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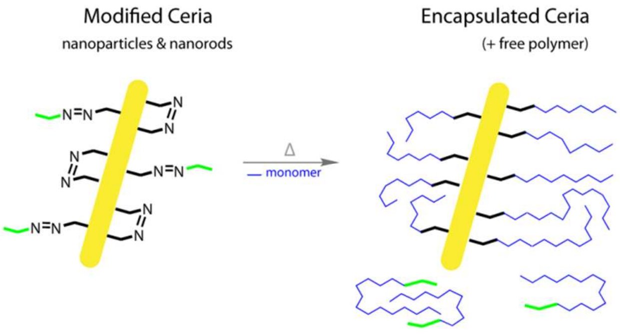
Radical Initiator Modified-Cerium Oxide Nanoparticles for Polymer Encapsulation via Grafting From the Surface

Eric Johansson Salazar-Sandoval[a,b], *Miren Aguirre*[c], *María Paulis*[c], *José R. Leiza*[c], *Mats Johansson*[b], *Anwar Ahniyaz*[a,]*

[a]SP Technical Research Institute of Sweden, Chemistry, Materials and Surfaces, Box 5607, SE-114 86 Stockholm, Sweden

[b]Department of Fibre and Polymer Technology, School of Chemical Science and Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

[c]Institute for Polymer Materials (POLYMAT) and Kimika Aplikatua saila, University of the Basque Country UPV/EHU, Joxe Mari Korta Zentroa, Tolosa Hiribidea 72, 20018 Donostia-San Sebastián, Spain



Abstract

The present paper describes a versatile route to modify and stabilize ceria nanoparticles with a radical initiator, 4,4′-Azobis(4-cyanovaleric acid) (ACVA), allowing a strong interface to be formed via grafting of polymers from the surface. This leads to the successful encapsulation of cerium oxides nanoparticles in a poly-(methyl methacrylate) matrix. The interaction between the radical initiator and the surface of ceria is studied by FTIR spectroscopy where a consistent shift of the carboxylate band, unequivocally demonstrates that the carboxylate groups of this acidic initiator complex the cerium ions on ceria surface by means of strong and stable ionic bonding.

Keywords: nano-ceria, radical initiator, 4,4′-Azobis(4-cyanovaleric acid), grafting from, encapsulation

Introduction

Ceria nanoparticles are of great industrial interest[1] for various applications, such as UV-screening[2] anticorrosion,[3, 4] and diesel additives[5]. Many of these applications require stabilization of ceria nanoparticles in either water or organic solvents. It is furthermore, in many cases, desired to incorporate ceria nanoparticles into a polymer matrix without agglomeration of the particles during the solidification process e.g. drying of a liquid coating. The most successful approach until now has been to utilize hydrophobic ceria nanoparticles that can be dispersed in a monomer phase prior polymerization of the monomer.[6-8] This allows for ceria nanoparticles being homogenously distributed in the final system. These blends however, do not offer any strong chemical interaction between the phases i.e. only physical interactions at the particle – polymer interface are present in these systems. A weak interface may result in reduced performance of the composite material if the material is subjected to harsh environments and/or mechanical stresses. A more preferred approach to enhance the chemical interaction at the organic-inorganic interface in composites, is the incorporation of reactive functional groups on the surface of the inorganic nanoparticles to allow forming a strong chemical bond in the final material. Functional groups, such as vinyl or azo moieties, have been used to allow for subsequent covalent coupling of the modified inorganic surface to polymeric materials. Such approaches have successfully accomplished the encapsulation of silica[9], calcium carbonate[10] and zinc oxide.[11] Previous studies on stabilization of ceria nanoparticles have shown very strong and stable ionic bonding between ceria and carboxylic acids.[12] The ionic bond, in this case, showed great stability and strength; suggesting that this general strategy can be used as a route to obtain a strong interaction at the nanoparticle–polymer interface, if the selected acid is capable to react with the monomer during polymerization. In the literature, studies on the modification of ceria with active RAFT-agents of different structures, including acidic oligomers, have been described.[13-15] Depending on the specific molecular structure of the RAFT-agent, the resulting hybrid assembly after polymerization either resulted in ceria coupling to the surface of polymer particles[13, 14] or incorporation of the ceria nanoparticles inside the polymer particles.[15] As an attempt to overcome the limitations of RAFT polymerization, such as low polymer molecular weights and consequent worsening of mechanical properties; in a very recent work it was considered combining a successful ceria stabilizer, nitrilotriacetic acid (NTA), with 4,4'-Azobis(4-cyanovaleric acid) (ACVA) as ceria modifiers.[7] However, only polymer particles growing perpendicularly to the ceria nanoparticle surface were observed. Nevertheless, the resulting polymer particles were effectively stabilized by anionic surfactants and because NTA-modified ceria is also extremely stable in aqueous solution, the resulting hybrids showed good stability.

