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Irradiation Induced Modification of Nano-Porous Metal Organic Frameworks

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Metal organic frameworks (MOFs) are a class of nano-porous materials built from nodes of metal clusters connected by organic ligands. The high specific area and abundant nano-pores have made MOFs promising in application such as gas storage, molecular separation, heterogeneous catalysis and drug delivery. In the present work, the irradiation effect and irradiation induced modification of MIL-101 (Cr) –a typical MOF material synthesized by the coordination of Cr (III) ions with benzene-1,4-dicarboxylate ligand was investigated. The results of electron spin resonance (ESR) showed that the free radicals generated on MIL-101 (Cr) after gamma ray irradiation were benzoyl free radicals and the concentration of benzoyl radicals decayed with time upon storage. The reactivity of the benzoyl free radicals on MIL-101 (Cr) was proved by the simultaneous graft polymerization of 2-hydroxyethyl acrylate (HEA) onto the surface of MIL-101 (Cr) initiated by gamma irradiation. The grafting kinetics of HEA on MOFs was similar to the conventional graft polymerization, which indicated the irradiation induced grafting method can be used to modify MOFs just like the irradiation induced modification of polymer materials. The PHEA graft chains significantly increased the hydrophilicity of MIL-101 (Cr) and the contact angle of water on MIL-101 (Cr) decreased from 156.7° to 61.5° (Figure 1). Brunauer–Emmett–Teller (BET) surface area measurements were performed to investigate the effect of grafting modification on the specific area of MIL-101 (Cr). The results showed the specific area of the modified MIL-101 (Cr) increased 50% compared to that of as prepared MIL-101 (Cr), which should be attributed to the accumulation of PHEA graft chains on the surface of the MOFs (Figure 2). X-ray diffraction (XRD) was used to investigate the crystal structures of the as prepared MOFs and the modified MOFs. The characteristic peak of the modified MIL-101 (Cr) was almost the same as that of as prepared MIL-101 (Cr), which indicated the nano-pore structure of MOFs was not damaged by irradiation. In conclusion, HEA was successfully grafted onto the surface of MIL-101 (Cr) initiated by gamma irradiation. The specific area increased without affecting the nano-porous structure of MIL-101 (Cr). The surface of MIL-101 (Cr) converted from superhydrophobic to hydrophilic. The present work provides a new method for the preparation of hydrophilic nano-porous materials.

Country/Organization invited to participate

China

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