EPR study of nanosized fumed silica incorporated with aged Zn(acac)$_2$ ethanol solution

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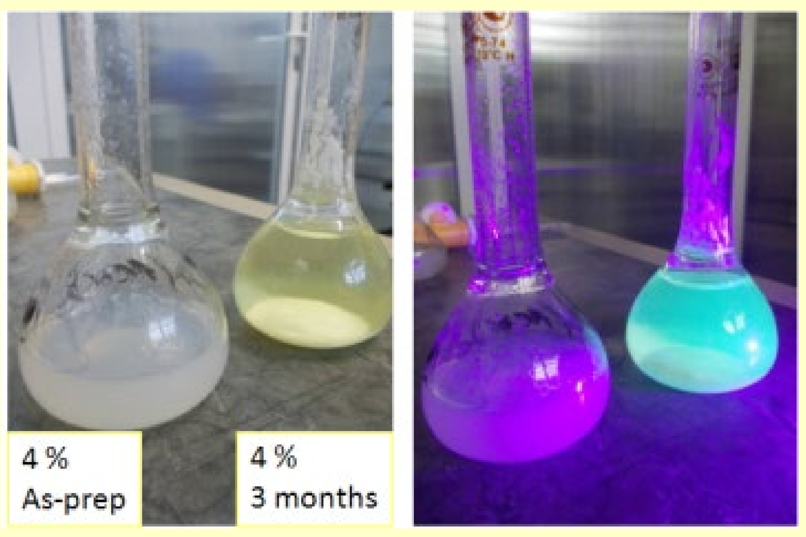
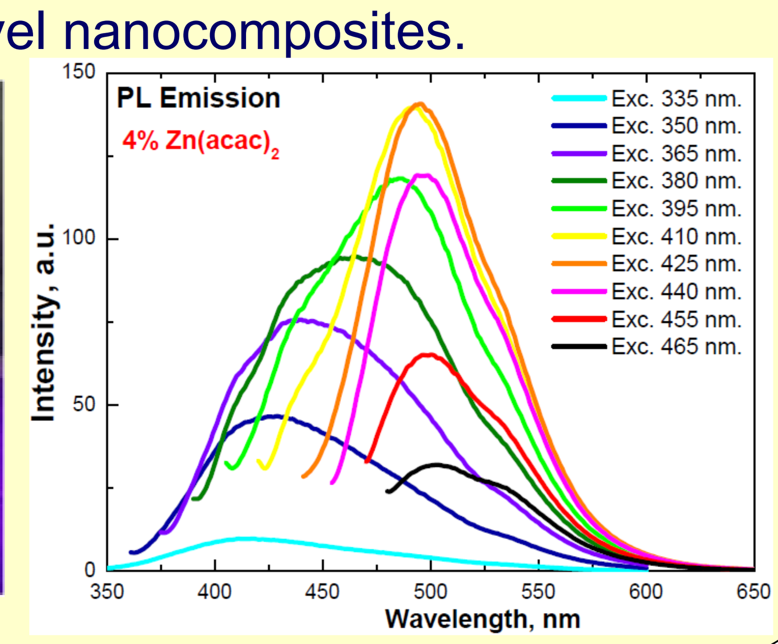
Introduction

Typically, pure pyrocarbon in hybrid carbonized silica (C/SiO$_2$) adsorbents possesses a relatively small number of active sites (oxidized groups) which could play an essential role in the bonding of polar molecules, as the carbon layer has mainly a non-polar pregraphite structure with the size of basal planes in graphene particles of several nanometers. To increase the amounts of active sites on hybrid adsorbent surfaces, additional oxidizing of pyrocarbon with the formation of COH, C=O, COOH, etc. groups, mixed **X**/SiO2 oxides as substrates (possessing a larger number of active sites than parent silica has), or organometallics as precursors can be utilized. The presence of carbon–metal compounds can change not only the topology but also other characteristics of C/**X**/SiO2 adsorbents, such as surface site distribution and catalytic and adsorptive abilities.

