Characterization of pure and composite resorcinol formaldehyde aerogels doped with silver

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Abstract. A series of Resorcinol Formaldehyde (RF) aerogels composites with nanoparticles of silver were prepared by the sol-gel method at different concentrations doped silver. FTIR spectra of pure and composite RF aerogels show six absorption bands attributed to –OH groups bonded to the benzene ring, stretching of –CH₂– bonds and aromatic ring stretching. FTIR results ensured that silver particles do not interact with aerogel network. UV-visible spectrum of pure silver show an absorbance peak at 420 nm attributed to the surface plasmon excitation of silver Nano spheres. UV-visible spectral of pure and composite RF aerogels shows a steep decrease of absorption with wavelength after 500 nm, making sample’s color reddish brown. TEM and SEM images of pure and composite RF aerogels revealed that the textural arrangement of RF aerogels can be described as densely packed small nodules.

Keywords: RF Aerogels, Porous Materials, Composite Materials, Sol-Gel, Infrared Spectroscopy.

1. Introduction
Aerogels are classified as nano-porous materials. The most interesting characteristics of aerogels are low bulk density, high surface area, continuous porosity and high crosslinking structure [1, 2]. Organic aerogels have most frequently been obtained by sol-gel polymerization of Formaldehyde and another reactive monomer Resorcinol, which is called RF aerogels [3]. Applications as thermal insulators, electrodes for super capacitors, nuclear particle detection, light guides and electronic devices have been suggested for RF aerogels [4-6]. The properties of RF aerogel as well as their application are related to synthesis and processing conditions [7]. Composites are two or more materials combined on a macroscopic scale to form a useful material. One of the utilized methods for synthesis the metal-aerogel composite involves mixing the desired metal (in the form of its salt) with the sol-gel mixture. An alternative method for preparation metal-aerogel composite involves replacement of resorcinol by its derivative containing an ion-exchange moiety. This technique generates an organic polymer with each repeat unit containing a binding site which can be used for incorporation of the desired metal ions through an ion-exchange process [8]. In this work we introduce an investigation on the synthesis and characterization of pure and composite RF aerogel doped with silver nanoparticles as a novel material.

2. Material and methods
2.1. Preparation of pure RF aerogel
The first step of preparing RF aerogel is the aqueous polycondensation of resorcinol (1, 3-dihydroxybenzene \( C_6H_4(OH)_2 \)) with formaldehyde (HCOH) at molar ratio 1:2 and KOH as a catalyst (0.024 wt. %). After stirring the solution for one hour, It was poured into glass tube which sealed by high temperature flame. Then the samples were stored in an oven at 90°C for seven days. During gelation, the solution progressively changed color from clear to yellow to orange to deep red as a
function of the reaction time. In general the solution gels within 12-16 hours, but the extended cure is necessary to complete crosslinking as much as possible. RF aerogels are dark red in color as a result of oxidizing products formed during the polymerization. Then the samples are placed in acetone bath and make several exchanges with fresh acetone to remove water before supercritical drying. In supercritical drying, samples are placed in a pressure vessel which is filled with liquefied CO₂ at a temperature of 15°C and a pressure of 900 psi. After a suitable time (an hour for each 1mm sample thickness), the system is closed and raised to 40°C, where it is left for about 10 minutes. Excess CO₂ is vented during heating. The chamber is bled slowly to atmospheric pressure.

2.2. Preparation of silver nanoparticles

A colloidal dispersion of silver nanoparticles was prepared by adding 75 ml of 1 M solution of NaOH to 125 ml of a 0.1 M solution of AgNO₃. AgNO₃ was transferred to the intermediate Ag₂O colloidal dispersion as follows:

$$2Ag^+ + 2NO^{-3} + 2Na^+ + 2OH^- \rightarrow Ag_2O \downarrow + 2NaNO_2 + H_2O$$ (1)

A dark brown precipitate of Ag₂O was formed immediately. Then, Ag₂O precipitate was dispersed in 125 ml deionized water containing 1.25 ml of 1 M solution of sodium dodecyle sulfate (SDS), after 10–15 min, a stable colloidal dispersion was formed. A 37% solution of formaldehyde was used as reduction agent. The reaction of Ag₂O with formaldehyde can be written as follows:

$$Ag_2O + HCOH + H_2O \rightarrow 2Ag \downarrow + CO_2 + 2H_2O$$ (2)

The formation process of silver colloidal dispersion of reaction (2) proceeds slowly. In fact, it takes several days at room temperature. However, the formation time can be reduced to a several hours by increasing the temperature of the solution and then conform its formation.

2.3. Preparation of RF aerogel composite with Ag

After preparing nano-silver colloidal as mentioned before, it has been added to aerogel during the preparation process of RF aerogel (at catalyst ratio 0.024 wt. %) at different Ag concentrations (1.2×10⁻⁴, 2.4×10⁻⁴, 3.6×10⁻⁴, and 4.8×10⁻⁴ wt. %). After stirring, for more than 30 min, the mixture was kept in the ultrasonic bath for 30 min. Finally, the mixture was poured into a test tube, which sealed by high temperature flame. The sealed tubes were kept for 7 days at a temperature 90°C. Then, the prepared composite aerogel was cut using diamond saw in a disk shape. The supercritical dryer, type–Quorum Technologies E3100 Series was used in order to get rid off any solvent for all samples.

