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The effect of sulfuric acid treatment on physicochemical properties of g-C₃N₄ and its efficiency for photocatalytic reduction of Cr(VI)

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INTRODUCTION: A great deal of interest is directed towards g-C₃N₄ (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 (Sp) 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 H₂SO₄ 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 H₂SO₄, by simple reflux method (2 h, 80 °C) Sample CN-P), b) very diluted H₂SO₄, by impregnation and evaporation method (sample CN-S), and c) concentrated H₂SO₄, 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-C₃N₄ structure was maintained after the acid-treatment, with some decreased interlayer spacing for CN-E. The Sp 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-C₃N₄ wasn't destroyed by the treatment, but the Sp was decreased. Concentrated H₂SO₄ was probably responsible for the different morphology of CN-E, drastically decreased Sp, 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 H₂SO₄ treatment.

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