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Title	Low temperature preparation and characterization of oxide-based functional composites from liquid phase via hot-water treatment

(800 words)

The low energy consumption production and environmentally friendly process are becoming a great concern in the materials engineering technology. Development of a simple synthetic methodology for preparation of advanced oxide-based materials is a major challenge till now. In the present study, a low temperature process using a soft chemical route from liquid phase via hot-water treatment (HWT) was conducted to synthesize crystalline oxide-based composite materials. Composites in SiO_2-TiO_2, polyaniline (PANI)-TiO_2, and ZrO_2 systems were prepared and studied to achieve better understanding on low temperature crystallization mechanism. In addition, preparation of high surface area of $BaZrO_3$ via modified HWT was carried out.

In the first study, to comprehend the precipitation mechanism of crystallized titania on the surface of SiO_2-TiO_2 coating, SiO_2-TiO_2 gel films were immersed in pure hot water at 90 °C. Concurrently, an external-field such as mechanical vibration or electrical voltage was applied. The dissolution of SiO_2-TiO_2 species into water, followed by migration and reprecipitation of TiO_2 species happened during the treatment. Upon the application of external-filed, both higher dissolution and lower precipitation rates of TiO_2 species were detected. Beside, the applied external-field provides a condition for TiO_2 species to precipitate on the surface of SiO_2-TiO_2 coating producing hydrated TiO_2 crystal with sheet-like morphology structure. The aspect ratio of precipitates formed was higher upon the application of external-field during HWT. By applying the external-field, the rate of water flow was increased, results in a higher collision rate between water molecules and the dissolved hydrolyzed titania species. Hence, the hydrolyzed titania species migrated to other areas of the coating. The hydrolyzed titania species were able to arrange themselves over a large area, which provided the possibility in producing higher aspect ratio of precipitates. By controlling the properties of the precipitates on the surface of the coating, an enhancement on hydrophilicity of the coating can be achieved. Furthermore, it can bring a significant development on anti-fogging coating and thin film catalyst application.

By utilizing the same concept, PANI-TiO_2 hybrids, which act as photocatalyst under visible light irradiation, were synthesized in the second study. The hybrid was prepared by combining the *in situ* aniline polymerization and the condensation-gelation reactions of the sol-gel derived TiO_2 in an acidic solution at 60 °C for 30 h. Structural studies on the obtained hybrids confirmed the presence of amorphous PANI along with crystallized anatase TiO_2. Low temperature crystallization of anatase was successfully conducted. The aging process at 60 °C during *in situ* aniline polymerization and the condensation-gelation reactions should allow the anatase crystallization. This crystallization occurred in a hot-aqueous condition. Similar with the HWT, the dissolution of hydrolyzed titania species which further rearranged themselves into a crystal structure occurred during the treatment.

In the third study, a similar HWT was conducted on ZrO_2 sol-gel system. The treatment conditions were modified to form ZrO_2 crystallites by substituting HWT with base-hot-water-treatment (BHWT) at 90 °C and at pH 14. The dry ZrO_2 gel was immersed in the 90 °C sodium hydroxide (NaOH) solution for 12 h. This process continued with additional stirring for 12 h. Consequently, tetragonal ZrO_2 (t-ZrO_2) with the surface area of 292 m^2/g and the crystal size of 7 nm was formed. The sodium ions played an important role in the formation of t-ZrO_2 by incorporating the Na^+ ions into the crystal structure during the treatment. Moreover, organic groups were effectively removed from the dry ZrO_2 gel, resulting in a porous structure of ZrO_2 powders. The obtained high surface area ZrO_2 powders show a high potential to be applied as support catalytic materials. In the fourth study, $BaZrO_3$ with high surface area was effectively produced via BHWT at relatively low temperatures. $BaZrO_3$ powders with BHWT showed surface area of 18.37 m^2/g which is nearly 8 times larger than those of the powders without BHWT after calcination at 1000 °C for 2 h. Upon BHWT, the organic compounds from the precursor, including amine groups and carbonate groups, were removed. The organic compounds removal provides a precursor with porous structure. The porous structure was relatively maintained during the calcination. Photocatalytic activities of $BaZrO_3$ powders upon decomposition of methylene blue in an aqueous solution under UV light irradiation were enhanced by the increment of their surface area. Based on all the studies, it can be concluded that HWT is a promising method for the preparation of an oxide-based functional composite at low temperatures.