Synthesis of TiO$_2$ Nanocrystals with a High Affinity for Amine Organic Compounds

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This article describes a different approach to the colloidal synthesis of TiO$_2$ nanocrystals using a polymer melt as a solvent. This approach allows us to obtain a colloidal dispersion with a high degree of stability in a polymeric solvent, resulting in a transparent colloid. Using this method, it was possible to obtain the TiO$_2$ nanocrystal with Bronsted acid sites and polymer chains chemically anchored on the nanocrystal surface. The acid surface of those nanocrystals has the chemical property to react in the presence of amine organic compounds and to maintain the colloidal stability. In this way, TiO$_2$ nanocrystals were combined with a molecular probe containing amine functional groups such as polyamine. Through the combination of the molecular probe and inorganic nanocrystals, we obtained a hybrid material with interesting chemical, optical, and electronic behavior, making it a promising material for photovoltaic, photochromic, and sensor devices.

Introduction

Titanium oxide nanocrystals have attracted considerable attention because of their importance in a wide variety of applications including photocatalysts, biosensors, and mainly in solar cells.¹–⁴ The synthesis of colloidal TiO$_2$ nanocrystals with controlled size and shape is the key step in these technological applications. The nonaqueous synthesis route of TiO$_2$ nanocrystals is a sophisticated method for producing nanoparticle with a narrow size distribution and high crystallinity.⁵–¹¹ Nevertheless, this method does not ensure the formation of colloids. The most important factor in colloid formation is the stability of the system, which depends on particle size and mainly the surface chemical composition. In particular, the control of a colloidal surface is not a simple task, and many studies have revealed the achievement of the colloidal stability of TiO$_2$ nanocrystals via chemical surface modification using a specific ligand, such as carboxylic acid, organosilanes, or phosphorus organometallics.¹²–¹⁶ Organic molecules with carboxylic acid groups have been the principal compound used to modify the surface of inorganic nanocrystals because this compound acts as a chelating agent.¹⁷ In many situations, the carboxylic acid is only a functional group anchoring the specific part of the molecule.¹⁸ However, there is a huge variety of amine compounds with interesting biological and chemical properties that could be directly anchored to the TiO$_2$ surface, resulting in a material with different functionality. For example, some ruthenium organometallics or bioligands¹⁹,²⁰ could be chemically incorporated onto the TiO$_2$ surface without the addition of a carboxylic acid functional group to the molecular structure. However, the amine group shows a weak affinity for the surface of TiO$_2$ obtained in aqueous media or via the synthesis method that uses surfactants as ligands.²¹,²²

The inherent acid–base property of the solid surface is a critical parameter in evaluating the interactions with chemical compounds.²² Miyamoto et al. have shown that the terminal hydroxyl groups on the surface of vanadium pentoxide act as Bronsted acid sites for ammonia adsorption and that these acid sites are more energetically stable.²⁴ Typically, the chemical strategy for increasing the affinity between the inorganic surface and amine compounds is to increase the degree of dissociation of the Bronsted acid sites on the solid surface. In addition, the number of the acid sites depends on the surface area, crystallographic planes, and residual ligands.²⁵–²⁷ In general, the synthesis approach used in

the nanocrystals synthesis is the key factor in controlling the acidic nature of the surface. It is well accepted that some surfactants and solvents inactive the acid sites during the synthesis process, drastically reducing the density of acid sites and the affinity with specific compounds in a posterior synthesis step.28–30

In this article, we introduce a different concept of the TiO2 surface, using appropriate synthesis methods that allow us to obtain an oxide undergoing a strong interaction with an amine organic compound without additional postprocessing steps. We synthesized anatase TiO2 nanocrystals with Brønsted acid sites; consequently, this surface has a strong affinity for basic organic compounds such as organic molecules with amine functional groups. The TiO2 nanocrystals were prepared in a polymer melt as a solvent, and they play an important role in the reaction process, such as reagent and solvent.31 To identify the Brønsted acid sites on the TiO2 nanocrystal surface, we select a molecular probe that presents a strong interaction with this kind of acid site and presents different properties after the protonation reaction. The polyaniline is a conducting polymer that is well known for its easy synthesis, environmental stability, and unique acid/base doping/undoping and oxidation/reduction chemistry. In the emeraldine oxidation state (emeraldine base), polyaniline becomes electrically conducting when doped with acid, leading to the formation of emeraldine salt.32 The tunable color and conductivity can be used to detect Brønsted acid sites on the solid surface. Many reports showed the combination of TiO2 and doped polyaniline using a simple mixing process.33–36 However, it is important to point out that we are using the undoped polyaniline as a molecular probe to characterize the strong acid sites on the surfaces of TiO2 nanocrystals and to obtain a hybrid material with polymer directly bound to the inorganic surface. Furthermore, these hybrid materials are an alternate path to obtaining new functionality as a result of the combination between organic and inorganic properties.37,38

