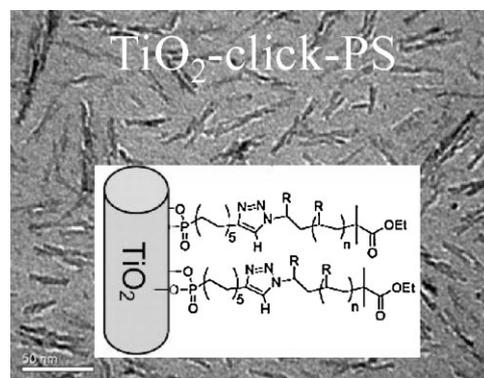


“Click” Dielectrics: Use of 1,3-Dipolar Cycloadditions to Generate Diverse Core-Shell Nanoparticle Structures with Applications to Flexible Electronics^a

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We have synthesized a “universal ligand” incorporating a phosphonate surface anchor and a terminal alkyne moiety which binds to TiO₂ nanoparticles and exhibits excellent dispersity in organic solvents. The alkyne functionality permits attachment of azide terminated polymer shells using “click” chemistry. Thus TiO₂ core nanoparticles have been encapsulated with both polystyrene and poly(*t*-butyl acrylate) shells. The TiO₂-poly(*t*-butyl acrylate) core shell nanoparticles are amenable to further chemical transformation into TiO₂-poly(acrylic acid) nanoparticles through ester hydrolysis. These TiO₂-poly-acrylic acid nanoparticles are dispersible in aqueous solution. The resulting core-shell nanoparticles have been incorporated as high *K* dielectric films in capacitor and organic thin film transistor devices and are promising new materials for flexible electronics applications.



Introduction

Flexible electronics based on organic thin film transistors is a rapidly advancing technology which is on the threshold of commercialization.^[1–3] Although much progress has been made towards the development of robust materials and processes to fabricate organic semiconducting devices, several outstanding materials challenges remain. One key

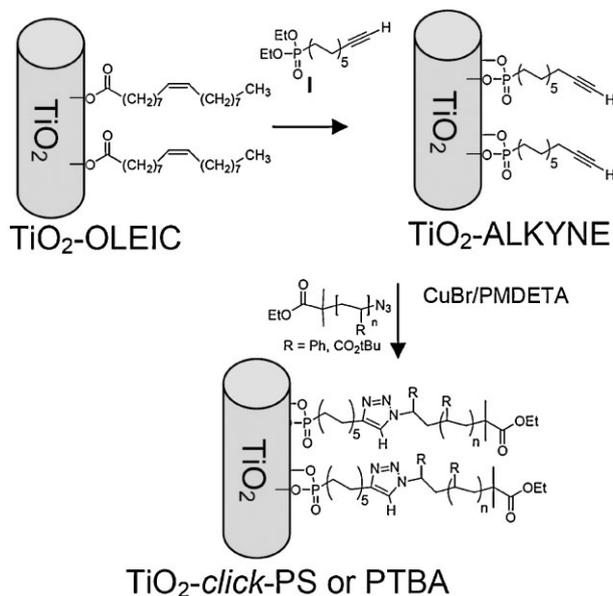
problem is that, due to the low mobilities in current organic semiconductors, high operating voltages are required. High *K* dielectric materials could reduce the operating voltages, but typical high *K* materials (inorganic oxides such as titanium oxide, barium titanate) are not compatible with flexible processing. Our previous efforts have provided a flexible high *K* dielectric through the use of core-shell structures in which a polymer (i.e. polystyrene) has been covalently attached to the surface of TiO₂.^[4] This method also permits the formation of films with high loading levels of TiO₂ (≈20 vol.-%) which are assembled from units of TiO₂-PS, thereby generating a pseudo-homogenous film which combines the high permittivity of TiO₂ with the desirable mechanical properties of polystyrene.^[4]

We sought to diversify the polymer shell used in these nanoparticle systems in order to tailor the properties of specific core-shell nanoparticle materials. However, due to

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^a Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mrc-journal.de>, or from the author.

