Investigating the effects of amine functionalized carbon balls in polybenzoxazine matrix

Periyasamy Thirukumaran[a], Asrafali Shakila Parveen[b], Seong-Cheol Kim[a*]

[a]*School of Chemical Engineering, Yeungnam University, Gyeongsan 38541, Republic of Korea*

[b]*School of Material Science and Engineering, Myongji University, Yongin, Korea*

*Authorfor the Correspondence: E-mail: sckim07@ynu.ac.kr

Materials

Eugenol, vanillin, stearylamine and paraformaldehyde were purchased from Sigma-Aldrich (USA). Ethylene diamine, potassium hydroxide (KOH), sodium hydroxide (NaOH) and dimethyl sulfoxide (DMSO) were purchased from Duksan Chemicals Co., Ltd. Republic of Korea. All chemicals were used without further purification

Instrumentation methods

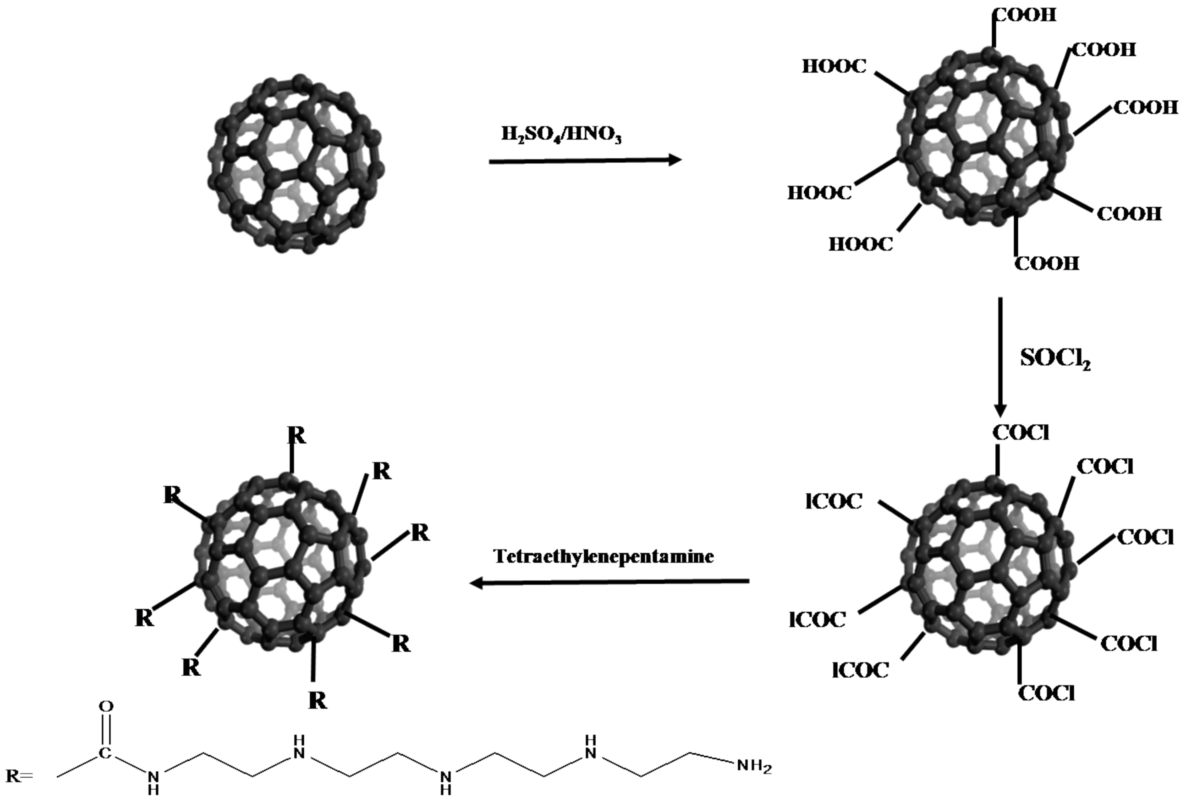
Fourier transform infrared (FT-IR) spectra were obtained with a Perkin Elmer MB3000 FTIR spectrometer. The spectra were obtained at a resolution of 4 cm^{-1} in the IR range of 400-4000 cm^{-1}. Samples were prepared by grinding with KBr and compressed to form discs. Nuclear magnetic resonance (NMR) spectra were recorded by using an Agilent NMR, VNS600 at a proton frequency of 600 MHz for 1H NMR and at a carbon frequency of 150 MHz for 13C NMR. Solutions were prepared by dissolving the samples in $CDCl_3$. Differential Scanning Calorimetry was performed in a TA instrument Q10 model using 5–10 mg of the sample at a heating rate of 10 ^{o}C min^{-1} in a N2 atmosphere The morphology of the material was examined by scanning electron microscopy (FESEM, Hitachi S-4800) at an accelerating voltage of 30 kV. . Surface area, pore size, and pore volumes were obtained from isotherms using the conventional Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) equations XPS spectra were achieved using a K-Alpha (Thermo Scientific). CasaXPS software was used for the deconvolution of the high-resolution XPS spectra. Dynamic mechanical analysis (DMA) was carried out using a Netzsch 242 DMA at a heating rate of 10 ^{o}C min^{-1} from 30 to 250 ^{o}C. Thermogravimetric analysis (TGA) was performed using a TA Q600 thermal analyzer. Cured samples were analyzed in an open silicon pan at a heating rate of 20 $^{o}C\ min^{-1}$ in a N_2 atmosphere, up to a maximum temperature of 800 ^{o}C.