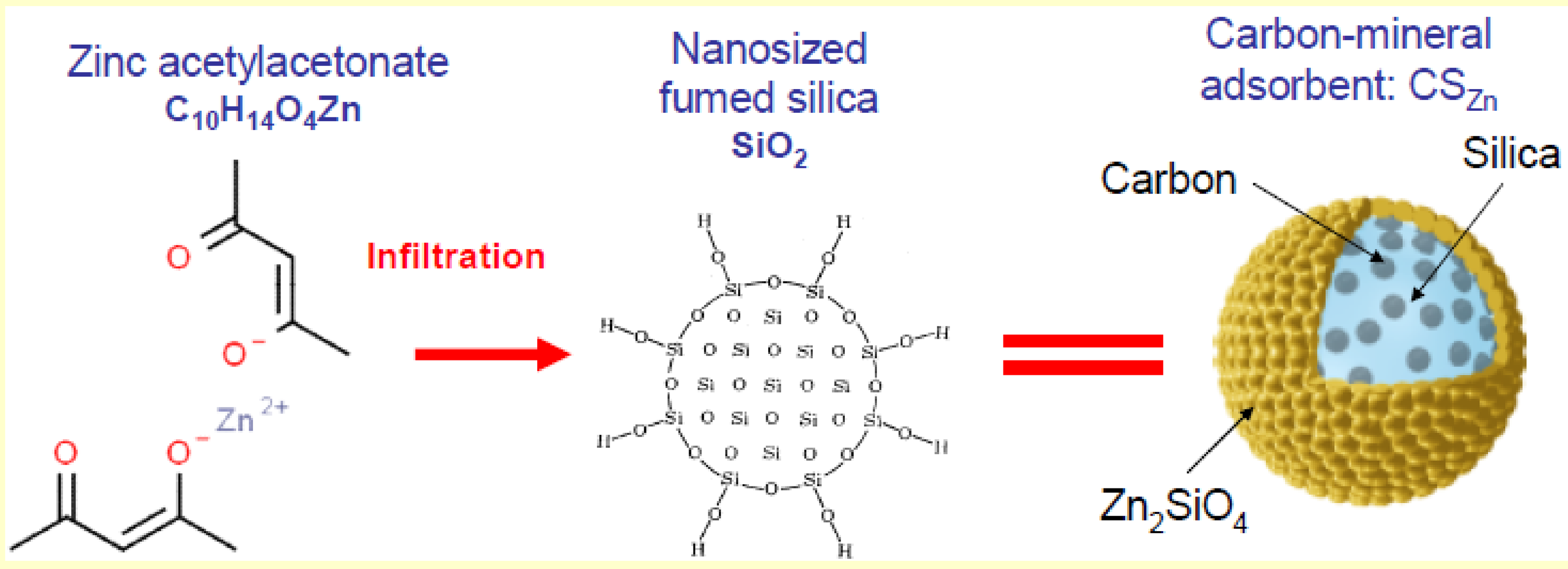
From the side, the functionalization of silica with aged Zn(acac)$_2$ solution that possesses intensive photoluminescence in the visible range can be perspective for the fabrication of modern luminophores. Therefore the study of the electronic structure of the defects is crucial for potential applications of this novel nanocomposites.





Materials and methods

The fumed silica (S~295 m^2/g, d~10-12 nm) was infiltrated with aged luminescent Zn(acac)$_2$ ethanol solution of different concentrations (1 wt.% and 4 wt.%). As a result, SiO$_2$:C nanocomposites with zinc silicate (Zn$_2$SiO$_4$) layer were obtained. The samples were annealed in the air at 600ºC. The electron paramagnetic resonance (EPR) spectra were measured at X-band frequency range (ν~9.4 GHz) on Bruker ELEXSYS E580 spectrometer.



