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Lamellar TiO_2 mesophase with an unusual room temperature photoluminescence

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A highly ordered lamellar TiO_2 mesostructure was obtained hydrothermally, in the presence of cationic surfactants under basic conditions. The resulted composite material shows an unusual room temperature photoluminescence.

Nanostructured inorganic–organic composites aroused great recent interest from the viewpoints of both application and fundamental research.[1,2] In the early nineties, with the discovery of a family of silicate mesophases,[3,4] a novel chemical synthetic approach was presented to organize inorganic species and organic surfactants into 2D and 3D superlattice structures.[5,6] In the past few years, this strategy was successfully extended to many non-siliceous elements and numerous ordered inorganic–organic composites with nanometer scale periodicities were obtained.[7] Among them are the lamellar mesophases, with the inorganic species intercalated between the organic layers which in turn offer a two dimensional host for the inorganic arrays. When the inorganic layers are constructed with semiconducting materials, a novel nanostructured semiconductor–surfactant superlattice may result and some novel properties could be thereby expected. In this respect, some metal sulfide based lamellar mesostructures templated by surfactants have been prepared.[8–10] However, their optical properties, relative to their unique structures, have rarely been mentioned. Herein, we report the synthesis of a mesostructured TiO_2, as well as its unusual optical property, *i.e.*, room-temperature photoluminescence, which is undetectable for the bulk TiO_2 phase.

Navrotsky[11] has previously reported a lamellar TiO_2 mesostructure, TMS, by using tetradecyl phosphate, under acidic conditions. However, due to the strong interaction between the phosphate headgroup and titanium, the inorganic layers may be expected to be constructed in part from titanium phosphate, whilst our synthesis is based on the cationic surfactant under basic conditions. The resulting inorganic fraction of the superlattice structure is constructed totally from TiO_2. Thus, 37 ml distilled water, 5.5 ml tetramethylammounium hydroxide solution (TMAOH, 10 wt%) and 1.6 g cetyltrimethylammonium bromide (CTAB) were combined at room temperature to give a homogeneous solution. Then 2.5 ml tetrabutylorthotitanate (TBOT) was added dropwise under stirring. The synthesis mixture, possessing a molar ratio of 1.0 TBOT : 0.60 CTAB : 0.82 TMAOH : 285 H_2O, was stirred for 4 h before being loaded into a Teflon lined autoclave and heated at 115 °C for 3–6 days. After this, the solid product was recovered by filtration, washed extensively with distilled water and air-dried. Elemental analysis, ICP (inductively coupled plasma emission spectroscopy) analysis and TGA measurement show that the as-synthesized product contains 40–45 wt% organic template, 2–5 wt% H_2O and 50–58 wt% TiO_2.

The powder XRD pattern of the as-synthesized mesostructured TiO_2 is shown in Fig. 1, and is indicative of a crystalline nature. As can be seen, only a series of (00*l*) peaks appear in the pattern, the peak intensity decreasing with increasing 2θ angle. These equidistant diffraction peaks have been recognized to arise from a lamellar mesostructure, such as the lamellar silicate[3,5] and aluminophosphate mesophase,[12,13] where both the inorganic species and surfactant molecules are arranged two-dimensionally, with the former sandwiched between the headgroups of the latter. The inter-layer distance of the TiO_2 mesostructure is determined to be 3.0 nm, on the basis of the XRD results. The clearly resolved six orders of the diffraction peak as well as the plain baseline in the 20–30° 2θ range suggest that the TiO_2 layers sandwiched between the surfactants are well crystallized. This high degree of condensation of the inorganic building units may be different from those of the silicate[3–5] and aluminophase mesophases[12,13] whose frameworks are amorphous in nature. On the other hand, the absence of peaks from anatase or rutile implies that there is no bulk TiO_2 crystalline phase present in the product. The superlattice structure is further confirmed by a TEM study, in which the lamellar structure can be clearly observed, with an inter-lamellar distance of 3.0 nm. Calcination in air at 350 °C leads to collapse of the mesostructure and upon calcination at 600 °C anatase was the only product, in contrast with the TMS,[10] in which titanium phosphate accounts for most of the calcination product.

Fig. 2 gives the room temperature photoluminescence (RTPL), spectra (collected on a RF-5301 PC spectrofluorophotometer, Shimadzu) of the resulting TiO_2 mesophase, after excitation at various wavelengths. The emission differs in intensity with changing the excitation wavelength, while the maximum position remains constant, centered at 475 nm. At

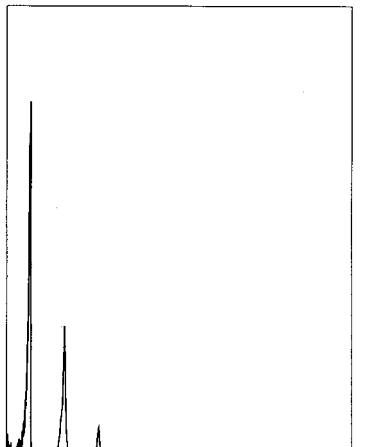

Fig. 1 XRD pattern of the as-prepared TiO_2 mesostructure.

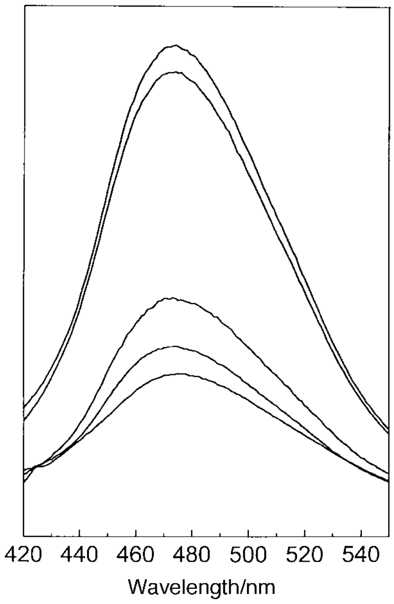

Fig. 2 Room temperature photoluminescence spectra of the TiO_2 lamellar mesophase, excited at (from bottom to top) 400 nm, 300 nm, 320 nm, 360 nm and 380 nm.

an excitation wavelength of 380 nm, the luminescence reaches its maximum intensity, with a FWHH (full width at half height) of 70 nm. The photoluminescence of bulk TiO_2 can only be detected at 77 K, with a maximum at 500 nm, while at room temperature, even a TiO_2 single crystal shows no detectable emission, due to its indirect transition nature.[14] In contrast to this, some nanometer-sized TiO_2 particles have been reported to exhibit RTPL.[14,15] We propose here that the unusual light emission of the mesostructured TiO_2 is induced by the interface effect between TiO_2 and surfactants, similar to the case reported by Zou.[15] Zou observed RTPL of surfactant coated TiO_2 nanoparticles and attributed this phenomenon to the modification of the surfactant molecules on the TiO_2 surface. Despite the dimension difference between the present TiO_2 mesophase and the coated TiO_2 particles of Zou, the interfacial effect between TiO_2 and the organic surfactant might be similar.

In conclusion, a highly ordered lamellar TiO_2 mesophase was prepared hydrothermally in the presence of a cationic surfactant *via* a cooperative organization route. The unusual emission features confirm the fact that this strategy could be employed to produce novel nanostructured materials with unique optical properties, which would be of both fundamental and practical interest.

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