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Synthesis of nano-scale TiO_2 particles by a nonhydrolytic approach†

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We describe a convenient nonhydrolytic approach to the preparation of uniform, quantum confined TiO_2 nanocrystals using an intramolecularly adduct stabilised alkoxide precursor. In contrast to established aqueous sol–gel techniques the processing in hydrocarbon solvents at high temperatures allows access to very small free standing crystallites, and opens up new possibilities for control over size distribution, surface chemistry and particle agglomeration.

Nanocrystalline metal oxides such as TiO_2 have potential and demonstrated applications in modern technologies including solar energy conversion, gas sensors, catalysis, and photocatalysis.[1] Due to this, in recent years, there has been increased interest in studying nano-scale TiO_2 materials as nanoparticles,[2] nanowires,[3] whiskers,[4] and nanotubes.[5] There are many synthetic routes for the creation of nanocrystals of oxides and the controlled hydrolysis of metal alkoxides is the most generalised solution-phase synthetic strategy.[6] TiO_2 nanocrystals prepared by the sol–gel method have fully hydroxylated surfaces and these hydroxyl groups have a strong influence on the catalytic and photocatalytic properties such as electron-transfer rates and reducing properties.[7] Increased photocatalytic activity was reported recently for TiO_2 prepared by ultrasonic irradiation and glycothermal methods.[8] Since the structural, catalytic and photocatalytic properties of nano-scale TiO_2 in general depend on the crystallinity and the nature of the nanocrystal surface, there would be a great scientific as well as technological value in the development of synthetic strategies to create nano-scale TiO_2.

Rapid thermal decomposition of molecular precursors in the presence of strong co-ordinating ligands such as tri-n-octylphosphine oxide (TOPO) at high temperatures yielded good quality metal[9] and highly crystalline semiconductor nanocrystals.[10] However, there are very few reports on successful synthesis of oxide nanocrystals employing similar nonaqueous/nonhydrolytic strategies.[11,12] Surface stabilisation of TiO_2 nanocrystals with capping ligands such as TOPO allows the possibility of ready exchange of capping ligands as well as manipulation of nanocrystal surface. In addition, organically capped nanocrystals are highly dispersible in hydrocarbon solvents and should provide better control over size, surface and prevent the aggregation of nanocrystals. Recently, the synthesis of TOPO capped TiO_2 nanocrystals was demonstrated, but this system does not exhibit quantum confinement.[13]

Alkoxides of titanium [$Ti(OR)_4$, (R = Et, Pr^i, Bu^t)] have been used as titanium precursors in metalorganic chemical vapour deposition (MOCVD) processes to fabricate thin films of TiO_2 and ferroelectric oxides such as $BaTiO_3$, $Pb(Zr, Ti)O_3$, $(Ba, Sr)TiO_3$ and these materials have several important applications in the microelectronics industry.[14] Replacing one or more isopropoxide groups in $Ti(OPr^i)_4$ with donor functionalised alkoxide ligands such as dimethylaminoethoxide ($OCH_2CH_2NMe_2$) (dmae) or diethylaminoethoxide ($OCH_2CH_2NEt_2$) (deae) leads to the formation of more fully saturated compounds such as $[Ti(OPr^i)_3(dmae)]$[15] **1**, $[Ti(OPr^i)_3(deae)]$ **2**, or $[Ti(OPr^i)_2(deae)_2]$ **3**. The conventional titanium alkoxide precursors are highly reactive towards air and water, but modified titanium alkoxide precursors like **1–3** have reduced air/moisture sensitivity compared to the parent alkoxides and are used as alternative precursors in liquid injection MOCVD.[16]

In this communication we describe a nonhydrolytic approach to the preparation of TiO_2 nanocrystals using the intramolecularly adduct stabilised titanium alkoxide precursor **1**. The organic passivating ligand TOPO was used as the reaction medium for the nucleation and growth of nanocrystals as well as a capping agent. Modified titanium alkoxide precursor **1** was synthesised according to the literature, whereas compounds **2** and **3** were synthesised for the first time and fully characterised.[17] Thermal properties of the precursors were analysed by thermogravimetry and differential thermal analysis (TG/DTA) and compared with the parent alkoxides.‡ In a typical synthesis of TiO_2 nanocrystals, 10 g of TOPO was heated to 200 °C, degassed periodically and flushed with argon. The temperature of the reaction flask was raised and stabilised at 325 °C and 0.35 g of the modified alkoxide precursor **1** was injected rapidly into the reaction flask under an Ar atmosphere. Immediately after the injection, the colourless solution rapidly changed to yellow-green and the temperature of the reaction was maintained at 300 °C for 15 min. The solution was cooled to 50 °C and treated with methanol to generate yellow-green flocculates, which were separated by centrifugation. The resulting nanocrystals could be readily dispersed in polar solvents like toluene or hexane.