**Experimental Section**

**Materials.** Titanium(IV) chloride (TiCl4, 99.99%, Aldrich), poly(1,4-butanediol) (HO(CHOH)2CH2CH2OH, H2), average molecular weight Mw = 1000 g/mol, Aldrich), emeraldine base (Mw ≈ 5000 g/mol, Aldrich), N,N-dimethylformamide (DMF), and acetone were used.

**Synthesis of TiO2 Nanocrystals.** TiCl4 (10 mmol) was injected into 20 g of poly(1,4-butanediol) at 80 °C in a nitrogen atmosphere. This transparent solution was heated to 120 °C under vigorous stirring and then kept for 6 h in a closed glass flask. The resulting TiO2 nanocrystals were cooled to 60 °C, after which 60 mL of acetone was added. This solution was then centrifuged at 1400 rpm for 5 min; after that it was washed several times with acetone. Part of the sample was vacuum dried at 60 °C for 6 h for later characterization. The other part of the sample was used to prepare a standard colloidal TiO2 solution by adding 10 mL of DMF to obtain a TiO2 concentration of 37 mg/mL.

**Molecular Probe Test.** Eight milligrams of emeraldine base was dissolved in 2 mL of DMF, forming a blue solution. This solution was then mixed with 2 mL of standard colloidal TiO2 solution, which instantly changed color to green. This green solution was centrifuged at 1400 rpm for 15 min and washed with DMF three times to remove excess polyaniline, after which 50% of the sample was vacuum dried at 70 °C for 18 h, yielding into a green powder that was subjected to characterization. The other half of the sample was dispersed again in DMF for characterization by UV−vis spectroscopy.

**Characterization**

**Transmission Electron Microscopy.** The size and morphology of the TiO2 nanocrystals were determined by high-resolution transmission electron microscopy (HRTEM), using a TECNAI F20 FEG microscope operating at 200 kV. The TiO2 nanocrystals were dispersed in ethyl alcohol, which was applied to an ultrathin 400 mesh carbon-coated grid.

**Powder X-ray Diffraction (XRD).** The crystallographic phase of the TiO2 nanocrystal powder was determined on a Rigaku D/MAX-2500 diffractometer using Cu Kα radiation (λ = 1.5418 Å). The scanning step size was 0.02° in 2θ with a counting time of 1 s per step.

**Dynamic Light Scattering (DLS).** DLS analysis was performed in a 90 plus particle size analyzer (Brookhaven Instruments) at a laser wavelength of 660.0 nm and a detection angle of 90° at 20 °C. The TiO2 was dispersed in DMF solvent, and the DLS analysis was adjusted to the viscosity and refractive index of this solvent.

**Infrared Spectroscopy.** Fourier transform infrared spectroscopy (FT-IR) analyses were obtained from a solid sample of TiO2 mixed with KBr powder using a Bruker Equinox 70 FT-IR apparatus in reflectance mode at a resolution of 4 cm⁻¹ over a 4000–500 cm⁻¹ spectral range.

**Thermogravimetric Analysis (TGA).** TGA was performed on a Netzsch model STA 409 to determine organic mass loss under an oxygen flux at a rate of 10 °C min⁻¹.

**UV−Vis Spectroscopic Analysis.** UV−vis spectroscopy was essential to garnering information about the absorbance behavior of TiO2-doped polyaniline nanocrystal. UV−vis absorption spectra were obtained using a Shimadzu 3100 UV−vis spectrophotometer.

**Photoactivity.** The photoactivity test was carried out with a 30 W UV lamp as the excitation source, exposing the samples to 30 min of ultraviolet radiation. A similar experiment was realized with a 150 W visible-light lamp.

