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MULTIDOPED PHOTOCATALYST IN DYES REMOVAL - A SHORT REVIEW

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Abstract : Application of multiple doped nanomaterials in wastewater treatment has received wide attention in recent years. This short review highlights recent developments in the use of multiple doped nanomaterials and their importance in mechanism of photocatalysis for the removal of dyes from aqueous medium. Recent publications emphasize on effectiveness of nonmetal with metal doping. Effect of N, S, C on photocatalyst is focused in current review.

Key words : Doped nanomaterials, wastewater treatment, photocatalysis, dye removal.

Introduction :

Organic pollutants constitute one of the largest groups of wastes released from industrial effluents. Dyes are extensively used in several industries including textile, painting, printing, cosmetic and pharmaceuticals. It is estimated that about 10%–15% of the dyes used in industries are lost in the effluents during the dying process (1).The discharge of highly colored wastewater into our ecosystem raises serious environmental and human health concerns. Many of the dyes are difficult to remove due to their complex nature (2, 3). Decolonization of dye effluents is difficult as they turn to pass through conventional treatment systems unaffected. Most popular methods for dye removal from waste water are Advance Oxidation Processe's (AOP's) since these methods break down the macromolecules into smaller and less harmful substances like N_2, CO_2, NH_3.etc. that is also known as mineralization. Photocatalyst like Fe_2O_3, CdS, WO_3, BiV_2O_5, Nb_2O_5. etc. are proven to be an efficient photocatalyst.

Although transition metal modified photocatalysts are active under visible-light irradiation, the efficiency is still low for practical use. Recently, doping nonmetal atoms, such as C, N and S, has received much attention. Theoretical calculations showed that the p-orbitals of these dopants significantly overlapped with the valence band of 2p-orbitals, which facilitated the transport of photo-generated charge carriers to the surface of the catalyst. Wang et al. (4) reported the shift of photo response of TiO_2 from UV to the infrared region by a carbon dopant. S-doped TiO_2 showed high activity for degradation of MB in water under irradiation at wavelengths longer than 440 nm. (5) Visible-light-active N doped TiO_2 photocatalyst has been prepared by thermal nitridation of TiO_2, amination of TiO_2, sputtering, and hydrolyzing titaniumprecursors in ammonia (6–10).

It is of great interest to investigate the synergetic effects of multiple dopants on the optical shift, crystallinity, surface areas, and activity of TiO_2. It was reported that N and F co-doped TiO_2 had higher visible-light activity than N-doped or F-doped TiO_2 since N dopant improved the visible-light absorption and the doped F atom enhanced the surface acidity and the adsorption of agents. (11) Tryba (12) synthesized C and Fe co-doped TiO_2 and it showed higher activity than TiO_2 for the decomposition of phenol in multiple uses. Our previous research showed two dopants had more beneficial effects than a single one for enhancing the absorption in the visible-light region and improving the photocatalytic activity of TiO_2 (13,14). In this work, multiple dopants modified TiO_2, namely, C, N, S, and Fe, were developed via a facile sol–gel process, which showed an enhanced activity compared to TiO_2 owing to the modification by these dopants.

Methods for Preparation of Nanomaterials :

Different methods are applied to dope Nitrogen, Carbon, Sulfur.etc. like nonmetal in photocatalyst. The methods differ according to sources of N, C, S. Few of them are mention below from current research articals.

[A] To prepare Gd,C,N,S-doped ZrO_2 photocatalysts, $Zr(NO_3)_4$ (1.0 mmol) was added to 0.1 M HNO_3. One millitre of polyethylene was added and the mixture stirred for 30 min. Then a calculated amount of $Gd(NO_3)_3.6H_2O$ was added to the mixture to give Gd:Zr of 0.3-1.0 % and the mixture further stirred for 1 h. This is followed by the addition of thiourea (3.0 g) and the mixture further stirred for 2 h. The Gd,C,N,S-doped ZrO_2 precipitates were separated by centrifugation after washing several times with DI water and ethanol to remove nitrate and organics.The precipitates were then dried in air in an oven at 100 oC for 12 h and further calcined at 500° C for 2 h. (14)

