



Fabrication of macro–mesoporous titania/alumina core–shell materials in oil/water interface



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ABSTRACT

A series of macro–mesoporous TiO₂/Al₂O₃ nanocomposites with different morphologies were synthesized. The materials were calcined at 723 K and were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscope (TEM), N₂ adsorption/desorption, Infrared Emission Spectroscopy (IES), X-ray photoelectron spectroscopy (XPS) and UV–visible spectroscopy (UV–visible). A modified approach was proposed for the synthesis of 1D (fibrous) nanocomposite with higher Ti/Al molar ratio (2:1) at lower temperature (<100 °C), which makes it possible to synthesize such materials on industrial scale. The performance–morphology relationship of as-synthesized TiO₂/Al₂O₃ nanocomposites was investigated by the photocatalytic degradation of a model organic pollutant under UV irradiation. The samples with 1D (fibrous) morphology exhibited superior catalytic performance than the samples without, such as titania microspheres.

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1. Introduction

Titania is regarded as one of the most important developing materials and has received considerable attention in numerous fields, such as heterogeneous catalysis [1–4], solar energy conversion [5,6] and hazardous waste remediation [7,8]. However, the relatively poor thermal stability and low surface area of TiO₂ have impeded its practical applications. Several strategies have been developed to circumvent the drawbacks of TiO₂, such as the synthesis of ZrO₂–TiO₂ mixed oxides [9], TiO₂ pillared clays [10] or supporting on mesoporous molecular sieves [11,12]. Preparing TiO₂/Al₂O₃ nanocomposites is a commonly used option and has been commercialized in the last decade because Al₂O₃ is cheap and possesses good thermal stability and large surface area [13–17].

Recent progress in catalyst preparation highlights a new research direction of catalytic nanoarchitecture design in which the accessibility of reactant molecule to catalytically active centers is emphasized and is viewed as an integral part of the catalyst design [18]. Particles with 1D morphology are regarded as an ideal building block for this purpose [19]. Firstly, the 1D nanocomposites is a preferential catalyst support for small nanoclusters or nanocrystallites because such active components, when supported

on traditional porous materials, are prone to block the apertures of the porous materials, which may generate steric hindrance for reactant molecules or even shut off the inner-pipe section from reaction [18]. Secondly, the stacking of 1D nanocomposites will generate large interparticle voids, which allows the large organic molecules to diffuse rapidly to the active sites of the catalyst. Therefore, creating nanocomposites with 1D morphology will be a promising strategy to optimize catalyst structure.

In our previous work, 1D hierarchical ZrO₂/Al₂O₃ nanocomposite was prepared with a specific core–shell structure using alumina nanofibres as hard templates. The stacking of resultant nanocomposite generates a hierarchically macro–mesoporous material: the evenly distributed ZrO₂ nanocrystallites on long bundles of alumina nanofibres form a layer of mesoporous zirconia with a relatively large surface area while the aggregation of 1D nanostructure gives rise to a novel macroporous framework. The core–shell structure of 1D ZrO₂/Al₂O₃ nanocomposite minimizes the exposed alumina surface at high Zr content, making the surface properties of nanocomposites close to pristine ZrO₂. We further developed this material into a strong acid catalyst by grafting sulfate ion on the surface of 1D nanocomposites. The catalyst with 50% Zr molar percentage exhibited an activity 1.4 times higher than that for the pristine sulfated zirconia. The success of developing zirconia nanocomposites into new class of solid acid catalyst motivated us to adapt the synthetic strategy to the preparation of fibrous TiO₂/Al₂O₃ nanocomposites. In this work, a series of TiO₂/Al₂O₃

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nanocomposites were synthesized with the Ti/Al molar ratio varied from 1 to 3. We modified our synthetic strategy allowing the fibrous TiO₂/Al₂O₃ nanocomposites to be prepared at relatively low temperature, which may benefit the production of such materials on industrial scale. The morphologies of resultant nanocomposites were investigated by SEM and the physicochemical properties of resultant nanocomposites were characterized by means of XRD, UV–visible, IES, and the N₂ adsorption/desorption isotherms.

The fibrous structure of TiO₂/Al₂O₃ nanocomposites should be an attractive material and has potential as catalyst or catalyst support to overcome the diffusion problem and rapid deactivation of catalyst suffered in some industrial process [14]. In present work, the structural superiority of fibrous TiO₂/Al₂O₃ nanocomposites was demonstrated by photocatalytic degradation of pollutant in aqueous solution under UV irradiation.

2. Principle for dispersion of boehmite nanofibres

Our preparation process starts with the preparation of dispersive system of boehmite nanofibres. The boehmite nanofibres can form a stable suspension in aqueous solution but usually flocculate in organic solution. Just as with normal colloid particles, the dispersion of boehmite nanofibres in an aqueous solution is a sensitive balance between repulsive interparticle forces associated with the electrical double-layer around the particles and the attractive van der Waals forces as described in Derjaguin–Landau–Verwey–Overbeek theory (DLVO). In this work, by adsorbing a thin layer of water molecules onto the surface hydroxyl groups of boehmite nanocrystallites, we can prepare evenly dispersed bundles of boehmite nanofibres in a hydrophobic organic medium.