Here, we describe the utilization of solely 4,4'-Azobis(4-cyanovaleric acid) as a suitable stabilizer for ceria nanoparticles that besides preventing –the otherwise inevitable– particle aggregation, provides a polymer initiating function on the surface of these ceria nanoparticles letting us graft a polymer from their surface which led to successful encapsulation of ceria nanoparticles in a selected polymer matrix.

Materials and methods

Reagents

Cerium (III) nitrate hexahydrate, ammonium hydroxide solution [28.0-30.0% NH_3], cerium bromide heptahydrate and 4,4′-Azobis(4-cyanovaleric acid) were purchased from Sigma-Aldrich. Hydrogen peroxide 30% was purchased from MERCK. Potassium hydroxide acquired from Alfa-Aesar. Methyl Methacrylate was kindly provided by Resiquímica. Dowfax 2A1 was generously supplied by The Dow Chemical Company. Double distilled water was used for all the experiments. All chemicals were used as received.

Synthesis

Synthesis of stabilized ceria nanoparticles with active stabilizers

A solution of 0.9 g of 4,4′-Azobis(4-cyanovaleric acid) (ACVA) in 20 mL of water at 4 °C was prepared by dissolving ACVA with gently stirring, by dropwise addition of NH_4OH to pH 5. This solution was kept at 4 °C and saved for later use.

5.40 g of $Ce(NO_3)_3{\cdot}6H_2O$ was dissolved in 150 mL of double distilled water in a 200 mL beaker. 11 g of a concentrated NH_4OH water solution was then added during stirring to precipitate (at pH 9 – 10) cerium hydroxides[16]. The suspension was centrifuged twice at 4.000 rpm for 15 minutes, washing the precipitate 10 times with 50 mL of double distilled water after each centrifuging cycle. The obtained cake was re-dispersed in 800 mL of pre-heated water at 80 °C, with help of a mechanical homogenizer (Ultra-Turrax from IKA Works GmbH). The heat was then turned off and when the temperature reached 76 °C, 6 g of H_2O_2 was added, all at once, while stirring to obtain ceria aqueous dispersion. The previously prepared ACVA solution was then added to the dispersion and was left under stirring for 20 more minutes to form an ACVA-functionalized ceria nanoparticle dispersion used for subsequent polymerization reactions.

Polymerization of methyl methacrylate using modified ceria nanoparticles as initiator

The ACVA-functionalized ceria nanoparticles were used directly after production as previously described. When the stirring was stopped, the nanoparticles tended to slowly precipitate and to collect them, they were centrifuged for 6 minutes at 4000 rpm and the supernatant was then decanted off. The obtained wet cake (containing ca. 1.8 g of ceria) was re-dispersed in 60 g of methyl methacrylate (MMA) using an ultrasonic probe for 10 minutes (pulses of 5 seconds at 60 % amplitude, with 5 seconds pauses; resulting in 5 effective minutes) in a 100 mL beaker. In a 100 mL beaker, 10 grams of the ceria-MMA dispersion were added to 50 grams of distilled water, together with 0.8 g of Dowfax 2A1 (mixture of anionic surfactants). This mixture was sonicated for 2 more minutes (again, pulses of 5 seconds with equally long pauses) to form an emulsion. The resulting emulsion was transferred to in a sealed flask where N_2 gas was flushed for 2 minutes and then polymerized with constant stirring in an oil bath at 70 °C during 4 hours.