[B] C, N and S doped TiO_2 photocatalyst was prepared by a simple hydrolysis process using titanium isopropoxide as the precursor for titanium and thiourea as the source for carbon, nitrogen and sulphur (26,34). In a typical preparation, 10 mL of titanium isopropoxide solution was mixed with 30 mL of isopropyl alcohol solution. This solution was added drop wise to 20 mL deionized water containing in a 250 mL beaker. The solution was tho- roughly mixed using a magnetic stirrer for 4 h. To this solution, required amount of thiourea, dissolved in 5 mL deionized water was added. The mixture was stirred for 6 h and dried in oven at 80°C for 12 h. The solid product formed was further calcined at 400°C temperature for 6 h in air to get C, N, and S doped TiO_2 photocatalyst. The weight (%) of thiourea doped TiO_2 was controlled at 0, 1, 3, 5, 10 and 15 wt% and the samples obtained were la-beled as TCNS0, TCNS1, TCNS3, TCNS5, TCNS10 and TCNS15 respectively (15).

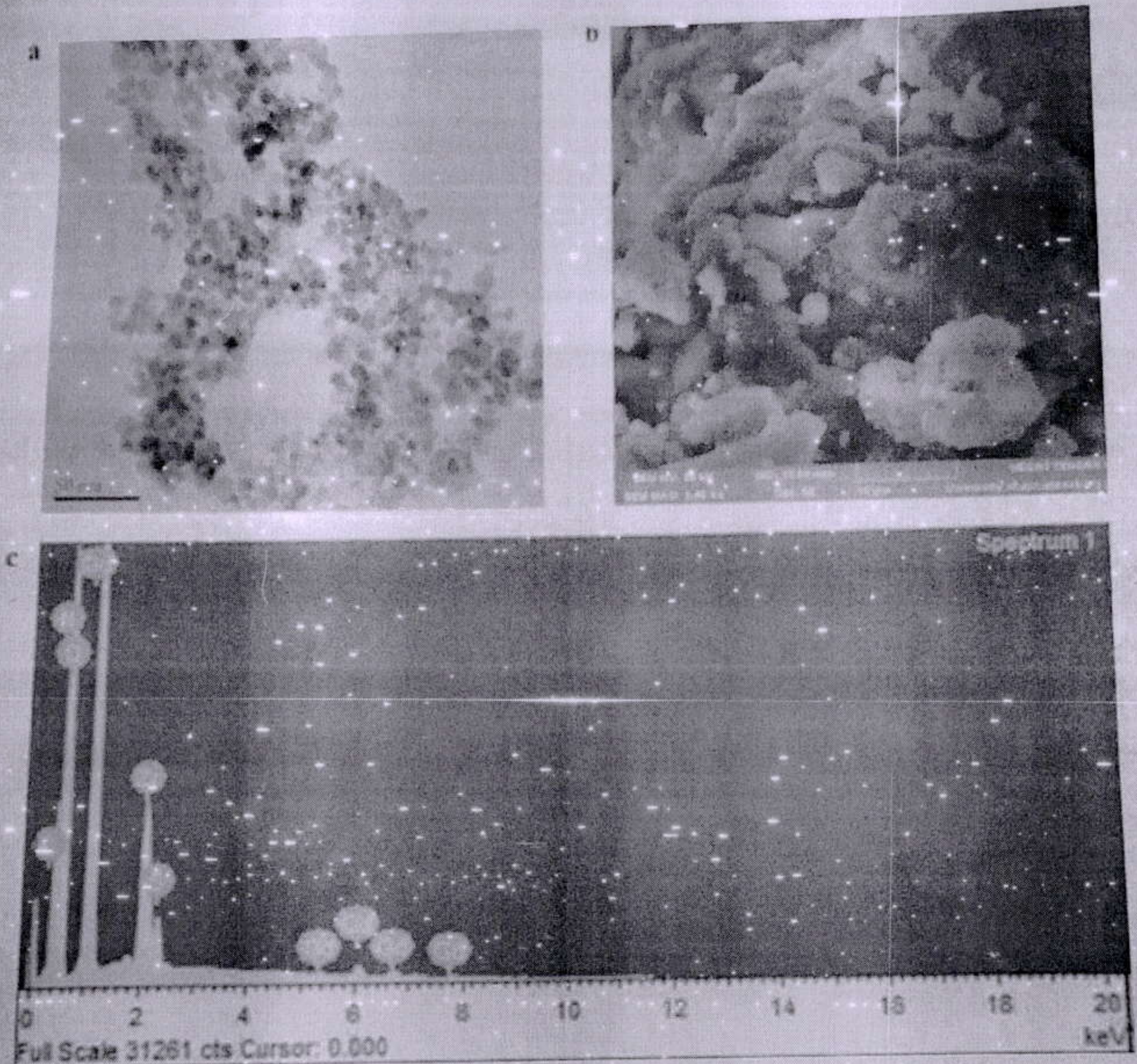
[C] C–N–S tridoped TiO_2 was synthesized using a sol–gel method. In a typical synthesis, 10mL titanium butoxide ($Ti(OC_4H_9)_4$) was added dropwise into 50mL absolute ethanol with certain amount of thiourea dissolved at ambient temperature. After magnetic stirring for 30 min, a mixture of 3mL MQ water, 3mL absolute ethanol and 1mL nitric acid was added dropwise into the above solution,followed by stirring for 6 h and aging overnight to obtain the gel. The gel was dried at 80° C for about 10 h in an oven, ground into fine powder, and calcined at 350, 450, 550 and 650°C for 2 h in a muffle furnace under air atmosphere to obtain the final products. The thiourea-to-Ti molar ratios were 0.03:1, 0.05:1, 0.10:1 and 0.15:1, and the as-synthesized TiO_2 were labeled as Tx–y, where x and y indicated the thiourea-to-Ti molar ratio and the calcination temperature,respectively. For comparison, carbon doped TiO_2 (CT) was synthesized with the same procedure without adding thiourea. In addition, nitrogen doped TiO_2 (NT) and sulfur doped TiO_2 (ST) were synthesized with the comparable contents of N and S using urea and sodium sulfate as dopant sources, respectively. CT, NT and ST were finally calcined at 450°C for 2 h in a muffle furnace under air atmosphere (16).

