ESR study of luminescent SiO_2:C nanocomposites prepared using sucrose solution

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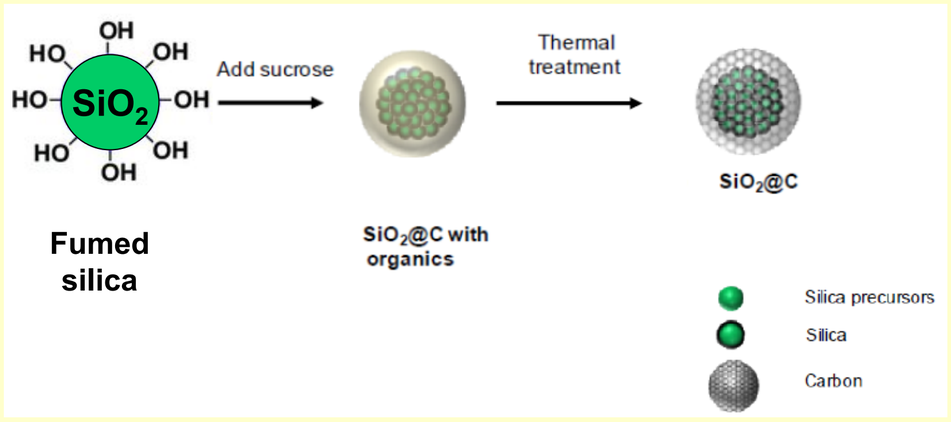
Introduction

Carbon dots (CDs), commonly identified as carbonaceous nanoparticles or graphene-like 2D nanocrystals, are among the best materials for achieving good electrical conductivity, high carrier mobility, and good dispersibility in a wide range of solvents. The use of carbohydrates as a starting material for synthesizing CDs is extremely attractive not only due to their abundance, availability, and heterogeneity but also due to their high water solubility, low-carbonization temperatures, low cost, and typically inherently lack toxicity. It is known that simple monosaccharides such as sucrose can be employed to prepare novel fluorescent CDs with improved properties using different methodologies.

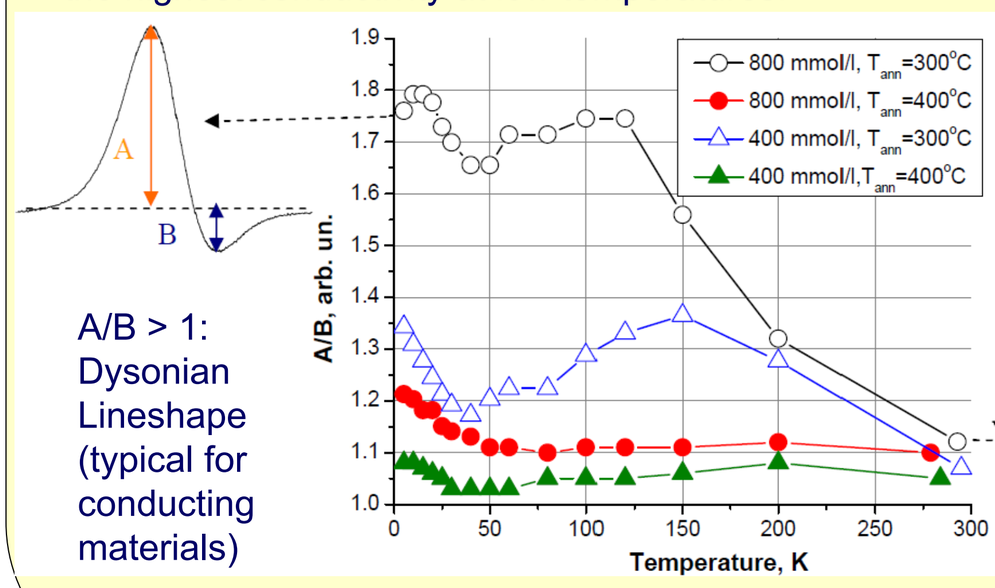
Materials and methods

The samples were prepared by the infiltration of fumed silica precursor (S~295 m^2/g, d~10-12 nm) by sucrose ($C_{12}H_{22}O_{11}$) water solution as a carbon source. Different concentrations of sucrose solution (800 mmol/g and 400 mmol/g) and annealing temperatures (300ºC and 400ºC in nitrogen flow) were used to study the effect of carbon incorporation. The electron spin resonance (ESR) spectra were measured at the X-band frequency range (v~9.4 GHz) on Bruker ELEXSYS E580 spectrometer.