**X-ray Photoelectron Spectroscopy (XPS).** The XPS measurements were taken in a VG Microtech ESCA3000 spectrometer with a base vacuum of 3 × 10⁻¹⁰ mbar, a 250 mm hemispherical analyzer with nine channelrons, and Al Kα nonmonochromatic radiation. Binding energy corrections were made to the raw spectra using the handbook reference of Ti 2p3/2 and the C 1s peak at 284.5 eV for the N 1s peak.

**Conductivity Measurement.** Four-probe pressed pellet conductivities for the TiO2−emeraldine salt sample were carried out using a Keithley 237 high-voltage source measurement unit at room temperature. The current−voltage curve of the pressed pellet exhibited nonlinear behavior. The conductivity measurement was carried out after the postpuncture voltage in the ohmic region.

**Photoluminescence (PL).** PL spectra were collected with a Jobin-Yvon, Inc. Fluorolog model FL3-12. A 450 W Xe lamp was
used for excitation, with the photon wavelength fixed at 250 nm. The PL spectra were collected in the 250–650 nm range using a photomultiplier tube detector. Measurements were conducted in quartz cuvettes of 1 cm path length. The excitation and emission slit widths were set at 3.0 nm.

Results and Discussion

Titanium oxide nanocrystals were synthesized by a modified synthesis route involving the reaction of titanium chloride with poly(ether glycol) of high molecular weight (i.e., poly(1,4-butanediol)). This synthesis is based on the formation of partially hydrolyzed titanium alkoxide and the elimination of organic halite and HCl via a subsequent polycondensation reaction, as illustrated in Supporting Information Scheme S1.[39,40] This reaction, which is performed at 120 °C, causes a stable colloidal dispersion of the TiO₂ nanocrystals in the polymer solvent. Apparently, there is no clear evidence of nanocrystal formation because the resulting products have transparent features in visible light. This transparency is caused by the high affinity of the nanocrystals for the melted polymer. The addition of ethanol, tetrahydrofuran, or DMF did not change the degree of stability. However, the TiO₂ nanocrystals in a melted polymer are easily destabilized by the addition of acetone or chloroform. The resulting turbid colloidal suspension is isolated by centrifugation in high yield and is washed several times with acetone.

Synthesized TiO₂ was characterized by high-resolution transmission electron microscopy and powder X-ray diffraction. The low-magnification HRTEM image in Figure 1a shows the formation of nanocrystals with a truncated tetragonal bipyramidal Wulff shape, and the highly magnified HRTEM image in Figure 1b indicates the formation of well-crystallized material. An anatase nanocrystal with the Wulff shape contains [101] and {001} facets. The XRD analysis (Figure 1c) confirmed the presence of the anatase TiO₂ phase only and a mean particle size of 8 nm, as estimated by the Scherrer formula. These nanocrystals form a very stable colloid in DMF with thixotropic behavior, as seen in Figure 1d. Apparently, the chemically attached polymer layer was able to transfer its solubility to the nanocrystal. The nanocrystal colloidal dispersion was used to perform DLS analysis, and the result shows a narrow particle size distribution with an average diameter of 9 nm (Supporting Information Figure 1S). This synthesis strategy makes promising TiO₂ nanocrystals with good phase and morphological control. However, we do not have information about the chemical surface characteristics. To obtain this information, a molecular probe test was performed. Polyaniline is an ideal molecular probe for identifying Brønsted acid sites because of the presence of amine groups and an optical effect in the presence of protons.

The molecular probe test proposed here is based on the simple reaction of the emeraldine base and TiO₂ in an organic solvent. The main idea is to promote the reaction of the amine group of polyaniline with the nanocrystal by means of a protonation reaction, as illustrated in Scheme 1. For this purpose, TiO₂ must have a superficial Brønsted acid site, namely, a hydroxyl group, and it must be soluble in a suitable organic solvent in which the emeraldine base is also soluble, such as DMF. To obtain the hybrid material, the TiO₂ solution was mixed with the emeraldine base solution at room temperature (Experimental Section). Mixing caused the solution to turn green, as illustrated in Figure 2c (vial 3c), indicating the protonation reaction and the formation of emeraldine salt. The resulting hybrid material kept its colloidal stability and can be easily centrifuged (Supporting Information Figure S2). It should be noted that the synthesis of TiO₂ nanocrystals and the processing of the hybrid material are carried out by simple, rapid routes using inexpensive raw materials.