Synthesis of cerium (III) – 4,4’-Azobis(4-cyanopentanoate) complex

The cerium (III) 4,4’-Azobis(4-cyanopentanoate) complex, abbreviated as Ce-ACVA or Ce_2ACVA_3 was prepared for comparison purposes. 0.1250 g of KOH was dissolved in 14 mL of water at 4 °C in a 28 mL vial. 0.3150 g of ACVA was then added to the alkaline solution while stirring on a magnetic stirrer. After complete dissolution of the ACVA, 0.3760 g of $CeBr_3$ was added. The vial was then sealed and left under magnetic stirring overnight at a 4 °C.

Characterization techniques

PXRD

Powder X-ray diffraction (PXRD) studies were conducted in a PANanalytical X'Pert Pro diffractometer using Cu radiation. An aliquot of the polymerized sample was first dried at room temperature for 72 hours. This yields a film which was rinsed with double distilled water to remove any residues of surfactants or even eventual dust deposited during drying. The dried film was placed onto silicon wafers on which a drop of chloroform was previously added to help attaching the film onto the wafer. The solvent evaporated at room temperature prior analysis.

TEM

A Jeol JEM-2100 transmission electron microscope (TEM) equipped with LaB_6 crystal as the electron source and operating at an accelerating voltage of 200 kV. A drop of the 40-fold diluted aliquot of the sample was deposited on ultrathin carbon film-coated copper grids supplied by TED Pella.

FT-IR

A PerkinElmer fourier transform infrared (FTIR) spectrometer, Spectrum One with Attenuated Total Reflection (ATR) sampling accessory was used with a MIR (mid-infrared) beam source. The instrument is equipped with KRS-5 and diamond ATR crystals on the top plate and with a MIR-DTGS (mid-infrared deuterated tryglycine sulfate) detector. When needed, samples were dried overnight in a vacuum oven at room temperature. A few milligrams of sample were placed directly on the ATR crystal. Spectra were recorded with 16 scans and a resolution of 2 cm^{-1}.

Results and discussion

Synthesis of stabilized Ceria nanoparticles with active stabilizers

The PXRD analysis corroborates that the characteristic cubic fluorite structure of ceria, with $Fm\bar{3}m$ space group was obtained and matches ICDD PDF 00-034-0394 reference pattern, Figure 1. This validates our synthetic approach for producing stabilized crystalline cerium oxide nanoparticles using

ACVA as a stabilizer. Transmission electron microscopy (TEM) was the technique chosen to verify the size and shape of the particles obtained.

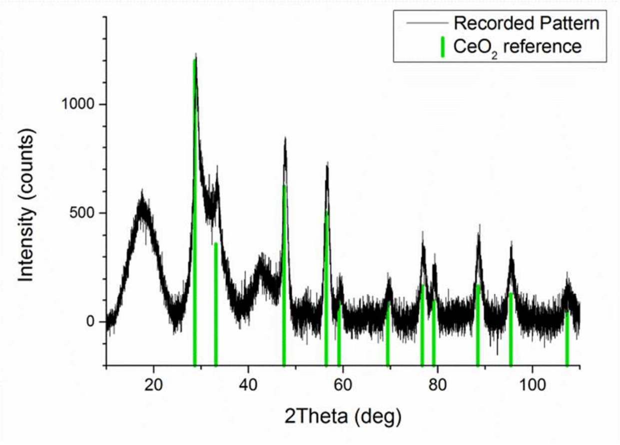


Figure 1. Powder X-ray diffraction pattern of the encapsulated ceria nanoparticles. Reference cerium oxide pattern represented as vertical green lines.

The TEM studies show that a mixture of spherical nanoparticles, between 5 and 20 nm, are obtained together with nanorods of 10 to 20 nm in their smallest dimension and between 100 to 200 nm in the longest, Figure 2. These values are consistent with a volume-averaged crystallite size of ca. 7.3 nm as calculated from the PXRD pattern, using the Scherrer equation with a shape factor of 0.9.