2.4. Characterization of the materials

FTIR spectra of the samples were recorded using Jasco FT/IR 4100 spectrometer in the range 400 - 4400 cm⁻¹. UV-Vis spectrum was recorded in the wavelength range 200-900 nm using Shimadzu UV-2450 Spectrophotometer. Morphology of the samples was performed using scanning electron microscopy (SEM) (Model JEOL JSM 6360 LA Analytical Scanning Electron Microscope).

3. Results and Discussions

Figure 1 shows FTIR spectra of pure and composite RF aerogel samples in wave number ranges from 400 to 4000 cm⁻¹. The results show the existence of six absorption bands, namely ν₁ at 3400 cm⁻¹, ν₂ at 2940 cm⁻¹, ν₃ at 1606 cm⁻¹, ν₄ at 1473 cm⁻¹, ν₅ at 1222 cm⁻¹, and ν₆ at 1090 cm⁻¹ respectively, which are in good agreement with that reported by others [9-11]. The broadband at 3400 cm -¹ can be attributed mainly to –OH groups bonded to the benzene ring, but may also be due to –CH₂OH groups connected to the resorcinol molecule, which did not take part in network formation [10]. The bands at 2940 and 1473 cm⁻¹ are attributed to stretching of –CH₂– bonds. The band at 1606 cm⁻¹ is attributed to aromatic ring stretching. The bands at 1090 and 1222 cm⁻¹ confirm the methylene ether C–O–C linkage stretching between two resorcinol molecules (phenyl rings), which is expected in the polycondensation reaction between resorcinol and formaldehyde [10, 11]. The change in transmission intensity can be attributed to aerogel concentration with respect to KBr. The differences of transmission intensity can be attributed to the concentration of the materials with KBr. This ensures that the silver particles do not affect the position of the absorption band of IR spectra. Figure 2 shows UV-visible spectra for pure Resorcinol with concentration 0.074 g per 250 ml of water. It is shown that the maximum absorption peak occurs at 273 nm representing an aromatic ring, which is in good agreement with literature [12], where the
maximum absorption for resorcinol occurs within wavelength range 273 - 294 nm depending on pH values.

**Figure 1.** FTIR spectra of pure and composite RF aerogels doped with Ag.

UV-visible spectra of pure and composite RF aerogel doped with different concentration of Ag are represented in figure 3. A shoulder occurs at ~500 nm after which the absorption decreases with increasing wavelength. Therefore, RF aerogel appears to be in reddish brown [13, 14]. The absorbance peak, which appears around 300 nm can be attributed to a lone pair of electron in oxygen atoms, while the peak at 250 nm is due to aromatic ring [13]. This means that the shift of the absorbance peak of aromatic ring in pure resorcinol (273 nm) to 250 nm (blue shift) in RF aerogel is an indication of formation of RF aerogel. The change in the intensity of absorbance can be attributed to catalyst concentration. After preparation of Ag nanoparticles under reduction of AgNO3 by formaldehyde, a UV-visible spectrum was recorded as shown in figure 4. The spectrum shows an absorption peak at 410 nm which can be attributed to the surface Plasmon excitation of silver Nano spheres, and could be taken as an indication of formation of silver nanoparticles [15,16].

**Figure 3.** UV-visible spectra of pure and composite RF aerogels doped with Ag.

**Figure 4.** UV-visible spectra of silver nanoparticles.

Figure 5(a) shows SEM image of pure RF aerogel. The morphology of pure RF aerogel has an open cell structure with continuous porosity with particle size ranging from 50 nm to about 150 nm. The result agrees with literature [17]. Figure 5(b-e) shows SEM micrographs of RF aerogel doped with silver. It is shown that the interconnection occurs in all directions of the network and there are many mezzo and macro pores among the interconnected channels which increase by increasing silver. The observed particle size ranges from 65 nm to 300 nm with large pore size which agrees with other [18]. These results reveal that the materials have a high surface area, which make them to be a good candidate as electrodes for supercapacitors.
4. Conclusion
Nano composite RF aerogels doped with Silver nanoparticles were prepared by the sol-gel process. The results of FTIR spectra show existence of six absorption bands for pure and composite RF aerogels and ensured that the silver particles do not affect IR spectra. UV-visible spectra for pure resorcinol show a maximum absorption peak at 273 nm which represent aromatic ring. UV-visible spectra for pure and composite RF aerogels show a steep decrease of absorption with wavelength after 500 nm and the peak of aromatic ring (273 nm) is shifted to 250 nm in RF aerogel. The shift of the absorbance peak of aromatic ring can be taken as an indication of formation of RF aerogel. UV-visible spectrum of Ag Nano particles shows an absorbance peak at 410 nm attributed to the surface plasmon excitation of silver Nano spheres. TEM images of pure and composite RF aerogels show that the textural arrangement of RF aerogels can be described as densely packed small nodules.

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