X-Ray diffraction (XRD) analysis of nanocrystals confirmed the anatase phase of TiO_2.§ The morphology of TiO_2 nanocrystals was examined by transmission electron microscopy (TEM). TEM analysis was carried out on a Hitachi-8100 scanning and transmission electron microscope operating at accelerating voltages up to 200 kV with a single crystal LaB_6 filament. X-Ray energy-dispersive spectra (EDS) were obtained from an attached EDX system, Oxford Link, with Si (Li) crystal and with an ultra thin window ATW 2. TiO_2 nanocrystals dispersed in toluene were deposited onto the porous carbon film on a Cu grid for TEM analysis. Typical TEM images, Fig. 1(a) and (b), revealed that the nanocrystals have a relatively spherical shape with a size distribution of 3–5 nm.

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†Electronic supplementary information (ESI) available: TG analysis of the precursors; particle size distribution analysis of TiO_2 nanocrystals dispersed in toluene; XRD analysis of TiO_2 nanocrystals with and without glass substrate background. See http://www.rsc.org/suppdata/jm/b2/b202767d/

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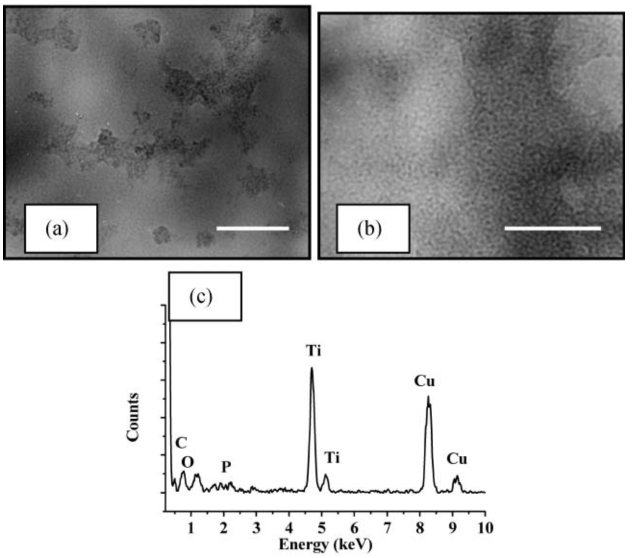

Fig. 1 (a) TEM image of TOPO capped TiO_2 nanocrystals, (b) at higher magnification (scale bar 50 nm), (c) EDX analysis of the nanocrystals showing the presence of Ti and O.

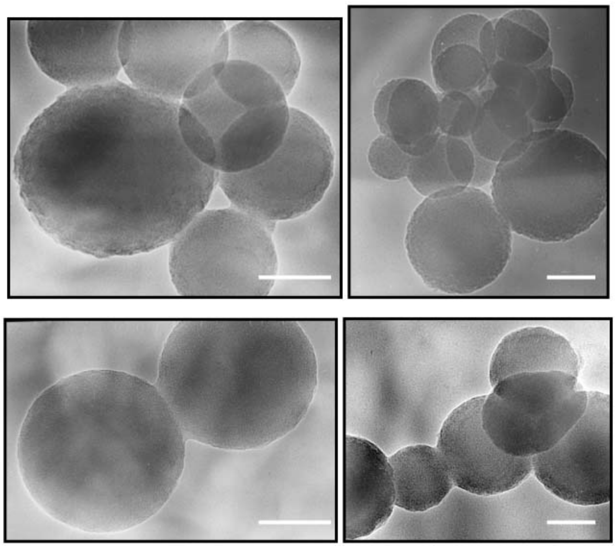

Fig. 3 TEM images of spontaneously self-assembled spherical aggregates of the primary TiO_2 nanocrystals (scale bar 50 nm).