the difficulties of dispersing titanium oxide nanoparticles in various solvents without aggregation, it was of interest to us to explore a ligand system that would not only dictate nanoparticle dispersibility but would also allow for further functionalization.^[5–6] We were aware of the extensive work on the application of the copper (I) catalyzed azide-alkyne cycloaddition “click” reaction^[7] to surface functionalization^[8–12] and to functionalization of nanoparticles of silica,^[13–15] gold,^[16] and other metals and other semiconductors.^[17–18] However, despite their importance as high *K* materials, successful “click” functionalization of titanium oxide and other high surface energy nanoparticles has to date not been reported presumably due to the difficult problem of aggregation. We sought to overcome this problem through ligand design. In our exploration of ligands for the first generation TiO₂-PS system, we determined that the use of a polar moiety (i.e. ester) as a ligand for TiO₂ resulted in aggregation and lack of dispersibility of the nanoparticles. We therefore designed and synthesized a nonpolar ligand with a phosphonate anchor^[19–22] to bind to the surface of the TiO₂, and an alkyne function at the other terminus to participate in a “click” reaction.^[6,7] This “universal ligand”^[5] was anticipated to have excellent properties for dispersion in organic solvents, as has been observed previously in the synthesis of polymer shell-iron oxide core nanoparticles. Alkyne functionalized TiO₂ nanoparticles served as a precursor to the “click” reaction with azide terminated polymer. (see Scheme 1) We have successfully attached poly(*t*-butyl acrylate) and polystyrene to titanium oxide. Furthermore,



Scheme 1. Functionalization of TiO₂-Oleic nanoparticles with dodec-11-ynyl-phosphonic acid diethyl ester (I) and subsequent CuAAC “click” reaction with azide terminated polystyrene and poly(*t*-butyl acrylate) to generate TiO₂-click-PS and TiO₂-click-PTBA.

we chose PTBA functionalization of TiO₂ since this allowed for the easy hydrolysis with trifluoroacetic acid^[23] to generate a polyacrylic acid shell structure, which is now dispersible in alcohols such as methanol and other polar solvents (e.g. water). We have successfully incorporated our polystyrene and PTBA functionalized TiO₂ into organic electronic devices, demonstrating their potential as new materials.

Experimental Part

Anatase phase titanium oxide nanoparticles coated with oleic acid (TiO₂-OA) were synthesized as reported previously.^[4,24] Dodec-11-ynyl-phosphonic acid diethyl ester (phosphonate-alkyne) (I) was designed with a phosphonate terminus for bonding to titanium oxide and an alkyne terminus for participation in the CuAAC reactions. The nonpolar nature of the ligand was thought to be essential to preventing aggregation of the resulting ligand capped nanoparticles. This was confirmed by good dispersion properties of TiO₂-alkyne in a variety of solvents (i.e. forms transparent dispersions that easily filter through 1 micron syringe filter). Phosphonate I was synthesized from 1,10-dibromodecane as described in the Supporting Information section.

Azide terminated polymers ω -azido polystyrene [$\overline{M}_n = 8100 \text{ g} \cdot \text{mol}^{-1}$, PDI = 1.18] and ω -azido poly(*t*-butyl acrylate) [$\overline{M}_n = 6483 \text{ g} \cdot \text{mol}^{-1}$, PDI = 1.05] were synthesized by ATRP from an α -bromoisobutyrate initiator and subsequent reaction with NaN₃ (see Supporting Information for details). Conditions were optimized for the CuAAC reaction in nonpolar solvent (DMF/toluene), since TiO₂-alkyne particles dispersed better in nonpolar solvents. Copper (I) bromide was used as catalyst for the “click” reaction with pentamethyldiethylenetriamine (PMDETA) as the ligand.^[25,26]

Infrared spectroscopy was used to monitor the extent of reaction (Figure 1). In the reaction of PS-N₃ with TiO₂-alkyne, peaks at 2150 cm⁻¹ due to the C-C triple bond and 2050 cm⁻¹ due to the N₃ moiety were used to determine the extent of reaction. Comparing these peaks to the 6-5 μ absorption for polystyrene at 1948 cm⁻¹ peak allows qualitative observation of reaction progress.^[27] After 48 h, the azide peak effectively disappears, indicating that the PS-N₃ is consumed. In the case of PTBA-N₃, overlap of the N₃ peak with the alkyne peak makes monitoring the reaction more difficult. However, after 48 h reaction time, the sharper alkyne peak remains, whereas the broader azide peak appears to be consumed. This is interpreted as the end of the reaction.

Films of TiO₂-click-PS can be made by either drop casting or spin coating. TiO₂-click-PS can be worked up via treatment with methanol. Centrifugation and washing with methanol removes copper and other impurities from the materials. In the case of TiO₂-click-PTBA, a methanol work-up results in aggregation of the nanoparticles. In this case, the reaction mixture is simply diluted with chlorobenzene and dropcast (no attempt is made to remove copper). Dropcast films are roughly 15 μm thick, whereas spun cast films are $\approx 500 \text{ nm}$ thick. TEM micrographs (Figure 2) show the TiO₂-alkyne as narrow cylindrical particles (average size = 20 \cdot 5 nm). Functionalization with either PS or PTBA improves dispersion and

