

SPECTRAL BEHAVIOUR OF NANOSIZED MATERIALS NANOTUBES/CERIUM OXIDE FOR UV PROTECTION OF SKIN

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Abstract

The nanomaterials developed by the authors were characterized in the optical absorption range with a focus on the UV range. Halloysite nanotubes (HNTs) and cerium oxide (CeO_2) have specific spectral absorption that has cumulative effect. The UV absorption of the HNTs@ CeO_2 composites exhibited maxima at 269–305 nm, with a much higher absorption intensity and a wider band than the original HNTs. A blue shift of the UV absorption band was observed for the small CeO_2 particles, and the shift was found to be nonlinearly related to the particle size. The nanoparticle sizes were within 1–15 nm. With electron microscopy it was shown that the CeO_2 particles were evenly distributed on the HNTs, resulting in low particle agglomeration. The creams showed effective protection against UV radiation and had additional healing properties, which were confirmed on the skin of guinea pigs.

Key words: halloysite nanotubes, cerium oxide, nanoparticles, UV protection

Introduction. Since the skin is the largest organ of the human body, the importance of maintaining homeostasis and protecting the skin from ultraviolet radiation is important. Imbalances can result in wrinkles, hair loss, blisters,

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rashes, life-threatening cancers, and disorders in immune regulation. Exposure to UV is not always considered bad. In fact, UV has been found to be particularly helpful in treating vitamin D deficiency, seasonal affective disorders, psoriasis, sarcoidosis, mycosis fungoides, and numerous other cutaneous conditions [1]. Some people are occasionally exposed to artificial sources of UV radiation (e.g., medical, industrial, disinfectant and cosmetic uses), but everyone is inevitably exposed to solar UV radiation. The skin is the first barrier between the body and the environment, and UV radiation acts first on the skin. Prolonged UV exposure poses significant health risks, and the resulting adverse effects manifest through a range of morphological, physiological, and biochemical features, varying from mild burns to metastatic neoplasia. In an environmental context, UV radiation stands out as the most critical modifiable risk factor for skin cancer and numerous other environmentally influenced skin conditions [2].

Cerium oxide (CeO_2 , ceria) is a semiconductor, and it has been shown to provide a strong UV barrier and absorption effect in a matrix of polylactic acid. When the content of CeO_2 was 2%, the UV transmittance was reduced to 0.47%. The study provided a potential solution for outdoor UV protection of skin [3]. The excellent morphological properties, low photocatalytic activity, and high absorption in the UV region of a related compound (CePO_4), have also been proposed as an alternative UV filter in sunscreen formulations, in order to substitute ZnO and TiO_2 [4]. Even if UV filters based on ZnO and TiO_2 are in general judged by the American FDA to be Generally Recognized as Safe (GRAS), there is an ongoing discussion about their potential toxicity and ecotoxicity [5]. CeO_2 nanoparticles have the unique ability to both refract UV light and act as potent biological antioxidants, making them possibly valuable for their potential anti-inflammatory, anti-ageing, and therapeutic properties. CeO_2 nanoparticles, via their $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$ redox couple, have been shown to potentially exert protection for UV-treated cells, buffering oxidation, preserving viability and proliferation, reducing DNA damage, and accelerating repair [6, 7]. When it comes to the cost of cerium, it can be noted that inorganic UV filters in sunscreen formulations are usually used in small quantities.

This manuscript studies HNTs@ CeO_2 -based materials as a component in sunscreen lotions.

Materials and methods. CeO_2 /HNTs nanocomposites with 0.5–5 wt% of CeO_2 were obtained by chemical precipitation in an alkaline aqueous medium in the presence of HNTs, NaturalNano, Inc. (HNTs@ CeO_2) according to the patent [8]. The materials were characterized by Scanning Electron Microscopy (SEM) with a ± 1 nm resolution at 10 kV using a MIRA3 LMU, Tescan device with inBeam mode and with an Oxford X-MAX 80 mm² energy dispersive spectroscopic chemical analysis system with an instrument uncertainty of $\pm 5\%$. The sample preparation was carried out by sputtering a gold conductive layer on its surface. The optical properties of the CeO_2 /HNTs nanocomposites were studied

by UV-VIS spectroscopy (UV-VIS-NIR-spectrophotometer UV-3600, Shimadzu) in reflection mode in the range of 220–3300 nm with an instrument uncertainty of ± 0.25 nm. Powders were prepared in the form of tablets.

