, Si-OH
MS II	- Peak at 1055 cm^{-1} (Si-O-Si), - broad band 3600-3200 cm^{-1} (Si-OH)
MS-NH_2	- Broad band between 2800-3400 cm^{-1} (comprise CH_2 from ATPES and N-H hydrogen bonds); Peaks from 1610, 1509 and 689 cm^{-1} from N-H specific vibration

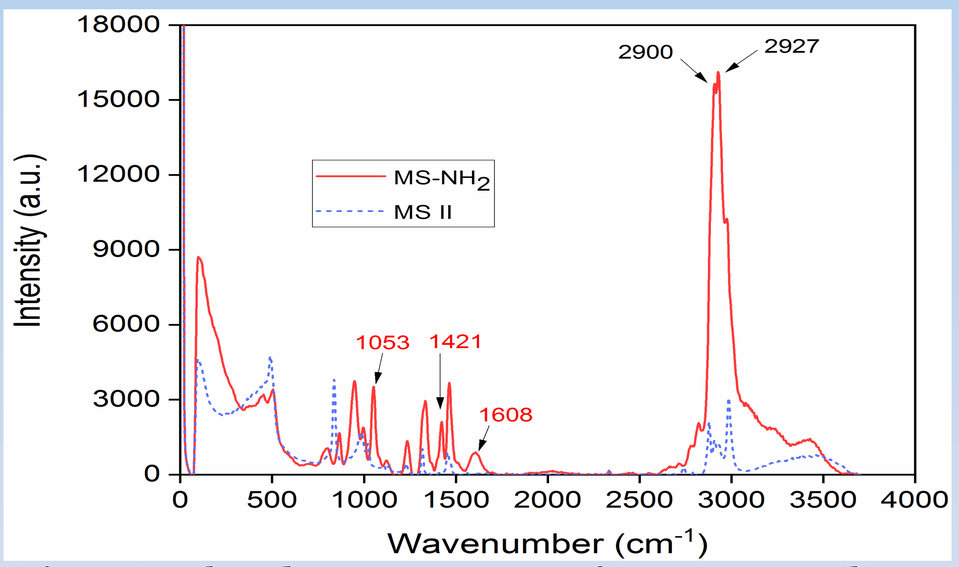


Fig. 3 Overlaped Raman spectra of mesoporous silica (MS II) and amino silica (MS-NH_2)

On notice different peaks in the region between 500-1500 cm^{-1} in the region of silica fingerprints and the intense duble peaks from 2900-2927 cm^{-1} in the Raman amino-silica spectra which due to the amino moieties.

Conclusions

- The characteristic peaks of silica in FTIR spectra are :

- the broad band between 3200-3600 cm^{-1} specific to the presence of adsorbed water;

- the strong adsorbtion peak (with sholders) from 1020-1090 cm^{-1} due to Si-O-Si stretching vibrations.

- The two peaks from 2922 and 2850 cm^{-1} due to stretching vibration of C-H from alifatic backbone of CTAB are present in the FTIR spectra of silica with CTAB (MS I) and disappear after the CTAB removal (MS II).

- The broad band between 3400-2800 cm^{-1} comprises the C-H (from aminopropyl) and the hydrogen bond, established between NH_2, too.

Also, peaks from 1610, 1509 and 689 cm^{-1} confirm the bonding of NH_2 on the silica (MS-NH_2).

- The Raman spectra of amino-silica (MS-NH_2) show some diferences in the silica fingerprints region (500-1500cm^{-1}) and a high, split peak, around 2900 cm^{-1}, characteristic for N-H vibration.

- The FTIR and Raman spectra of the silica compounds emphasised the removal of CTAB from the MS II silica mesopores (FTIR) and the presence of NH_2 groups in the aminated –silica (FTIR and Raman).

- Synthesized silica compound will be used as they are or by further functionalization for nanocomposite polymer electrolyte synthesis.

References

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Acknowledgments

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Further informations

Instruments:
FTIR, Agilent Cary 630 ATR-FTIR (from Agilent Technologies Inc., USA);
Raman, WITec alpha 300+ RAS (Ulm, Germania).

E-mail: irina.petreanu@icsi.ro