FT-IR spectra of the hybrid material in Figure 3 confirmed the presence of poly(1,4-butanediol) and emeraldine salt on the surface of TiO₂. The spectrum of TiO₂ nanocrystals shows a broad band at 3260 cm⁻¹, which is evidence of the terminal hydroxyl group of the polymer. The bands at 2967 and 2871 cm⁻¹ associated with the asymmetric and symmetric stretching modes of the C−H group. Two other important bands at 1649 cm⁻¹ associated with the hydroxyl group of titanium oxide and at 1104 cm⁻¹ associated with the −C−O− group,[41,42] relative to poly(1,4-butanediol), are observed.

The spectrum of the hybrid material (Figure 3) shows an intense signal at 1656 cm⁻¹ attributed to protonated =N⁺ (emeraldine salt) absorbed on the nanocrystals' surfaces and signals at 1572, 1492, 1377, 1305, and 1251 cm⁻¹ ascribed to polyaniline. This

analysis indicated that polyaniline and poly(1,4-butanediol) were attached to the metal oxide surface. It is important to point out that the infrared signals corresponding to the nitrogen bond showed a shift in relation to the infrared spectrum of the pure emeraldine salt. This shift must be associated with the strong interaction between polyaniline and the TiO$_2$ surface.

A thermogravimetric analysis of the hybrid material showed the presence of 12 wt % poly(1,4-butanediol) and 8 wt % polyaniline. The formation of emeraldine salt is a clear indication of the reaction of TiO$_2$ with the emeraldine base. Because the reaction took place in an aprotic organic solvent such as DMF, we believe that the presence of the OH supercial groups of the nanocrystal was the source of protons, acting as Bronsted acid

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**Scheme 1. Simplified Scheme of the Interaction of TiO$_2$ Nanocrystals with Emeraldine Base to Form a Hybrid Material**

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sites. For a better analysis of the reaction between the emeraldine base and TiO$_2$, the material was characterized by UV–vis spectroscopy, as indicated by the results in Figure 2a. This Figure depicts the spectrum of the emeraldine base (blue curve), which is a typical spectrum with two absorption peaks (325 and 625 nm), and the spectrum of TiO$_2$ (black curve) showing an absorption edge of around 430 nm associated with the electronic transition between the valence band (VB) and the conduction band (CB) of this metal oxide. Now, looking at the spectrum of the hybrid compound TiO$_2$–emeraldine salt (green curve), a shoulder at around 430 nm and a broad peak beginning at 520 nm are visible. These two features are the fingerprint of the emeraldine salt, confirming the formation of the electronically conducting form of polyaniline. In addition, note the red shift of the absorption edge of the TiO$_2$ nanocrystals, suggesting the formation of an interface with localized states. These localized states may be related to the trapped charge at the TiO$_2$–polyaniline interface.

The UV–vis and FT-IR spectroscopy analyses strongly suggest a protonation reaction between polyaniline and the TiO$_2$ surface. However, for a more detailed analysis of this interaction, the material was characterized by X-ray photoelectron spectroscopy, as shown in Figure 4. The XPS analysis shows the core-level spectrum of Ti 2p$_{3/2}$ of the hybrid compound, the TiO$_2$–emeraldine salt. This spectrum can be deconvoluted into two different curves, which can be ascribed to Ti$^{4+}$ bound to oxygen, with a peak at 458.8 eV, and a Ti$^{4+}$ ion with a higher negative charge density, with a peak at 457.7 eV. A plausible explanation for this lower-energy peak of Ti is the deprotonation of Ti–OH, resulting in Ti–O$^-$.

It is important to point out that the core-level spectrum of Ti 2p$_{3/2}$ of the pure TiO$_2$ nanocrystals showed the presence of a single peak centered at 458.8 eV (Figure S3 in the Supporting Information). The core-level spectrum of N 1s also showed relevant information about the protonation reaction, as illustrated in Figure 4b. The N 1s spectrum of polyaniline showed a single peak centered at 398 eV, typical of a benzenoid amine, nondoped polyaniline, whereas the TiO$_2$–emeraldine salt sample showed a spectrum with a peak centered at 401.5 eV associated with positively charged nitrogen atoms of doped polyaniline.

