The effect of sulfuric acid treatment on physicochemical properties of g-C_3N_4 and its efficiency for photocatalytic reduction of Cr(VI)

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INTRODUCTION: A great deal of interest is directed towards g-C_3N_4 (CN) for the photocatalytic reduction of Cr(VI), due to its high stability in acidic conditions and medium band gap (~2,7 eV), but its practical application is limited because of the high recombination rate of electrons and holes. Sulfuric acid treatment is considered as one of the methods for optimizing properties of CN by certain surface and possibly structure modifications which would lead to an increased specific surface area (*S*p) and more active sites, anchoring electronegative groups to enhance charge separation, exfoliated bulk CN into the nanosheets, *etc*. The aim of this research was to investigate the influence of H_2SO_4 concentration and other experimental conditions (temperature and time) on physicochemical properties and photocatalytic efficiency of CN.

EXPERIMENTAL: For the synthesis of CN from urea, direct thermal polymerization (550 °C, 4 h, 10 °C/min) was applied. CN was modified with: a) 1 M aqueous solution of H_2SO_4, by simple reflux method (2 h, 80 °C) Sample CN-P), b) very diluted H_2SO_4, by impregnation and evaporation method (sample CN-S), and c) concentrated H_2SO_4, by mixing (2 h, 80 °C) and pouring the mixture to cold water (sample CN-E) [1-3]. The properties of the samples were studied by FESEM, FTIR, BET, DRS and PL analysis, as well as by determination of particle size distribution, the point of zero charge (pH_{PZC}) and the number of acidic functional groups. Photocatalytic reduction of Cr(VI) was tested at pH=3, under the UV and simulated visible (Vis) irradiation, in the presence of citric acid as a hole scavenger.

RESULTS AND DISCUSSION: The typical g-C_3N_4 structure was maintained after the acid-treatment, with some decreased interlayer spacing for CN-E. The *S*p and mesopore volume decreased for all modified samples, while only CN-E had completely different morphology with respect to the pure CN. Particle size distribution revealed that most of the particles were micro-size and for the CN-E much bigger. All acid-treated samples exhibited blue shift in the absorption edge, corresponding to an increase in the bandgap (BG) energy, which was confirmed with both DRS and PL analysis. Compared with CN, modified samples had lower pH_{PZC} and higher content of surface acid groups. Apart from CN-E, the modified samples showed slightly improved photocatalytic reduction of Cr(VI) under Vis irradiation.

CONCLUSIONS: The main structure of g-C_3N_4 wasn't destroyed by the treatment, but the *S*p was decreased. Concentrated H_2SO_4 was probably responsible for the different morphology of CN-E, drastically decreased *S*p, as well as wider BG, hence reduced photocatalytic activity under Vis irradiation. Still, photocatalysis under UV irradiation was improved, meaning that widening of the BG was crucial parameter, not the rest of the changes achieved by H_2SO_4 treatment.

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REFERENCES

[1] Patnaik S., Martha S., Madras G., Parida K., The effect of sulfate pre-treatment to improve the deposition of Au-nanoparticles in a gold-modified sulfated g-C_3N_4 plasmonic photocatalyst towards visible light induced water reduction reaction, *Physical Chemistry Chemical Physics*, 2016., 18, 28502-28514. https://doi.org/10.1039/C6CP04262G

[2] Zhang L., Liu D., Guan J., Chen X., Guo X., Zhao F., Hou T., Mu X., Metal-free g-C_3N_4 photocatalyst by sulfuric acid activation for selective aerobic oxidation of benzyl alcohol under visible light, *Materials Research Bulletin*, 2014., 59, 84-92. http://dx.doi.org/10.1016/j.materresbull.2014.06.021

[3] Teng Z., Lv H., Wang C., Xue H., Pang H., Wang G., Bandgap engineering of ultrathin graphene-like carbon nitride nanosheets with controllable oxygenous functionalization, *Carbon*, 2017., 113, 63-75. http://dx.doi.org/10.1016/j.carbon.2016.11.030

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