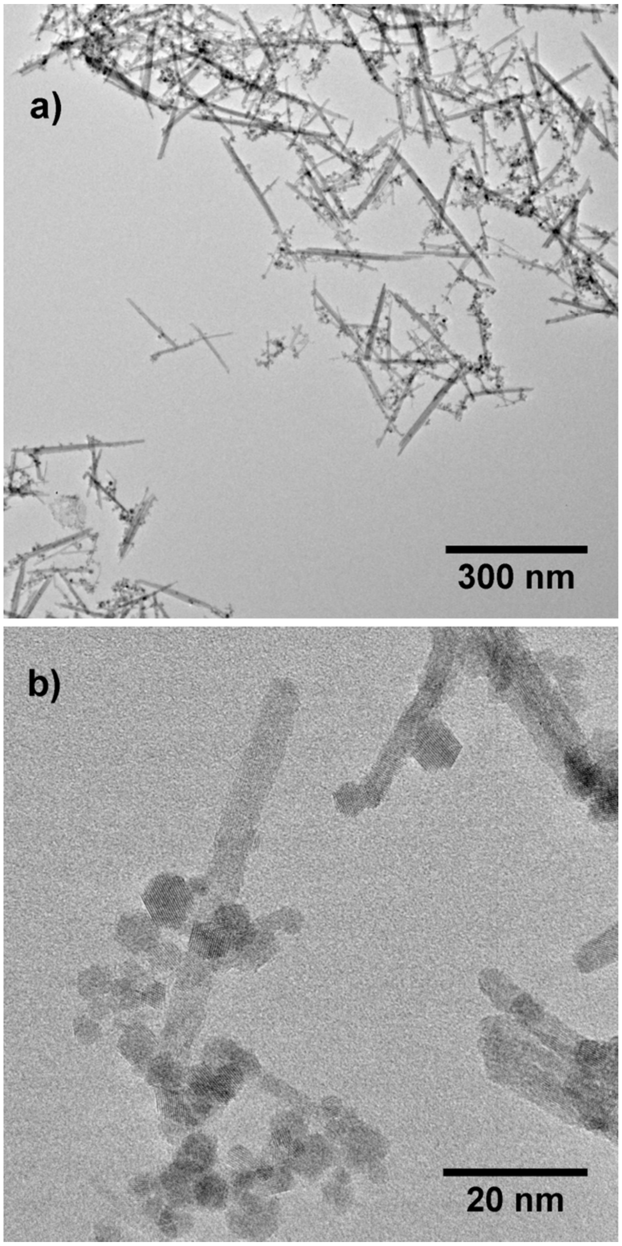


Figure 2. TEM images of ACVA-modified cerium oxide nanoparticles. Image a) lower magnification; b) higher magnification

In order to investigate the interaction between ACVA and the surface of ceria nanoparticles, FT-IR studies were conducted. The carboxylic groups in ACVA, when protonated (as represented in Chart 1a), show an asymmetric vibration band (ν_{as}) at 1705 cm^{-1}, Figure 3a. This ν_{as} band shifts to 1545 cm^{-1} when ACVA complexes the cerium ion (forming the complex represented on Chart 1b), as a consequence of substituting the protons of the carboxylic groups by cerium ions, Figure 3b. Interestingly, we observe a similar shift to 1536 cm^{-1} when ACVA is added to ceria nanoparticle dispersions, Figure 3c. This points out that, at the molecular level, the carboxylic group of ACVA interacts with the surface cerium ions of ceria as represented by Chart 1d. This is consistent with the model we have previously proposed.[12] The small band at 1709 cm^{-1} in Figure 3b indicates minor presence of either free protonated ACVA as in Chart 1a or partially coordinated as in Chart 1c. Similarly, the band at 1715 cm^{-1} in Figure 3c, signifies the presence of either free ACVA, or more likely, ACVA partially coordinated to ceria surfaces as in Chart 1e. The blue dash lines in Figure 3 highlight the presence of hydration water that could not be removed upon drying during sample preparation. Interestingly, the presence of hydration water seems to slightly affect the position of the carboxylic and carboxylate bands. Particularly, as water content increases, the carboxylic band shifts to higher wavenumbers while the carboxylate shifts on the opposite direction.