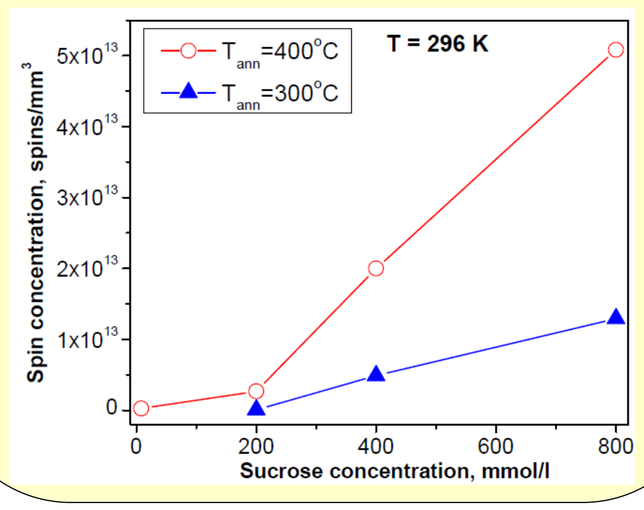
Temperature-dependent ESR lineshape

As the asymmetry ratio *A*/*B* is proportional to the electrical conductivity of the probed spins, we can assert that SiO_2:C nanocomposites prepared with sucrose concentration of 800 mmol/l and annealed at 300°C have the highest conductivity at low temperatures.



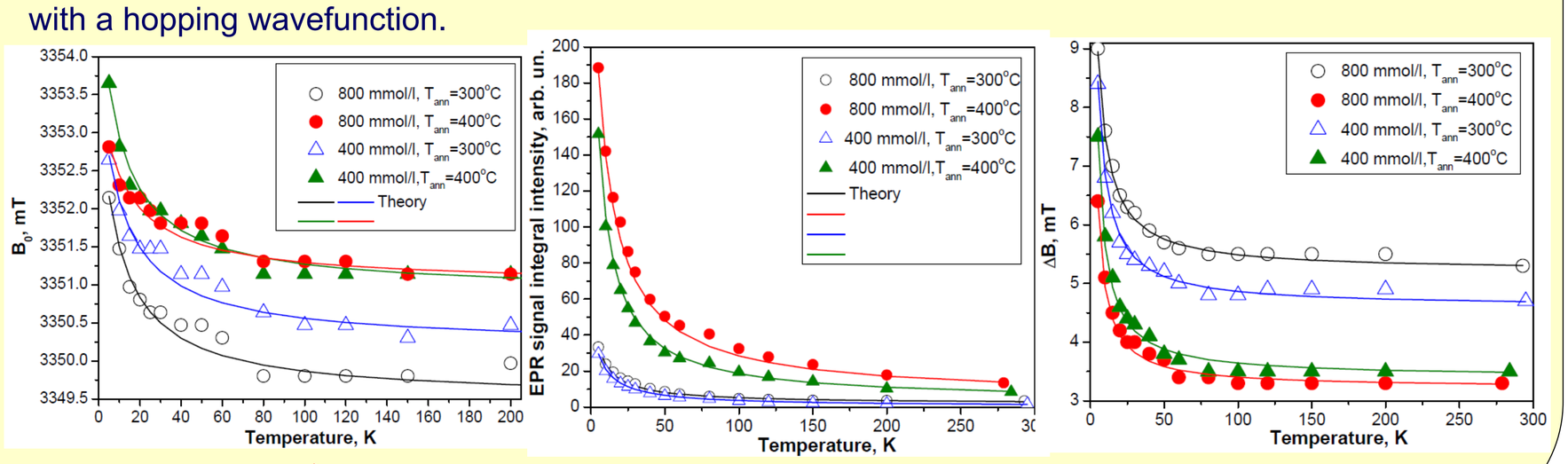
Spin concentration of the paramagnetic centers in SiO_2:C nanocomposites

No ESR spectra were observed in SiO_2:C nanocomposites before thermal annealing. The spin concentration of the single ESR line increases with the sucrose concentration, while the thermal annealing from 300ºC to 400ºC quadruple the spin concentration.



Temperature-dependent integral intensity, resonance field position and width of the single ESR line

There is a strong exchange interaction of conduction electrons (non-localized spins) and localized spins resulting in an appearance of a single line in the ESR spectrum. The observed exponential decrease of the single ESR line was described by combining Anderson's motional narrowing relation with a hopping wavefunction.



Sucrose concentration	$T_{ann.}$	g_{NS} (non-localized spins)	g_{LS} (localized spins)	Curie-Weiss temperature, K	Spin dephasing time, ns	Activation energy for hopping motion, meV	Average time each spin spends at each hopping location, fs	Number of jumps before phase coherence is lost
800 mmol/l	300°C	2.0045(3)	1.9985(3)	-6	11	0.39	1688	$6 \cdot 10^3$
	400°C	2.0036(3)	1.9986(3)	-9	18	0.14	4702	$3 \cdot 10^3$
400 mmol/l	300°C	2.0041(3)	1.9981(3)	-7	12	0.30	2194	$5 \cdot 10^3$
	400°C	2.0036(3)	1.9976(3)	-6	17	0.15	4388	$3 \cdot 10^3$

CRD **CDs** **Antiferro-magnetic interaction** **↑ T_{ann} ⇨ ↓ the rate of hopping between localized and non-localized states**

Conclusions

Carbon related defect (CRD) with non-localized electrons hopping between CDs was observed in annealed SiO_2:C nanocomposites. The Dysonian EPR lineshape of CRD was explained by the high conductivity of SiO_2:C nanocomposites caused by the presence of the CDs. The rise of the T_{ann} leads to the decrease of the conductivity, possibly due to the formation of carbon clusters

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