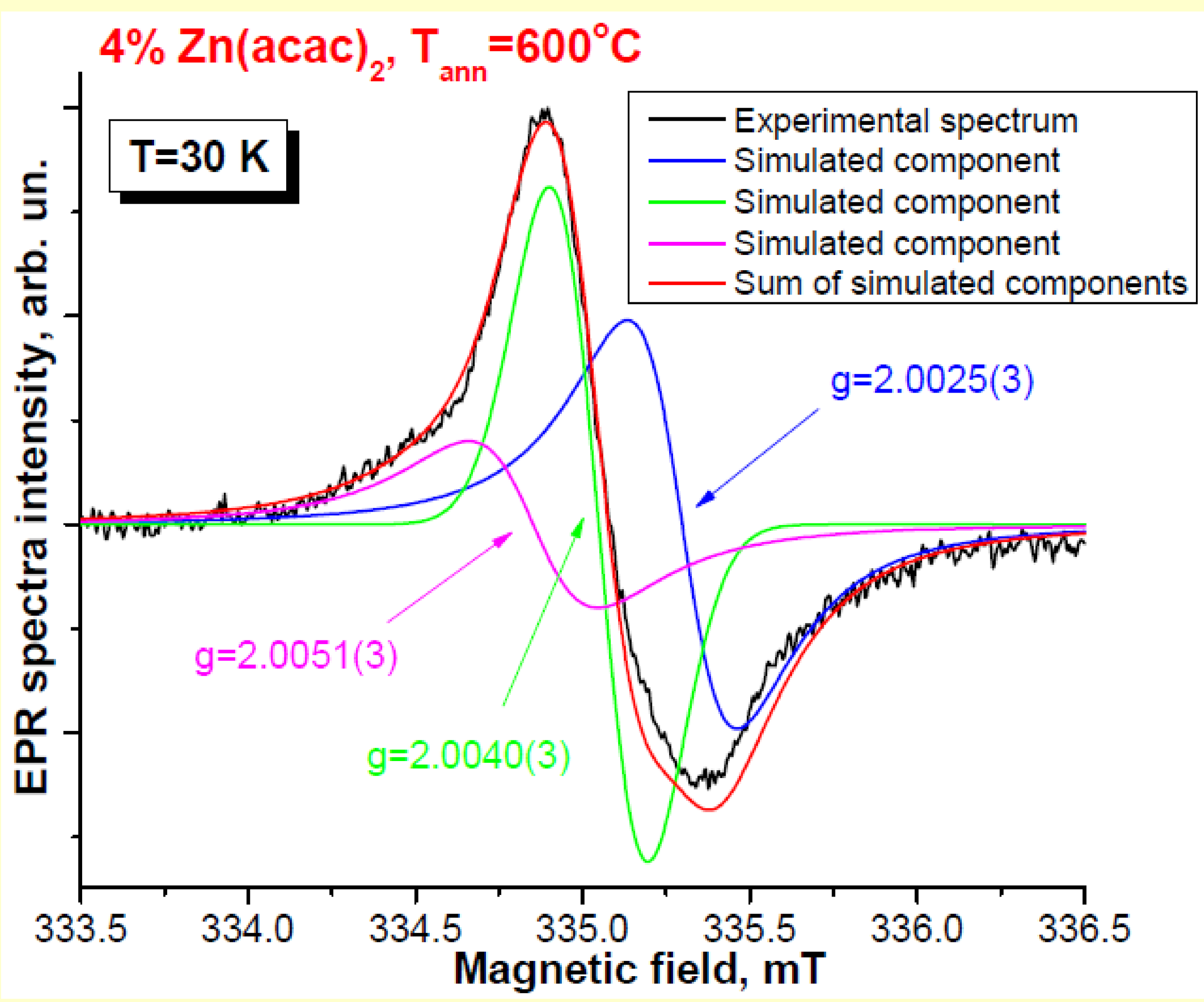
Spin concentration of the paramagnetic centers in CS$_{Zn}$ nanocomposites at T=295 K

In the CS$_{Zn}$ nanocomposites prepared with 1% of Zn(acac)$_2$, no EPR spectra were observed. After thermal annealing of those samples at 600ºC, the spin concentration of the paramagnetic centers at 295 K was very low: N_S~5.4·10^9 spins/mm^3.

In the CS$_{Zn}$ nanocomposites prepared with 4 wt.% of Zn(acac)$_2$, the paramagnetic centers had N_S~3.1·10^{11} spins/mm^3, while the thermal annealing at 600ºC doubles it: N_S~6.7·10^{11} spins/mm^3.

EPR spectra decomposition

The single EPR line at g=2.0040(3) dominates the EPR spectra, and its shape varies from Lorentzian in the initial CS$_{Zn}$ nanocomposites prepared with 4% of Zn(acac)$_2$ to Gaussian after thermal annealing at 600ºC. The EPR signal at g=2.0025(3) with temperature-dependent linewidth and intensity was detected as well. In addition, a weak broad signal at g=2.0051(3) was observed.



EPR spectra assignment

The weak EPR signal with g=2.0051(3) and Lorentzian lineshape can be tentatively attributed to silicon dangling bonds that can be formed at the interface of Zn$_2$SiO$_4$ layer and carbonized silica or at the Zn$_2$SiO$_4$ surface layer.

The intense signal at g=2.0040(3) should be related to carbon-related defect with an adjacent oxygen atom. The transformation of its EPR lineshape from Lorentzian to Gaussian one with the increase of the thermal annealing temperature can be explained by the appearance of the superhyperfine interaction of this defect with surrounding nuclei (e.g. ^{1}H).

The third Lorentzian EPR signal with g=2.0025(3) can be assigned to carbon-dangling bonds in the *sp*^{2} hybridized state.

At the same time, no EPR signals that can be related to the defects usually observed in ZnO particles were detected.

Conclusions

EPR spectra consist of three paramagnetic centers: two of them are related to carbon-related centers located in uniform carbon layer that cover silica nanoparticles, and another one is attributed to silicon dangling bonds raised from the formation of Zn$_2$SiO$_4$ layer.

The spin concentration of the paramagnetic centers rises with the increase of Zn(acac)$_2$ concentration and annealing temperature.

This work was supported by the MES of Ukraine (Project **F2211**) and the OP RDE by ESIF and the Czech MEYS (Research infrastructure SAFMAT – **CZ.02.1.01/0.0/0.0/16_013/0001406**)