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Organic Geochemistry and Photodegradation of Organic Pollutants in the Environment
環境中有機汙染物的有機地球化學及其光催化降解研究

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) belong to a class of organic contaminants of great environmental concern. They have grasped much attention due to their carcinogenic potential and ubiquitous presence in the environment. The main pathway for PAHs to enter human bodies is via breathing polluted air or through the food chain. Various forms of PAHs in coals or from coal combustion may affect human, especially indoor coal combustion. In the meantime, PAHs in raw coal can reduce or even poison the activity of catalysts in the refinery, making the stockpile of liquid product unstable. Many literatures concluded that most of the PAHs come from fossil-fuel combustion. However, their pollution from raw coal were usually neglected. The movement and distribution of PAHs in the environment depends on properties such as how easily they dissolve in water, and how easily they evaporate into the air.

The abundances of sixteen polycyclic aromatic hydrocarbons (PAHs) on the priority list of U.S. Environmental Protection Agency (USEPA) have been determined in fourteen Chinese and American coals. The ranks of the samples range from lignite, bituminous coal, anthracite to natural coke. Soxhlet extraction was conducted on each coal for 48 h. The extract was analyzed on gas chromatograph-mass spectrometer (GC-MS). The results show that the total PAHs content ranged from 0.31 μg/g to 57.6 μg/g coal (on a dry basis). It varied with coal rank and is highest in the maturity range of bituminous coal rank. High-molecular-weight (HMW) PAHs are predominant in low-rank coals, but low-molecular-weight (LMW) PAHs are predominant in high-rank coals. The Low-sulfur coals have a higher PAHs content than high S coals. It may be explained by an increasing connection between disulfide bonds and PAHs in high-S coal.

In addition, it leads us to conclude that the PAH content of coals may be related to the depositional environment.

Fly ash and bottom ash samples were collected from a coal-fired power plant located in Anhui province, China. Mineral phases and morphologies of the samples were determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. 16 polycyclic aromatic hydrocarbons (PAHs, 16 compounds specified on “EPA Method 610”) properties in the ash samples were investigated. In the fly ashes, the $\sum_{16}$PAH (total amount of 16 PAHs) and the CPAHs (total amount of eight carcinogenic PAHs) levels varied from 0.93 μg/g to 2.08 μg/g, 0.26 μg/g to 0.87 μg/g, respectively. In the bottom ashes, $\sum_{16}$PAH and the CPAHs levels varied from 2.83 μg/g to 5.32 μg/g, 1.76 μg/g to 3.76 μg/g, respectively. The CPAHs levels of some ashes, especially for the bottom ashes, are above the limits regulated by several countries, indicating that this type of coal combustion product need special treatment before landfill. Fly ashes were dominated by medium molecular weight (MMW) PAHs and low molecular weight (LMW) PAHs, while bottom ashes were abundant in the 5- and 6-ring PAHs species.

Thirty-three soil samples were collected from the Luling, Liuer, and Zhangji coal mines, in the Huaibei and Huainan areas, Anhui Province, China, in 2007. The concentrations of 16 polycyclic aromatic hydrocarbons (PAHs), identified as priority pollutants by the USEPA, were determined by gas chromatography-mass spectrometry (GC-MS). The sum of 16 US-EPA PAHs ranged from 0.13 to 3.54 μg/g (dry weight basis) with a mean concentration of 0.84 μg/g. Among the three sampling sites selected around the coal mines, the site at the Luling Coal Mine revealed maximum concentration of PAHs, while minimum concentration was observed at the site at Zhangji Coal Mine. In general, low molecular weight PAHs were predominant. Gob pile and coal preparation plant are the sources of PAHs pollution in surface soils in the vicinity of coal mines. The crops in rice paddies may adsorb some PAHs and reduces the PAHs content in soils from paddyfields. Vertical distribution of PAHs in two soil profiles indicates that PAHs contamination in soil profiles tends to occur high in the surface soils and markedly decreases with soil depth. For all depths, PAHs showed a similar distribution pattern, which is an indicator of a similar origin. Total B[a]P equivalent concentration (B[a]Peq) was found to be maximum at the Luling area, while it was minimum at Liuer zones.

