Synthesis of N-modified TiO_2 nano powder by plasma spray for visible light photocatalysis

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Nano particles of N-modified TiO_2 photocatalyst for visible light catalysis have great potential application on the environmental and energy industry (Chen *et al*., 2007). The preparation for the titania-based visible light photocatalyst usually are carried out by liquid phase synthesis, while with the drawbacks, including long reaction time (1-24 hr), residual carbon matter, and high cost of precursors. Rapid gas phase synthesis of titania is not easily for control of operating condition and size distribution. Moreover, the modification of titania need be performed via multiple stages.

In this study, a clear and transparent $H_2O/TiCl_4$ solution was sprayed as nano aerosols into the reactor for rapid (< 1 sec) thermal synthesizing N-modified TiO_2 ($TiO_{2-x}N_x$) particles by using an atmospheric-pressure microwave plasma torch. The continue microwave plasma system was assembled by a commercially available magnetron (National Electronics YJ-1600, 2.45 GHz) with maximum stationary power of 5 kW. A quartz tube are intersected the waveguide (ASTEX WR340) and the resonator perpendicularly. The powders were collected by 14-stage impactors (MOUDI).

The experimental conditions are as follows: inlet $H_2O/TiCl_4$ molar ratio = 8, the applied power = 900 W, and the inlet $NH_3/N_2/O_2$ molar ratio = 0.5/13.5/1.5.

In order to avoid blocking the atomizer, the precursors must be in the form of a clear and transparent liquid. Moreover, the clean solution reduces the amount of Cl atoms in the feedstock or N-TiO_2. The results show that at an initial $H_2O/TiCl_4$ volume ratio of 8, the final stock solution with a [Ti^{4+}] concentration of 1.14 M and a Ti/Cl atomic ratio of 0.9 is clear and transparent. Yellow ($Ti(OH)_xCl_{4-x}$) or white ($Ti(OH)_4$) was found for other $H_2O/TiCl_4$ volume ratios via the following reaction (Ritala *et al*., 1993):

$$TiCl_4 + H_2O \rightarrow Ti(OH)_xCl_{4-x} + xHCl \quad 0 \leqq x \leqq 4$$

The mass-fractionated particle samples were collected by 14-stage impactors (MOUDI). The results showed that the most of particles (in number) were in 5-10 nm stage impactor, reaching 97.8% of total particle number. Though the most of the mass was contributed by particles in the size of 0.54-6.2 μm, reaching 63.6% of the total mass (Table 1).

The photographs of powders show that the spherical TiO_2 with a primary particle of about 10 nm was found, and the secondary particles were aggregated by the primary particles. In addition, the XRD patterns show that the structural characteristics of powders were mainly anatase crystallization.

Elemental analysis by EDS shows that N atoms were doped in TiO_2. Chemical bonding analysis by XPS confirms the N-doping. The N_{1S} peak could be fitted to three line shapes with binding energies at 395.8, 399.1, and 401.5 eV. These different binding energy peaks are fitted to N^{1+} at 395.8 eV, N^{2+} at 399.1 eV and N^{3+} at 401.5 eV, respectively.

UV-Visible absorption spectrum was used to confirm the red shift of band gap for N-TiO_2. The photocatalytic efficiency of unmodified and N-doped TiO_2 is consistent with commercial P25 powders for the duration of UV-light degradation. By visible light degradation, the conversion of methylene blue is much higher for N-doped TiO_2 than P25, indicating that by using MW plasma torch for producing N-modified, nano TiO_2 powders is an excellent approach.

Table 1. Size distribution of N-TiO_2 powders prepared by $NH_3/N_2/O_2$ MW plasma

Size distribution, μm	Medium size Dp, μm	TiO_2 particles no. percentage n', %	TiO_2 mass percentage, M',%
0.005~0.01	**0.008**	**97.77**	3.06
0.01~0.018	**0.014**	**1.812**	0.37
0.018~0.032	0.025	0.32286	0.37
0.54~1	0.770	0.000463	**15.72**
1~1.8	1.400	0.000115	**23.51**
1.8~2.5	2.150	0.000009	**6.62**
2.5~6.2	4.350	0.000003	**17.71**
6.2~10	8.100	0.000000	12.54

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