This case should be regarded as a hydrated aggregation of hydrophilic particles dispersed in a hydrophobic medium. Since the Van der Waals attraction force on close approach of two nanoparticles is extremely large, separating the aggregation of nanoparticles inevitably requires some considerable force. The repulsive hydration force, which arises between two surfaces when water molecules orient with and bind to the hydrophilic surface forming a hydration layer around nanoparticles, is necessary to separate the hydrophilic surface of two overlapped particles. Meanwhile, the lack of corresponding repulsion is just the fundamental reason that dry boehmite nanofibres are prone to aggregation in oil phase [20].

The repulsive hydration force is a short-range force. This force increases with the water molecule in the hydration layer around nanoparticles being squeezed out. The strength of this force depends largely on the energy required to dehydrate these hydrophilic groups. Empirically, the repulsive hydration energy (per unit area) follows an exponential decay:

$$W_a^H(D) = W_0 \exp\left(-\frac{D}{\lambda_0}\right)$$

where D is a surface separation, $W_0 = 3\text{--}30 \text{ mJ m}^{-2}$ and λ_0 , 0.6–1.1 nm, is the decay length. As measured experimentally, the effective range of hydration forces is $\sim 3 \text{ nm}$ [21].

The amount of water distributed on the boehmite nanofibres, in our work, is strictly controlled. In practice, we restrict the thickness of the water layer to 2–3 nm by calculation, assuming that the water is evenly distributed on the surface of each boehmite nanofibre. For boehmite nanofibres, the hydration repulsive force strongly depends on the orientations of boehmite nanofibres. The hydration repulsive energy is strongest for the parallel orientation of two overlapped nanofibres. As the hydrated boehmite nanofibres are restricted closely by the limited amount of water, there is a strong hydration repulsive force acting between two parallelly

orientated nanofibres. As shown in Scheme 1, they are prone to align to minimize overlapped areas in order to achieve a balance between hydration repulsive energy and van der Waals attractive energy. Therefore, the long bundles are made up of a collection of boehmite nanofibres with a hydration repulsive force acting between them.

The toughness of each bundle is maintained by the Van der Waals force between each of the interconnected nanofibres. As these hydrated nanofibres are dispersed into oil phase, the toughness of each bundle is strongly enhanced by the Laplace pressure, which is the pressure difference between the inside and the outside of a droplet, expressed by the following Young–Laplace equation:

$$\Delta P \equiv P_{\text{inside}} - P_{\text{outside}} = \gamma_{ow} \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

where in the case of R_1 being equal to R_2 ,

$$\Delta P = \frac{2\gamma_{ow}}{R}$$

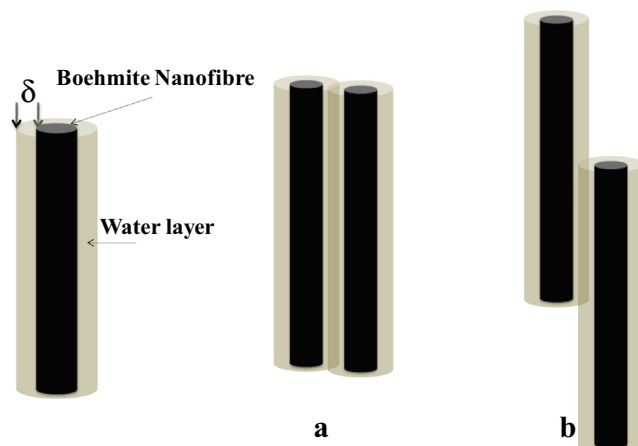
where P_{inside} is the pressure inside the droplet, P_{outside} is the pressure outside the droplet, γ_{ow} is the water/oil interfacial tension, R is the radius of the bubble.

Indeed, the long bundle of boehmite nanofibres is restricted in a droplet possessing a large aspect ratio. As shown in Scheme 2, the bend of the bundle will give rise to the interfacial curvatures and generate pressure differences. As the radius of curvature, generated by nanomaterials, is on a nanometer scale, according to the equation the pressure difference will be extremely large. It will result in an attractive force between two nanofibres. Therefore, the bended bundle will readily restore into the linear arrangement of interconnected nanofibres [22]. By this way, a self-supporting network structures can form in oil/water interface. This network is fairly stable allowing the sedimentation of metal oxide.

3. Experimental section

3.1. Materials

Boehmite nanofibres were synthesized by steam-assisted solid wet-gel method according to previous reports [23]. n-Butanol was purchased from Ajax Finechem and Titanium (IV) butoxide was purchased from Aldrich. All these chemicals were used as received without further purification.



Scheme 1. A schematic illustrating the linear arrangement of boehmite nanofibres driven by hydration repulsive force (a) the strongest hydration repulsive force acting between two parallelly orientated nanofibres (b) change to linear arrangement to minimize the hydration repulsive force.

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