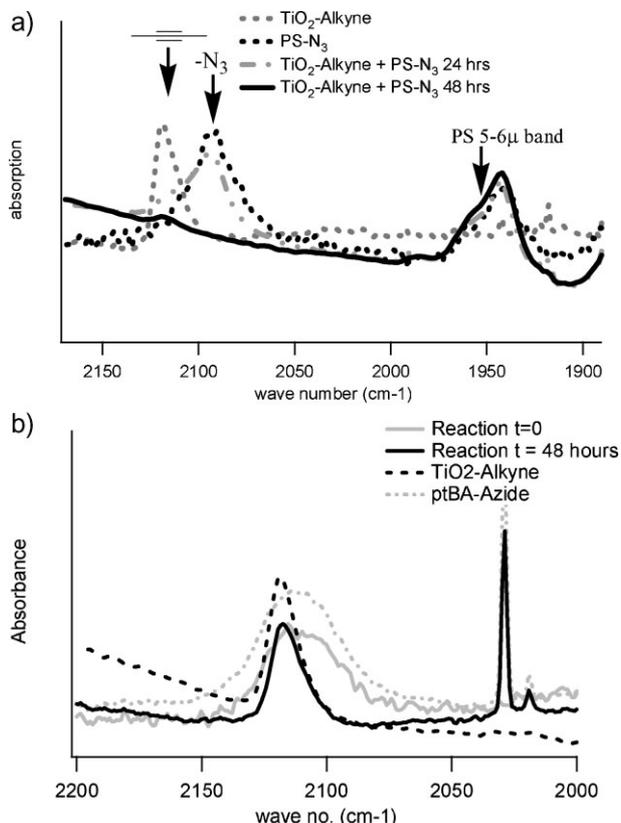


Figure 1. Infrared monitoring of "click" reaction a) for TiO_2 -click-PS and b) for TiO_2 -PTBA.

film forming ability of these particles. The TEM data further indicates that no large aggregates form.

Results and Discussion

Capacitors were fabricated from TiO_2 -click-PS and TiO_2 -click-PTBA. TiO_2 -click-PS was spun into films on ITO/glass, and gold top contacts were evaporated to create metal-insulator-ITO devices. Effective dielectric constants were calculated from measured capacitances using the equation:

$$K_{\text{eff}} = Cd/A\epsilon_0$$

The effective dielectric constant ($K \approx 6.5$; see Figure 2) correspond to titanium oxide loadings of approximately $\approx 15\%$ (using a parallel capacitor model), which are slightly lower than measured previously.^[4] However these devices have not been optimized. Larger K values are anticipated upon reducing either the loading of PS- N_3 or reducing the chain length of PS- N_3 used. The degree of polymer coverage can be estimated based on our measured dielectric constants and comparison with our previous work with TiO_2 -PS.^[28] Thus measured K values of 6.5 for TiO_2 -click-PS correspond to titanium oxide loadings of 15% by volume. This results in a weight percent of PS in the composite of 61%. Using this weight percent, the length of the polystyrene chains, and the size of our nanoparticles (*vide supra*), we can estimate the number of polymer chains

per nm^2 titanium oxide surface to be ≈ 0.5 PS chains $\cdot \text{nm}^{-2}$. This value is below what would be expected for functionalization of each possible ligand site (estimated to be ≈ 4 sites $\cdot \text{nm}^{-2}$) and corresponds to 12.5% of surface sites covered with polystyrene chains.^[19] The number of alkyne sites on the titanium oxide surface is anticipated to be slightly larger, since the azide terminated polymer is the limiting reagent as seen by IR spectroscopy (see Figure 1). TiO_2 -click-PTBA did not form good films when spin coated, but did form good dropcast films. Capacitors made from dropcast films show high K (≈ 8) and flat frequency response. The higher K_{eff} for TiO_2 -click-PTBA as compared to TiO_2 -click-PS is expected, due to the larger K of pure PTBA (≈ 3.5 vs. 2.5 for PS).^[29]

Thin film transistors (TFTs) built from TiO_2 -click-PS dielectrics show moderate mobility in unoptimized