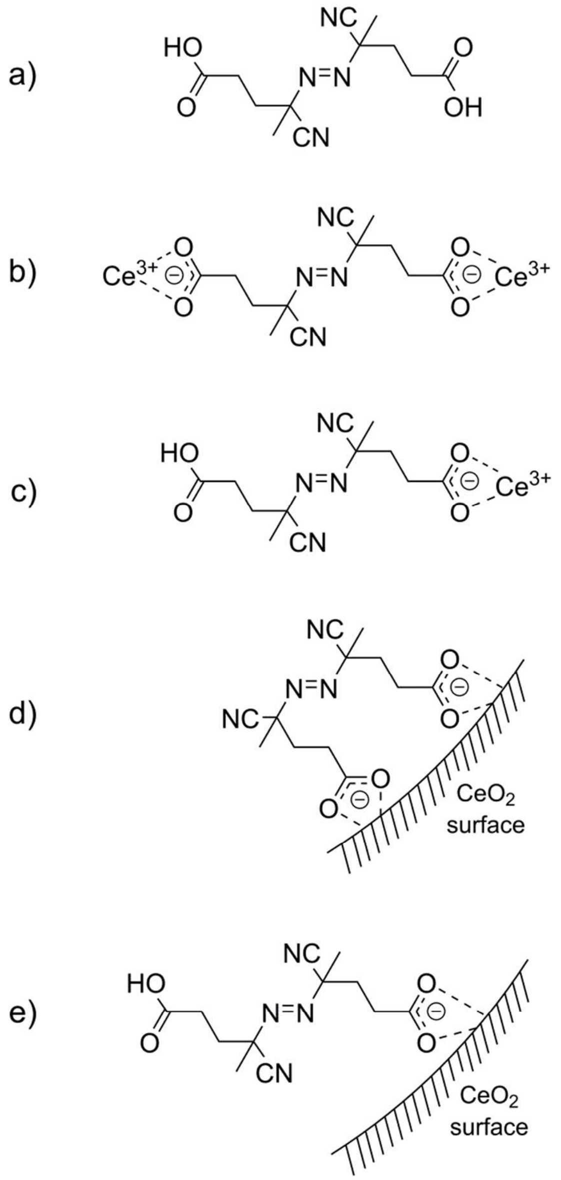


Chart 1. Representations of the ACVA molecule, complexes and surface complexes. a) ACVA protonated; b) ACVA forming a complex with two cerium (III) ions; c) ACVA as a monoligand, complexing one cerium (III) ion; d) ACVA chelating ceria surface; e) ACVA complexing ceria surface as monoligand.

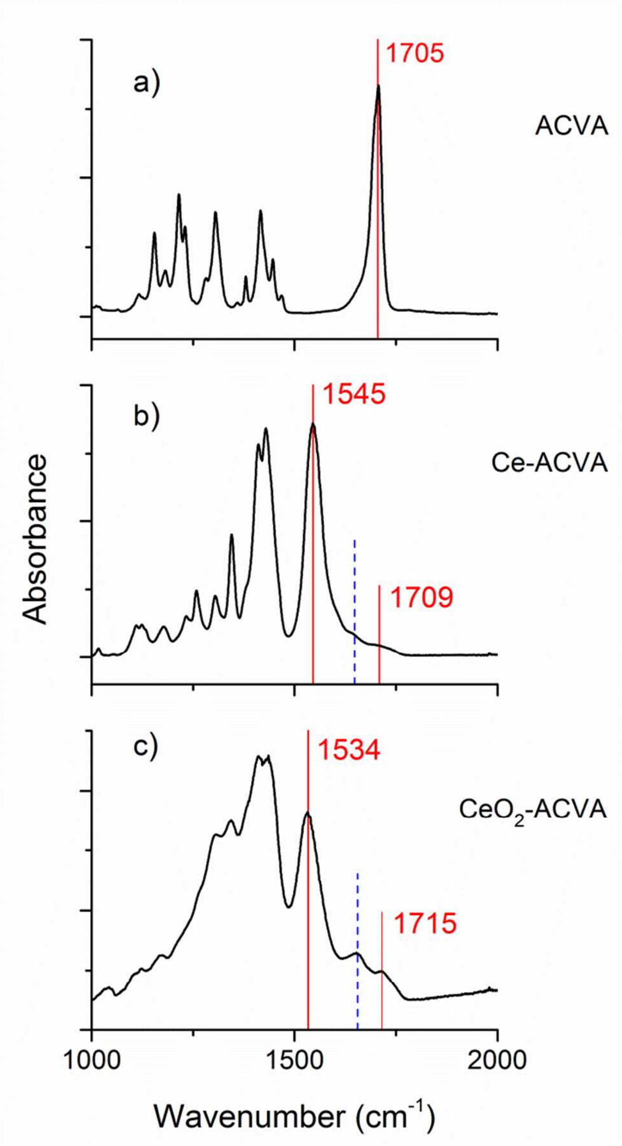


Figure 3. FTIR of the a) ACVA molecule; b) cerium (III) 4,4'-Azobis(4-cyanopentanoate) complex; c) ACVA-modified ceria nanoparticles. The red vertical lines correspond to carboxylic and carboxylate bands while the blue dashed line highlights the presence of water.

