

Hybrid Material Based on Colloidal Cerium Oxide and N,N'-(N,N'-dimethylethylene-N''-butyl)-1,4,5,8-di-naphthalimide

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Abstract – A hybrid cerium oxide-organic material was obtained by interaction between N,N'-(N,N'-dimethylethylene-N''-butyl)-1,4,5,8-di-naphthalimide (DC4) with colloidal CeO₂ in alkaline medium (pH 8). This hybrid composite shows a new luminescence behavior with relation to the DC4 solution spectrum. The intensities enhance with pH increase and also red shifts. Present findings highlight the peculiar ambient that cerium oxide surface furnishes to the organic substrate, given raise to a novel luminescent behavior through favorable like excimer-like induction in aqueous alkaline media.

The formation of hybrid species by the incorporation or sorption of naphthalimides in nano and meso scales have been exploited. Such confinement brings significant changes on IR and UV-Vis spectra, photochemical behavior, and on charge- and energy-transfer processes [1]. Presents work deals with preparation and characterization of Cerium oxide/N,N'-(N,N'-dimethylethylene-N''-butyl)-1,4,5,8-di-naphthalimide (DC4) hybrid material.

Synthesis of CeO₂ dispersion was carried by out drop wise addition of NH₄OH (1 M) to 1 L of aqueous Ce(NO₃)_{3(aq)} (4.45 mM) under stirring, until pH 11. The resulting colloidal dispersion was centrifuged and washed with deionized water, followed by peptization in deionized water. The final pH of the CeO₂ dispersion was adjusted to 8 and the size and polydispersity of the particles were measured by dynamic scattering (Fig. 2). Dicationic diimide DC4 was prepared by conventional methods and characterized according [2]. For hybrid material obtaintion, DC4 (4.6 x 10⁻⁴ M) was *in-situ* reduced (with sodium ditionite) into the CeO₂ dispersion (30 mL). This dispersion was lyophilized for obtaintion of the respective precipitate and further characterizations were made (IV, UV/Vis, Fluorescence, Powder X-Ray).

UV/Vis and fluorescence characterizations were performed in solution and point out to the formation of diimide like-excimer species that are stabilized on the oxide surface (Figure 1 and 2). The diimide luminescence intensities enhance with increasing pH, an unusual behavior since these molecules have high hydrolysis rate constant in alkaline media (above pH 8) which causes luminescent fading [1]. The pH-dependent luminescence showed to be reversible. The results suggest that high pHs, above isoelectric point, makes the CeO₂ surface negatively charged, which promotes the stabilization of an excimer-like aggregated constituted by two cationic DC4 diimide molecule (Figure 3).

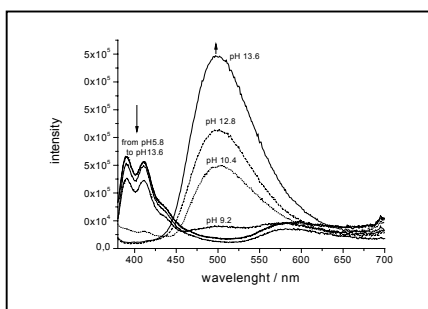


Figure 1: The pH-dependent luminescence spectra of the CeO₂-DC4 in aqueous media.

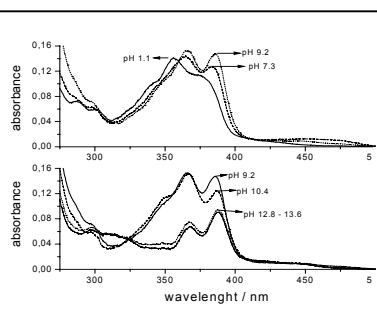


Figure 2: The pH-dependent absorbance spectra of the CeO₂-DC4 in aqueous media

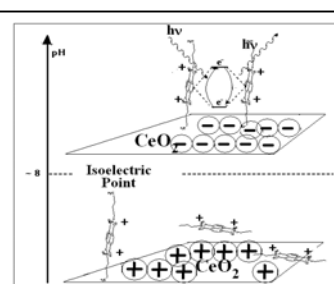


Figure 3: Illustration of the mechanism of DC4 ordered aggregation onto CeO₂ surface

References

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