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Full Length Article

Graphene and g-C_3N_4 based photocatalysts for NO_x removal: A review

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ABSTRACT

NO_x liberated into atmosphere from automobile exhausts and fossil fuel combustion, comprise the major air pollutants. They are responsible for serious environmental problems such as acid rain, ozone accumulation, haze and photochemical smog. Besides they contribute to the deterioration of human health by causing decrease of the lung function and respiratory problems. The application of photocatalytic methods in order to mitigate the presence of NO_x in the atmosphere is preferable as they are environmentally friendly, mild and low cost. Therefore, in this review, the photocatalytic activity of g-C_3N_4 and graphene based composites towards NO_x removal was discussed.

NO_x oxidation to non volatile nitrates on the surface of graphene and g-C_3N_4 based photocatalysts has attracted much interest during the last years due to their structures with unique features such as large specific surface area, thermal and chemical stability and enhanced visible light utilization. The formation of 2D-2D intimate heterojunctions between graphene or g-C_3N_4 and other components ensures the enhanced charge transfer, lifetime of electron/hole pairs and thus photocatalytic activity. The increased visible light harvesting also contributes to their usefulness as effective photocatalytic materials. In the present work, the advantages of these novel photocatalysts and the differences/similarities between them were exhaustively highlighted. The role of graphene as catalyst promoter, electron reservoir, support and photosensitizer in its photocatalytic composites was emphasized. The effect of g-C_3N_4 doping and copolymerization with metals/semiconductors on its photocatalytic activity towards NO_x oxidation was thoroughly discussed. Besides, the preparation methods, photocatalytic efficiencies, type of irradiation, utilization of appropriate cocatalysts, and reaction mechanisms during the photocatalytic NO_x removal by graphene and g-C_3N_4 composies, were summarized. It was demonstrated that in the vast majority of graphene and g-C_3N_4 based photocatalysts, the dominant reactive species on their surface during photocatalytic NO_x removal, are $O_2^{\bullet -}$ radicals.

1. Introduction

In recent years, the releaseof NO_x in the atmosphere has become one of the major environmental problems. NO_x (mainly 90% NO and 10% NO_2) are also called "fresh" nitrogen oxides because they reach atmospherein this form. NO, the major component of NO_x, is less toxic than NO_2 but it is readily converted to the latter, via reaction with oxygen. NO_x are emitted from natural processes which are the volcanic activity and decomposition processes of organic matters. They are also emitted from human activities such as automobile exhausts (55%),chemical industry and fossil fuel combustionin power plants (45%).

It is reported that on-road diesel vehicles produce one fifth of global antropogenic NO_x emissions. Studies in Poland, in 2007, showed that the total nitrogen oxide emissions reached 890 Gg but following the accession to the EU, it was agreed to reduce the limits of NO_x emission below 200 mg/m^3. Averages concentrations of NO_x equal to 142 μg m^{-3} (24900 particles cm^{-1}) and 136 μg m^{-3} (27100 particles cm^{-1}), at highway and kerbside stations respectively, have been reported in Denmark in 2008. In 2013, in London street, the highest levels of NO have been found equal to 600–700 ppbV, far away from the target for NO_x levels which is 105 ppbV (EU directive for the protection of human health).

NO_x are responsible for serious environmental problemssuch as acid rain, ozone accumulation, haze, photochemical smog, tropospheric ozone, ozone layer depletion and global warming caused by N_2O. Besides, NO_x as very poisonous, harmful and prominent air pollutants, contribute to the deterioration of human health by causing decrease of the lung function, respiratory problems and increase of the response to allergens [1–7]. For all these reasons, a plethora of new technologies for the lowering of NO_xconcentration

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Fig. 1. NO_x emitted from human activities [7] .

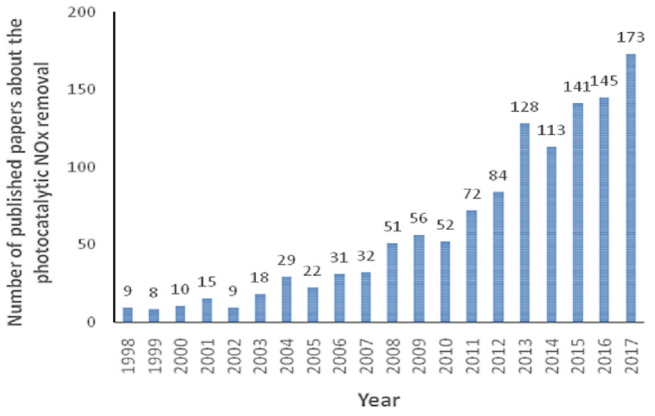

Fig. 2. Number of published papers per year, in the field of the photocatalytic NO_x removal (Science Direct June 2017).

in the atmospher eehave been evolved and their potentials are continuously getting improved (Fig. 1) [7].