ACVA is an azo initiator which decompose at higher temperatures to release N_2(g) forming initiating carbon centered radicals. The decomposition rate at ambient pressure is within a similar range as AIBN having a half-time of 4.8 h at 70 °C[17]. This implies that great care is needed in controlling the time and temperature for the different procedures to minimize premature decomposition of the initiator.

Treatment with reduced pressure will also increase the decomposition rate. The employed procedures were chosen to minimize these issues although there is an undeniable possibility that the spectra we obtained correspond to the cleaved and recombined ACVA molecule. However, our hypothesis is that it does not affect significantly the position of the carboxylate bands because the azo bond should be sufficiently away from the carboxylic groups.

The performed FTIR studies confirm that ceria was indeed modified by ACVA. However, FTIR alone cannot verify that the azo function is still present and available to form the necessary radicals to trigger a grafting polymerization and to corroborate our assumption, a trial polymerization was performed.

Polymerization of methyl methacrylate using active ceria nanoparticles as initiator

Grafting a polymer from the surface of ACVA-modified ceria, results in the encapsulation of the nanoparticles in polymer particles of sizes ranging from 50 to 100 nm, Figure 4. It is also remarkable that the encapsulation occurs around small aggregates or clusters of nanoparticles and nanorods and when the polymer particles coalesce to form a film the cerium oxide nanoparticles end up evenly distributed in the film, Figure 5. By comparing Figure 2a against Figures 4b and 5, one realizes that the aggregation seen on Figure 2a shall be due to drying on the TEM grid during sample preparation. After polymerizing, the nanorods seem to be better dispersed. The total absence of non-encapsulated ceria nanoparticles strongly suggests that the surface modification of the nanoparticles is very efficient and that practically no unmodified nanoparticles are present. This will allow for a very efficient coupling of the nanoparticles into the polymer matrix as demonstrated on Figures 4 and 5.