Synthesis of carbon balls

In a three-neckedround-bottomed flask equipped with a magnetic stirrer and a reflux condenser, paraformaldehyde (1.8 g, 0.06 m) was taken and 20 mL of DMSO was added to it. It was then allowed to stir while maintaining the temperature at 50°C. Ethylenediamine (1.34 mL, 0.02 m) was added dropwise to the stirring mixture. In the meantime, a solution containing eugenol (3.28 g, 0.02 m) in 10 mL of DMSO was prepared separately. After complete addition of ethylene diamine, the solution of eugenol was added dropwise to the reaction mixture. The temperature was then slowly raised to 120°C. The reaction was then continuously stirred for 3h at this temperature. On completion of the reaction time, a transparent pale yellow colored solution was obtained. This solution was then cooled to room temperature and precipitated in water and ethanol mixture. The precipitate thus obtained was washed with NaOH solution and distilled water several times, filtered and finally dried in vacuum at 50°C for 12h to obtain Eu-Bzo monomer. This Eu-Bzo monomer was used to synthesize carbon balls. Step-wise curing of Eu-Bzo at 100, 150, 200 and 250°C, each for an hour was adopted to produce polybenzoxazine. Carbonization of the obtained PBz material was done under a nitrogen atmosphere by heating at 600°C for 5h with a ramp of 5°C min^{-1}. Activation of the obtained carbonaceous materials was done by thoroughly mixing in an aqueous KOH solution in a weight ratio of 2:1 (KOH: carbonized material), followed by evaporation at 120°C to remove the water content. Further, it was activated by heating in a tubular furnace at 600°C for 1h. Metal-freenitrogen-rich glassy carbon thus obtained was denoted as CBs.

Synthesis of amine functionalized carbon balls

Amine functionalized carbon balls were prepared by way of oxidation, alkylation and amination of pristine carbon balls (CB). Pristine carbon balls were dispersed in a mixture of conc. H_2SO_4 and HNO_3 (3:1) and sonicated at 120°C for 2h. Afterwards, the reaction mixture was filtered, washed with distilled water several times, until a neutral pH was obtained. The filtrate was further dried in vacuum oven at 80°C overnight to obtain acid functionalized CB [CB-COOH]. This was then reacted with thionyl chloride to form acyl functionalized CB [CB-COCl]. Tetraethylene pentamine (TEPA) was used as the amine source to produce amine functionalized CB. Amine functionlized CB was prepared by solvo-thermal reaction, where 2 g of CB-COCl was dispersed in ethylene glycol and sonicated for 30 minutes to obtain homogeneous dispersion. Then, TEPA (10.08 g) was added to the dispersion and stirred at 200°C for 10h. After completion of the reaction, the reaction mixture was cooled to room temperature, filtered, washed with distilled water and ethanol and finally dried in vacuum at 60°C to obtain amine functionalized CB [CB-NH_2] (Scheme S1).



Scheme S1. Synthesis of amine functionalized carbon balls