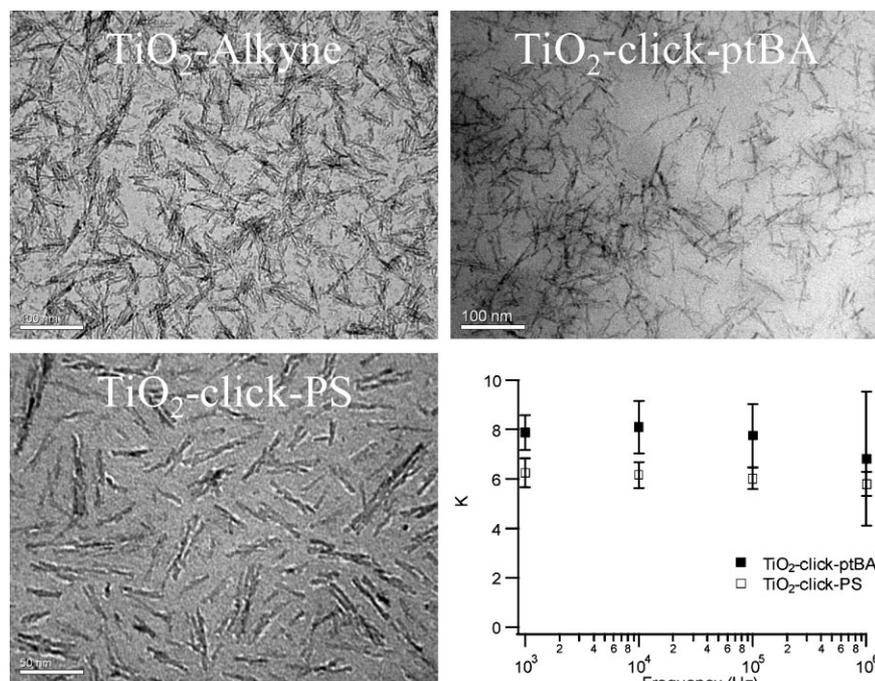


Figure 2. TEM images of TiO_2 -ALKYNE, TiO_2 -click-PS, TiO_2 -click-PTBA, and effective dielectric constant as a function of frequency for TiO_2 -click-PS and TiO_2 -click-PTBA capacitors.

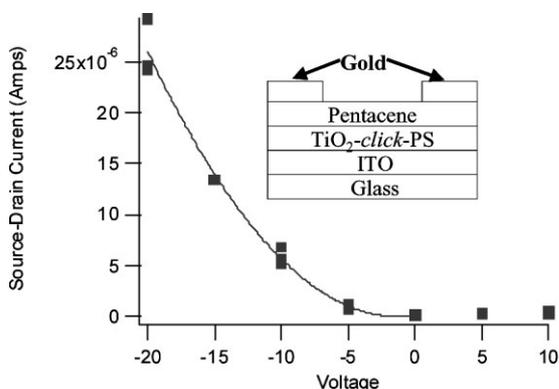


Figure 3. Source drain current versus gate voltage for an evaporated pentacene FET.

devices (Figure 3). Mobilities on the order of $0.02 \text{ cm}^2 \cdot \text{Vs}^{-1}$ and low leakage currents were observed for these TFTs. We have not as of yet been able to fabricate TFTs with TiO_2 -click-PTBA dielectrics that have acceptable performance, a challenge most likely due to leakage pathways in the TiO_2 -click-PTBA, which we attribute to incomplete removal of copper from the polymer. Efforts are underway to successfully remove copper from TiO_2 -click-PTBA films, and thus generate better quality TFT devices.

TiO_2 -click-PTBA is amenable to hydrolysis in the presence of trifluoroacetic acid to generate TiO_2 -click-PAA [PAA = poly(acrylic acid)], a water soluble TiO_2 -core polymer-shell nanoparticle. These nanoparticles form transparent dispersions in water that filter easily through a $1 \mu\text{m}$ syringe filter. The properties of these water soluble core-shell materials are under further investigation for interesting properties and potential applications to photo-voltaics (dye sensitized cells), and sensors applications.

Synthesis Protocols and Characterization Data are available as Supporting Information.

Conclusion

In order to tailor the properties of polymer inorganic oxide nanocomposite materials to various applications, a robust methodology is required to coat inorganic oxide nanoparticles with polymer in a well defined manner. The propensity of high surface energy nanomaterials, such as titanium oxide, to aggregate makes it difficult to control the dispersion properties of these materials. In order to avoid optimizing each polymer coating of a titanium oxide nanoparticle, our approach has been to coat these nanoparticles with a low polarity, alkyne terminated layer which allows for excellent dispersion in organic solvents. Using the versatility of the CuAAC reaction, we

have been able to generate a diversity of core-shell structures including acrylate, styrenic and polyacid coated core-shell structures. Further combinations are possible, and are limited only by the ability to generate a suitable azide terminated polymer precursor. This methodology should be applicable to the generation of many different types of core-shell nanostructured materials, and should be amenable to other high surface energy inorganic oxides.

Acknowledgements: This work was supported in part by the MRSEC Program of the National Science Foundation under Award Number DMR-0213574.

Received: June 4, 2008; Accepted: July 8, 2008; DOI: 10.1002/marc.200800346

Keywords: "click" chemistry; core-shell; dielectric properties; flexible electronics; nanocomposites

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