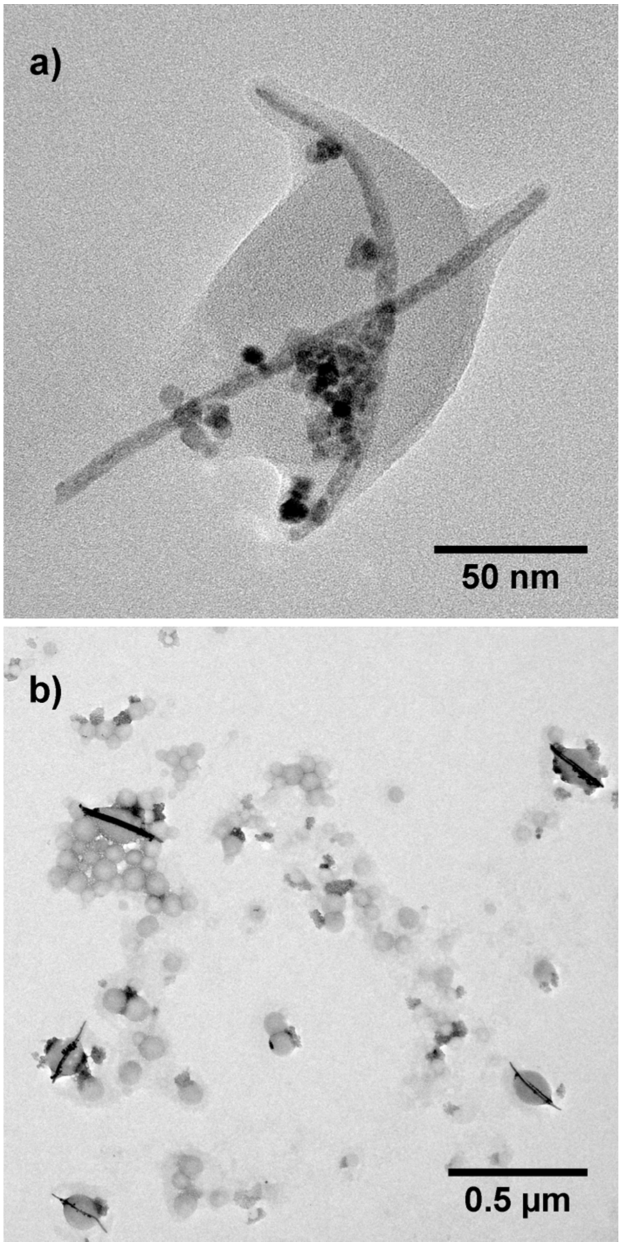


Figure 4. TEM micrographs of cerium oxide nanoparticles encapsulated in poly-(methyl methacrylate). a) an aggregate of nanoparticles and nanorods that has been encapsulated during the emulsion polymerization process. b) emulsion containing several polymer particles with and without encapsulated ceria nanoparticles

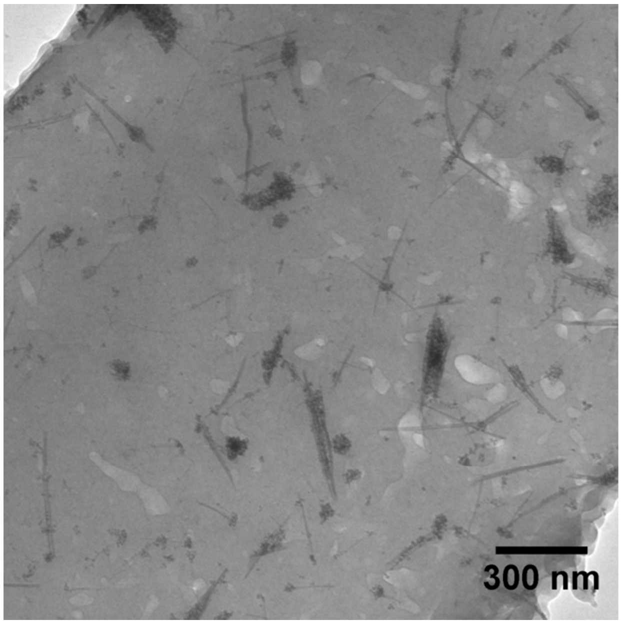


Figure 5. TEM micrograph of dried ceria-polymer hybrid film.

The successful incorporation of ceria nanoparticles into the polymer strongly reinforces our interpretation of the FTIR results demonstrating that the active azo-initiator is bonded to the surface of the ceria. This results can explain observations found in other studies where ceria nanoparticles either stick to a carboxylic acid functional polymer particle[13, 14, 18] or are incorporated into polymer matrices using acidic oligomers.[15] Altogether, it demonstrates that a delicate balance of several factors needs to be accurately controlled. Variations in the molecular structure of the chelating agents, pH, concentrations and steric constraints all affect the final structure of the hybrid material.

It is worth mentioning that we do see empty polymer particles that do not encapsulate any ceria nanoparticles; presumably originated from free ACVA in solution (not coordinated to ceria surfaces) or from ACVA that is only partially bond to ceria (acting as a monoligand towards ceria), Chart 1e. This is consistent with observing carboxylic bands (1715 cm^{-1}) on the FTIR for the ceria-ACVA dispersions, Figure 3c. After cleaving, any eventual uncoordinated end of the initiator would trigger the polymerization separately from the inorganic particles, i.e. it would start a polymerization in the aqueous phase; which explains the presence of polymer particles not encapsulating any ceria (see ESI† for more details).

Conclusion

The present study has shown that it is possible to modify ceria nanoparticles using 4,4′-Azobis(4-cyanovaleric acid). This endows ceria with the ability to trigger a graft polymerization from its surface, resulting in the formation of nanocomposites where the inorganic nanoparticles are chemically bonded to a surrounding polymeric matrix.

When comparing the infrared absorption spectra of both the Ce^{3+}–ACVA complex and the CeO_2–ACVA system, the consistent shift of the carboxylate absorption frequency confirmed our assumptions regarding the strong ionic bond formed between ceria and the ACVA initiator.

We believe this general strategy can be applied to the encapsulation of other metal oxides.

Author Information

Corresponding author

*Anwar.Ahniyaz@sp.se

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