Organic pollutants in water have been causing serious environmental problems. Photocatalytic degradation of these pollutants using solar energy is an attractive solution to this global problem. Metal oxide semiconductor nanoparticles have been used as high activity photocatalysts; such as ZnO, TiO_2, CdS, Fe_2O_3 and $HNbO_3$. These semiconductors, however, can only be excited by UV light due to their large band gaps. For better utilization of sunlight and indoor illumination, it is desirable to develop photocatalysts that can be excited by visible light. We propose to develop a series of highly efficient visible light nano-photocatalyst of niobates and tantalates as well as doping these semiconductors with various metals and non-metals. Additionally, doping with metals can lead to increased photocatalytic efficiencies, while doping with non-metals can shift the optical absorption of the photocatalysts to the visible region. Our research should lead to the development of a novel, practical and marketable nanotechnology for environmental remediation.

Nitrogen doped $KNbO_3$ micro/nanostructures was synthesized by the following two procedures: First, $KNbO_3$ micro/nanostructures were synthesized by a hydrothermal process using KOH and Nb_2O_5 as starting materials; The effects of KOH concentration on the morphology and particle size of $KNbO_3$ micro/nanostructures were carefully studied. It was found that lower concentration of KOH lead to formation of nanorod, further increase of KOH concentration leads to formation of $KNbO_3$ microcubes from the nanorod, and then the portion of the cubes increases as the reaction advances until all of the products become nanocubes. Second, nitrogen doped $KNbO_3$ nanocubes (N-cube), that firstly exhibited good visible light photocatalytic activity of $KNbO_3$ species, were synthesized by solid-state reaction of $KNbO_3$ micro/nanostructures with urea at 425 ℃.

Photocatalytic experiment results showed that 1) different morphology and particle size of $KNbO_3$ can cause the change of recombination rate of photogenerated chargers and specific surface area, thus have a significant influence on the photocatalytic activity; 2) The as prepared N-cube exhibited greatly enhanced activity in the visible-light photocatalytic degradation of varies of organic contaminants and photocatalytic reduction and oxidation of water for H_2 and O_2 generation, which were mainly attributed to the improved surface area and increased optical absorption properties arises from the N 2p levels above the O 2p levels of the valence band. A mechanism for the photodegradation of organic contaminants by the N-cube photocatalyst under visible light is also proposed.

The visible-light-sensitive photocatalyst of $Ag_{1.4}K_{0.6}Ta_4O_{11}$ nanoplates was synthesized by a facile molten-salt method, and the photocatalytic activity is evaluated by decomposition of aqueous organic contaminants containing orange G (OG), rhodamine B (RhB) and pentachlorophenol (PCP) as well as photocatalytic reduction of water for H_2 generation under visible light irradiation. The $Ag_{1.4}K_{0.6}Ta_4O_{11}$ nanoplates exhibited higher photocatalytic activity on photodegradation of OG and PCP than that of Degussa TiO_2 P25, but slower on the photodegradation of RhB. In addition, the activity of the $Ag_{1.4}K_{0.6}Ta_4O_{11}$ nanoplates is improved significantly by the modification with lanthanum ions. The optimal modifying content is 1mol% corresponding to the highest photodegradation percentages for photodegradation. On the other hand, the 5% La^{3+} modifying content exhibited highest photocatalytic activity for H_2 evolution. The enhancement of photocatalytic activity after La^{3+} modification is attributed to the formation of nanowires, which further promote charge separation and transfer capability in the La^{3+} modified $Ag_{1.4}K_{0.6}Ta_4O_{11}$ nanocomposites.

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