[D] To synthesize carbon-sulfurcodoped TiO_2 particles, 11.65 g (0.3 mol) of thiourea (99.0%,SCR) and 9.10 g (0.3 mol) of urea (99.0%, SCR) were dissolvedin 150 mL of pure water and magnetically stirred for 30 min.At that point, 26 mL (0.075 mol) of tetrabutyl titanate (98.0%,SCR) as the precursor was slowly added to the solution whileit was surrounded by an ice bath. Then, the mixed solution wasstirred for 12 h and aged for 24 h, and the water was removed at 80°C in air. The precipitate was finally calcined at 500, 550,or 600°C for 3 h in a muffle oven at a heating rate of 5°Câ min-1. The obtained catalysts are denoted as TCS1, TCS2,and TCS3, respectively. To compare the effects of the preparation methods on the activity of the photocatalyst, codoped TiO_2 photocatalysts were also prepared directly by calcining amorphousTiO_2 or anatase TiO_2 with a mixture of thiourea and urea at 600°C; these samples are denoted as TCS4 and TCS5,respectively. The powders before calcination are denoted asTCS1/p, TCS2/p, TCS3/p, TCS4/p, and TCS5/p, respectively. Pure TiO_2 was prepared by direct hydrolysis of tetrabutyl titanate in water surrounded by an ice bath (17).

Given characterization is from E.S. Agorku et al. Materials Today: Proceedings 2 3909 – 3920 (2015) which show incorporation of nonmetal with metal in nanoparticals.

Conclusion :

Nanomaterials proving to be an important pollutant removing materials. Recently nanomaterials are prepared



(a)TEM image; (b) SEM image; (c) EDS spectrum of Gd, C, N, S-doped ZrO_2 (0.6% Gd)

by various doping methods and doping agent but nanomaterial doped with nonmetals are showing their importance in photocatalysis because of their light absorbing capacity and effectiveness after reganaration.

Previously single nonmetals where doped in base nanomaterials, then modified metal plus nonmetals doped photocatalyst are developed, now a days multidoped (N, C, S tridoped) photocatalyst are extensively prepared for efficient photocatalysis.

The introduction of p-orbital in solar energy absorption is an important breakthrough in photocatalysis, because of this factor photocatalyst are more and more applicative in wide range of uv-visible saolar radiation.

Considering all these aspects, it is important to focus on multidoped photocatalysis process because of their surface and light trapping capacity. Multiple sources can be used for the introduction of Nitrogen, Carbon, Sulfur, Boron.etc. nonmetals which include enzymes, low cost chemicals like urea, polyethylene, ammonium chloride.etc.can be used and more cheaper sources can be investigated in near future.

This possibility may be favorable for extensive use of photocatalysis in pollution prevention in future.

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