Another method we applied to investigate the average diameter of the particles was dynamic light scattering (DLS) also known as photon correlation spectroscopy (PCS). DLS analysis of TOPO capped TiO_2 nanocrystals dispersed in toluene gave the average diameter of the TiO_2 nanocrystals as 3.3 nm ± 0.8 nm.¶ EDX analysis (Fig. 1c) was performed in order to determine the composition of nanoparticles and mainly Ti and O peaks are obtained along with Cu peaks (from the grid). UV-Vis spectroscopy (Perkin-Elmer Lambda 9) was used to characterise the TiO_2 nanocrystals and the inset of Fig. 2 shows the UV-Vis absorption spectrum of the TiO_2 nanocrystals dispersed in toluene. The spectrum indicates that the onset of absorption appears at 370 nm. The blue shift in the onset of optical absorption of TiO_2 particles relative to the bulk anatase TiO_2 (E_g = 382 nm) implies the quantum confinement of TiO_2 nanocrystals. With decreasing particle size, an increase of the band gap energy and therefore a blue shift in the absorption edge was encountered in many studies as quantum size effects for very small ($d < 4$ nm) TiO_2 particles. The emission from the TiO_2 nanocrystals dispersed in toluene at room temperature was obtained by excitation of the sample. A Fluoro Max-2 instrument with a continuous ozone-free xenon lamp (150 W) and a R928P photomultiplier tube as a detector was used for the analysis. A broad emission spectrum was obtained and a sharp increase in the emission intensity at 320 nm is observed, reaching a maximum around 370 nm (Fig. 1). This type of blue light emission (band-to-band transition) was reported earlier for specially synthesised aqueous TiO_2 colloids (d = 3 nm).[18] Emission spectra were recorded using different excitation wavelengths (275–295 nm) to confirm that the broad band (300–550 nm) is due to very small TiO_2 particles. These results suggest that the TiO_2 particles show the effect of quantum confinement.

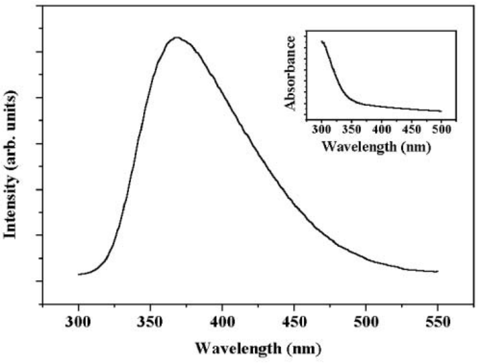

Fig. 2 Luminescence spectrum of TiO_2 nanocrystals dispersed in toluene. Inset: UV-Vis spectrum of TiO_2 nanocrystals in toluene.

Highly monodispersed TOPO capped semiconductor nanocrystals as well as thiol capped metal nanocrystals exhibited spontaneous self-assembly to form well ordered two-dimensional lattices. Previously, Fitzmaurice *et al.*[19] suggested that the polarity of the liquid medium affects the wetting properties and subsequently influences the aggregation of nanocrystals. The mechanism of solvent dewetting in annular ring structures formed by drying a metal colloid on a substrate was examined by Ohara *et al.*[20] and Gelbart *et al.*[21] The slow evaporation of a dispersion of TiO_2 nanocrystals in toluene (minimum amount) on a TEM grid leads to the formation of monolayers/bilayers of ordered spherical structures (Fig. 3). These spherical aggregates of nanocrystals are well ordered and we believe that the formation of these self-assembled structures and the degree of ordering depends on the polarity of the solvents, the rate of solvent evaporation, and the concentration of the nanocrystals.

In conclusion, TiO_2 nanocrystals exhibiting the quantum confinement effect were successfully synthesised using an intramolecularly adduct stabilised titanium alkoxide precursor by a non-aqueous route. Since many metal alkoxide precursors of this type are readily available, we are at present extending this approach of systematically modifying the metal alkoxide precursors for the controlled synthesis of different oxide nanocrystals by non-aqueous routes.

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Notes and references

‡Thermogravimetric and differential thermal analysis (TG/DTA) of precursors **1** and **2** were carried out using a Seiko TG/DTA 6300S11 in an argon atmosphere (100 mL min^{-1}) under ambient pressure employing a heating rate of 5 °C min^{-1}.

§XRD analysis (BRUKER AXS) was carried out on a sample prepared by placing the TiO_2 nanocrystals (dispersed in toluene) on a glass substrate and slowly heating the substrate to 350 °C.

¶Dynamic light scattering (DLS) experiments were performed on a commercially bought ALV photon correlation spectrometer (ALV/DLS/SLS/5000E compact Goniometer system from ALV-Laser Vertriebsgesellschaft mbH Lagen, Germany). A He–Ne laser (Uniphase; 22 mW) was used as the light source. TOPO capped TiO_2 nanocrystals were dispersed in spectroscopic grade toluene and filtered through a 0.2 μm filter (Millipore). Experiments were carried out at room temperature by placing the sample filled quartz cuvette in the centre of the scattering cell surrounded by the index matching liquid (toluene). The scattering intensity autocorrelation functions were obtained at a scattering angle of 90° using a detector (HIGH QE APD) and analysed using a ALV-5000/E Multiple Tau digital correlator. CONTIN method was used for the data analysis.

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