1.1. NO_x abatement methods

As far as it concerns NO_x emissions, several restrictions have been imposed by Gothenburg and Kyoto Protocols which refer to the development of new technologies and/or the improvement of currently existing methods.A large number of technologies for NO_x abatement have been applied. These are categorized to pre-combustion, combustion and post combustion techniques. Pre-combustion is a high cost modification which embraces fuel purification, choose of fuels with decreased amounts of nitrogen or replacement of the air in the combustion process by oxygen. Combustion techniques (such as Low Excess Air (LEA), Burners Out of Service (BOOS), Over Fire Air (OFA), Low NO_x Burner (LNB)) are performed via the alteration of operational conditions in order to lower the formation of NO_x by creating oxygen deficiency, lower flame temperature etc.Post-combustion methods succeed in the NO_x removal of the flue gas and the NO_x destruction. They include chemical processes such as reduction (SNCR −Selective Non Catalytic Reduction- or SCR-Selective Cataytic Reduction- with ammonia, or NSR-NO_x storage/reduction, also known as lean NO_x trap-) and oxidation (NTP-Non Thermal Plasma-, PCO-Photocatalytic Oxidation) processes and physical processes (adsorption on activated carbon, absorption in alkaline solutions). A variety of 3D ordered macroporous nanocatalysts has been synthesized, such as transition metal oxide nanosheets on macroporous Ni foam substrate and K-Mn/$La_{0.8}Ce_{0.2}FeO_3$ perovskites for the oxidation of NO_x [8,9]. Hematite supported on alumina (Fe-Al) has also been used as catalyst for NO_xremoval via the generation of OH·radicals from the decomposition of H_2O_2 [10]. $Ni_xZn_{1-x}Ga_2O_4$ systems have been synthesized for NO_x reduction and it has been demonstrared that the ratio of Ni/Zn strongly affects their microstructure, surface morphology and composition and consequently their operating temperature [11]. MnO_2/TiO_2 was studied as catalyst for selective catalytic reduction of NO_x with NH_3 at temperatures 90–330 °C and the role of the poisoning effect of potassium ions in the form of KNO_3, KCl and K_2SO_4 was studied. It was deduced that KNO_3 exhibits the strongest deactivation effect as it provokes a significant decrease in the specific surface area and pore volume and furthermore, K^+ ions decomposed by KNO_3 react with Bronsted acid sites and reduce their reduction power [12].

These technologies are characterized by several important disadvantages, for example, they are efficient only for high concentration NO removal and usually in high temperatures, whereas often their surface modification needs improvement. In case where

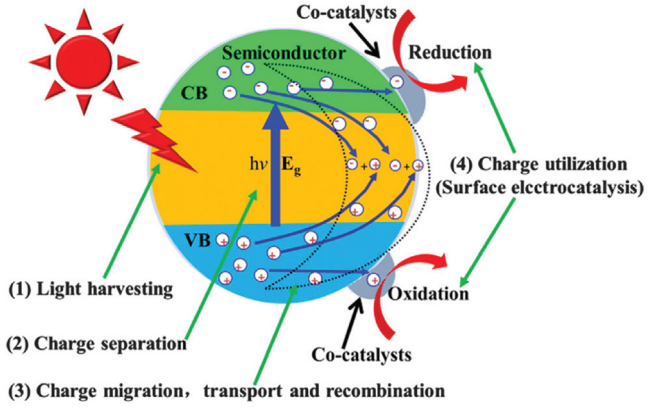

Fig. 3. Four different stages in heterogeneous photocatalysis [20].

alkaline solutions are used, NO_2 is absorbed by them, but the primary necessary oxidation of NO to NO_2 becomes very slow when NO concentration falls to 10 ppm at room temperature. As each of the above methods displays important limitations, they are usually combined in order to obtain improved results [1,13–17].

The photocatalytic oxidation of NO_x constitutes the most convenient way to remove this kind of air pollutants even at parts per billion (ppb) levels by using solar energy, which is cheap, abundant and environmental friendly, in contrast to the conventional methods which are rather expensive and environmental burdensome. A great advantage of the PCO of $NO_x$is that they are oxidized to nitrate (NO_3^-) on the surface of the photocatalyst, which can be easily washed off by water. Besides, very high photocatalytic activities have been recently performed due to the preparation of novel, significantly efficacious photocatalysts [18,19]. The scientific publications during the last 20 years on photocatalytic NOx oxidation are continuously growing as is shown in Fig. 2.

1.2. Heterogeneous photocatalysis/Reaction mechanisms of the photocatalytic NO_x removal

Heterogeneous photocatalysis consists of the following major processes: a) light harvesting, b) charge separation, c) charge migration, transport and recombination d) charge utilization by reduction and oxidation reactions, as shown in Fig. 3 [20]. Namely, under UV/VIS irradiation of an inorganic semiconductor, photoinduced electrons are transferred from the valence band (VB) to the conduction band (CB) giving holes in the VB. The photogenerated electron/hole pairs travel from the bulk to the surface of the catalyst in order to accomplish the appropriate redox reactions