The XPS analysis corroborated the UV–vis and FT-IR results, strongly supporting the protonation reaction between the superficial OH group of TiO$_2$ and the emeraldine base, resulting in the emeraldine salt.

The aforementioned results suggest that the hybrid material possesses the characteristics of the doped emeraldine salt, thus the hybrid material should present good electronic conductivity. Four-probe pressed-pellet conductivity for the TiO$_2$–emeraldine salt was 0.6 S cm$^{-1}$, which is lower than the pure conventional HCl-doped emeraldine powder with conductivity ranging from 1 to 10 S cm$^{-1}$. However, lower conductivity than that of pure emeraldine salt was expected because the total amount of polyaniline was only 8 wt %. Considering that the electronic conductivity of the hybrid material followed a phase role relationship and that the electronic conductivity of polyaniline is much higher than the conductivity of TiO$_2$ anatase that ranges from $10^{-4}$ to $10^{-12}$ S cm$^{-1}$, the conductivity of the hybrid material should range from 0.2 to 2.0 S cm$^{-1}$. On the basis of this analysis, the conductivity measurement corroborated the presence of doped material.

Figure 5 shows the photoluminescence (PL) spectra of the TiO$_2$ nanocrystal in DMF and the TiO$_2$–emeraldine salt hybrid material. This kind of characterization can supply information about the correlation of energy levels between polyaniline and TiO$_2$. The PL spectrum of the TiO$_2$ nanocrystals showed a broad asymmetric band with a maximum intensity at 380 nm (3.3 eV). This band can be associated with the emission process related to free exciton electron–hole recombination (i.e., the maximum intensity must be associated with the band gap energy) of TiO$_2$.

The PL spectrum of the hybrid material showed two broad asymmetric bands, one of lower intensity with a maximum at 413 nm (3.0 eV) and the other with a maximum at 493 nm (2.5 eV). The pure polyaniline did not show any PL in the UV–vis range of the spectrum. A plausible explanation for this PL emission behavior is as follows. The first band is presumably associated with emission from the localized states at the TiO$_2$–polyaniline interface to the VB of TiO$_2$. The emission band at 413 nm supported the formation of localized states at the interface, corroborating the UV–vis results in Figure 2a. The second band can be ascribed to an emission process from electrons in the π orbital of the emeraldine salt to the VB of the TiO$_2$. On the basis of the PL measurement and on the optical transition of the emeraldine salt, we can propose that an electronically active interface was generated between polyaniline and TiO$_2$, as illustrated schematically in Figure 5b, considering electronic transitions, energy levels, and electron trapping. The relative positions of the electronic energy levels proposed here make this hybrid material a good candidate for use in photovoltaic devices.

The colloidal suspension of the hybrid material showed interesting optical activity when irradiated with UV or visible light. As indicated in Figure 2b, when the green solution was irradiated with UV light it turned blue and when it was irradiated with visible light it became purple. This photochromic behavior is likely related to light-induced oxidation. The UV–vis spectra of these solutions (Figure 2b) confirm the color change. Note, also, that the ratio of the absorption edge in both samples, suggesting a strong interaction between polyaniline and TiO$_2$ nanocrystals.

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Conclusions

The reaction between poly(1,4-butanediol) and TiCl₄ led to the formation of colloidal nanocrystals with a polymer layer and acid sites on the surface during the synthesis process. The polymer chemically attached to the nanocrystals’ surfaces and Brønsted acid sites allowed high stability in DMF and the capacity to react with an amine compound, such as polyaniline. A colloidal dispersion of the hybrid material showed interesting optical activity when irradiated with UV or visible light. As indicated in Figure 2, when the green solution was irradiated with UV light it turned blue and when it was irradiated with visible light it became purple. This photochromic behavior is likely related to light-induced oxidation. The UV–vis spectra of these solutions confirm the color change. Note also the red shift of the absorption edge in both samples, suggesting a strong interaction between polyaniline and TiO₂ even after oxidation took place. It is also important to note that the hybrid material retained its colloidal stability after its color changed.

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Supporting Information Available: Reaction mechanism, DLS analysis, photograph of centrifuged hybrid material, and Figures of XPS spectra of TiO₂ nanocrystals. This material is available free of charge via the Internet at http://pubs.acs.org.