Synthesis and photoproperties of edge-selectively modification of zeolite-templated carbon with bromine or carbazole groups

(Okayama Univ.) GOTO, Haruko; TAJIMA, Tomoyuki; KOBAYASHI, Kazumasa; TAKAGUCHI, Yutaka; (Tohoku Univ.) NUEANGNORAJ, Khanin; KYOTANI, Takashi; NISHIHARA, Hirotomo

[Introduction] Recently, we reported zeolite-templated carbon (ZTC), which can be obtained as a negative replica of a zeolite, as a new class of the graphene-based material having 3D regular network of nanosized curved-graphene sheets.[1] From the point of view of nanoscience and nanotechnology employing ZTC, versatile chemical modification method is required and necessary. However, covalent functionalization of ZTC has scarcely reported. This paper describes an edge-selective functionalization of ZTC introducing carbazole moieties as fluorophores via the preparation of edge-brominated ZTC (ZTC-Br) and Suzuki-Miyaura coupling. A unique solvent-dependent photoproperty of carbazole-modified ZTC (ZTC-Cz) is also discussed.

[Results and Discussion] The edge selective bromination of ZTC was achieved using dibromoisocyanuric acid (DBI) in chloroform. In a typical run, a solution of ZTC (80 mg) and DBI (160 mg, 558 µmol) in chloroform (25 ml) was stirred at 50 °C for 72 h to give ZTC-Br (99 mg). The bromine content of ZTC-Br was estimated to be 2.24% (atomic%) by X-ray fluorescence spectrometry. Subsequently, N-phenyl carbazole groups were introduced into the edge of ZTC using Suzuki-Miyaura coupling (Scheme 1). The reaction of 4-(9-carbazolyl)phenyl boronic acid (35 mg, 122 µmol) with ZTC-Br (30 mg) in the presence of Pd(0)(PPh₃)₄ (30 mg, 26.0 µmol) in DMF (5 ml) at 80 °C gave ZTC-Cz (38 mg). It is notable that ZTC-Br and ZTC-Cz were well dispersed in DMF and DMSO. However, ZTC-Cz was not dispersible in water as contrasted to ZTC-Br. The structures of ZTC-Br and ZTC-Cz were confirmed by X-ray fluorescence spectrometer, elemental analysis, Raman spectrum, XRD, and XPS.

Scheme 1. Synthesis of ZTC-Br and ZTC-Cz.

Existence of a zeolite-like structure in ZTC-Cz is supported by the XRD patterns. Sharp peak around 6.4° observed in the XRD profile of ZTC, which shows the inherited periodicity (1.4 nm) of the zeolite template, weakened but remained clearly at about the same position.
This result indicated that zeolite-like structure still remained after the chemical modification of ZTC.

In order to explore potential applications of the edge-modified ZTC, we investigated the photoproperty of ZTC-Cz. The fluorescence spectrum of ZTC-Cz shows red-shifted emission ($\lambda_{\text{max}} = 380$ nm), which may due to a covalent attachment of carbazole moieties to ZTC, comparing with those of N-phenyl carbazole ($\lambda_{\text{max}} = 361$ nm) and the mixture of 4-(9-carbazole)phenyl boronic acid and ZTC ($\lambda_{\text{max}} = 361$ nm), although their carbazole moieties exhibited the same absorption maxima at 293 nm. Furthermore, we found that the fluorescence intensity of ZTC-Cz in binary DMF/water solvent was dramatically changed depending on the ratio of water to DMF (Figure 1). The higher ratio of water, the lower intensity of emission was observed at 380 nm. This result indicated that the zeolite-like structure of ZTC-Cz showed a swelling-shrinking behavior in binary DMF/water solvent, i.e., adding water into DMF dispersion of ZTC-Cz lead to shrinking the zeolite-like structure, which caused the fluorescence self-quenching of carbazole moieties. Such structural change was observed by means of XRD using ZTC powder that was wetted with DMF or water. After wetting ZTC with water, characteristic broad halo corresponding to the average of interlayer spacing of graphite ($d = 0.34$ nm) along with the small peak of zeolite-like structure ($d = 1.4$ nm) was observed.[2] On the other hand, the XPD pattern of ZTC wetted with DMF exhibited halo of $d$-spacing maxima at 0.45 nm, which is larger than that of water-wetted ZTC (Figure 2).

![Fluorescence spectra of ZTC-Cz in different ratio of DMF and H$_2$O. ($\lambda_{\text{ex}} = 293$ nm).](image1)

**Figure 1.** Fluorescence spectra of ZTC-Cz in different ratio of DMF and H$_2$O. ($\lambda_{\text{ex}} = 293$ nm).

![The XRD patterns of ZTC powder that was wetted with DMF or water.](image2)

**Figure 2.** The XRD patterns of ZTC powder that was wetted with DMF or water.
