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PAPER SLUDGE DERIVED NITROGEN-DOPED POROUS CARBON FOR EFFICIENT HEXAVALENT CHROMIUM ADSORPTION

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Abstract:

Paper sludge has been converted to activated carbon, however the adsorption capacity is still limited. We herein present a facile ethylenediamine dihydrochloride assisted activation of paper sludge in producing nitrogen-doped porous carbon adsorbent for hexavalent chromium removal. The characterization results have categorically confirmed the addition of ethylenediamine dihydrochloride effectively introduces nitrogen dopant and enlarges specific surface area. The best-performing nitrogen-doped porous carbon adsorbent endows with a large specific surface area (1244 m²/g) and high Cr(VI) adsorption capacity (193.6 mg/g). The adsorption experiment verifies a spontaneous endothermic chemisorption process with pseudo-second-order kinetic, consistent with a Langmuir model. Further X-ray photoelectron spectroscopy (XPS) results indicate a reductive Cr(VI) adsorption onto the nitrogen-containing functional groups on the nitrogen-doped porous carbon. The present work exemplifies a chemical assist activation of paper sludge into high performance porous carbon adsorbent for hazardous metal removal.

AN POSSIBLE MECHANISM OF THE AGGREGATION-INDUCED EMISSION IN COUMARINS COMPOUNDS

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The most organic chromophores with highly fluorescent in solution at low concentration shows a sharp decrease in their emission efficiency in the solid state. This behavior is usually associated with intermolecular interactions, which provide ways for the nonradiative decay of the electronic excitation energy. A new

photophysical phenomena associated with the aggregation of chromophores - aggregate-induced emission (AIE) was first reported in [1]. In 2002, Park *et al.* reported about enhanced emission phenomena caused by aggregation under similar conditions [2]. Since then, these two effects have attracted considerable attention of researchers, since solid organic luminescent materials are of interest both from the point of view of fundamental research and practical applications, due to their important role in such diverse fields as solid-state light-emitting electrochemical cells, chemosensors, and photocatalysts for hydrogen generation, biochemical probes, and organic light-emitting devices.

To explain the nature of AIE, a number of mechanisms have been put forward, among which the most popular is the mechanism of Restriction of intramolecular rotation, which was later supplemented by the Restriction of intramolecular vibrations mechanism and the Restriction of intramolecular motions mechanism [3]. The implementation of all the presented mechanisms mainly comes down to the mobility of molecules restriction, due to which nonradiative channels are blocked and self-quenching (different motions, rotations, vibrations, conformations changes) is effectively suppressed through the environment effect (change in polarity, viscosity of the solvent and temperature of the system), resulting in the formation luminescent aggregates.

The effect of temperature on fluorescence intensity with a possible mechanism of fluorescence quenching in solutions of heteroaromatic molecules is described in the paper [4]. However, it is not always possible to explain the different fluorescence intensity at the same temperature only by the temperature dependence of the intramolecular degradation of the electronic excitation energy.

This indicates that the medium viscosity has a certain effect on the fluorescence intensity. Quantitatively, the viscosity effect is described: $k_{fl} = \text{const}(T/\eta)^{1/4}$. As can be seen, the fluorescence quantum yield increases inversely with the fourth root of the temperature relative to the viscosity of the solvent. For different molecules, this temperature range may vary, since the molecules exhibit different sensitivity to the solvent polarity and viscosity. Turning to the mechanism describing the dependence of the fluorescence intensity on the medium viscosity, we can conclude with confidence that this is the level inversion mechanism proposed by us in our work [5]. In our studies show that both the temperature and the solvent polarity affect the energy gap between the lowest singlet and triplet levels, which in turn determines the probability of the intersystem crossing between these levels. Thus, theoretically, we assumed that the change in the molecules fluorescence intensity caused by aggregation is determined by the relative position of the energy levels of the lowest electronically excited states.

Many of our experimental and theoretical works are devoted to the study of the spectral-luminescent properties of the coumarins compounds [6,7]. Recently, Wang and co-workers report AIE active coumarin-based Schiff bases [8,9]. However, the coumarin molecules with AIE properties, none of the mechanisms proposed in [4] cannot fully describe the features of fluorescent characteristics.

To explain AIE process, the first step is to learn emission quenching of single molecules of AIEgens by radiationless processes in the solution state. In this respect we carried out theoretical calculations of the absorption spectra of the model series: coumarin, 3,4-benzocoumarin, 4,9-dioxapirene-5,10-dione (DPD) .

The quantum-chemical calculations of the energy parameters of the model compounds were performed employing the program package GAUSSIAN 03W within density functional theory (TD-DFT) B3LYP method and basis set 6-31G (d). On the calculations results, the dependence of the energy levels of electronically excited states position of model compounds and the energy gap value between the $S_{\pi\pi}$ and $T_{n\pi}$ levels on the π -system size was established.

It was confirmed that the effect of temperature should be associated with a change in the length of the C=O fragment and, correspondingly, a change in the relative position of the energy levels of the lower electronic-excited states.

The discussion of the possible mechanism of the AIE-coumarin molecules was based on the established basic regularity of the change in their spectral-luminescent properties, which is determined by the relative position and proximity of the energy levels of the lowest electron-excited states of different orbital and spin nature. This mechanism can be used to explain AIE in compounds whose fluorescence is associated with the various location of energy levels of different orbital and spin nature ($\pi-\pi^*$ and $n-\pi^*$).

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