Results. Electron microscopic examination of the HNTs@CeO₂ materials. We estimated by analyzing the SEM images that the particles of HNTs and a typical HNTs@CeO₂ nanocomposite (3 and 5wt% CeO₂) had HNTs particles with a width of approximately 60–90 nm and a length of approximately 450–550 nm (Fig. 1a). According to the elemental mapping analysis of the HNT_s@CeO₂ nanocomposite, the cerium was evenly distributed on the carrier surface (Fig. 1). Hence, we inferred that the CeO₂ nanoparticles were uniformly distributed on the HNTs surfaces. The aggregation of the nanoparticles had been suppressed, and we linked this to the fact that the HNTs particles had prevented direct contact between the CeO₂ particles and, hence, their agglomeration during the preparation of the composites. It should be noted that the UV-blocking efficiency has been shown to be seriously weakened as an effect of severe aggregation of CeO₂ nanoparticles [9], and it is important in this context to limit the aggregation.

NIR spectroscopic characterization of the HNTs@CeO₂ materials. When it comes to the chemical composition of the HNTs, please note that the outer surface of HNTs consists of siloxane (Si-O-Si) groups. On the inner surface between the layers there are aluminol (Al-OH) functional groups, which are localized in the cavities of the nanotubes. It can also be noted that silanol (Si-OH) and additional aluminol functional groups are formed in structural defects and fractures of silicates [10]. The formation of CeO₂ nanoparticles occurs mainly on the hydrophobic surface of nanotubes that is close to silica by its nature. The NIR spectra of the pure and modified halloysite have similar absorption maxima and relative band intensities as can be seen in Fig. 2. No significant influence of the CeO₂ modifier on the NIR bands of hydroxyl groups of the HNTs were observed. A number of bands are detected as shown in Fig. 2 but natural clays contain numerous impurities, which prevents the interpretation of absorption bands with high accuracy. The bands in halloysite at 2263, 2205, and 2167 nm are assigned to the $(\nu + \delta)_{\text{Al-OH}}$ absorption combination of “inner hydroxyl” and “inner surface hydroxyls” [11]. The band 1908 nm is to be interpreted as absorbed water vibration modes of a higher order. The NIR signal at 835 nm is in the the region for the fundamental overtones of organic impurity [12]. The broad bands observed at 1553 and 1401 nm are assigned to halloysite and the overtone of -OH stretching vibration of water molecule in the halloysite layer also provide evidence for the existence water in the halloysite layer. The other bands were attributed to the overtone of the -OH stretching vibration [13]. Near infrared rays have been reported to promote photoageing and potentially leading top negative effects such as muscle thinning in relation to absorption in myoglobin [14]. Therefore, it is speculated that preventing deep absorption in the near infrared range may be important in protecting human skin [15].

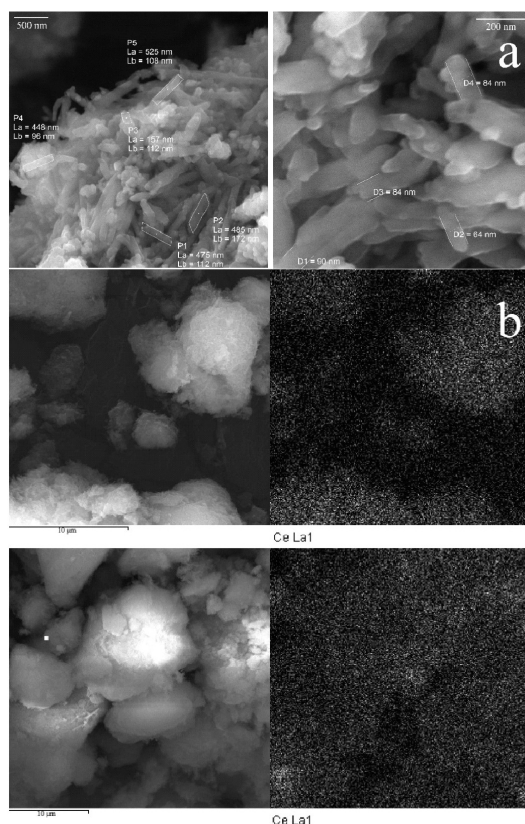


Fig. 1. SEM images of HNTs: (a) synthesized HNTs@CeO₂ nanocomposites (left) and cerium distribution (right) with 3 and 5 wt%, (b) the cerium oxide modifier

UV spectroscopic characterization of the HNTs@CeO₂ materials.

The mechanism of the absorption action of the inorganic filter involves UV light absorption and scattering. The absorption of UV light in CeO₂ occurs by the transitions into valence and conduction band while the scattering depends on the particle size. The maximum light scattering happens when the particles diameter is nearly identical to the incident wavelength of the radiation [4]. The size of the particles up to 15 nm for the synthesized HNTs@CeO₂ materials provides mainly an absorption mechanism of the UV protection, so we focused on that.

The UV absorption spectra of the HNTs/CeO₂ nanomaterials have absorption in the UV range up to 400 nm, and the signal maxima at 269–305 nm for all synthesized samples were in the close range (Fig. 3). The absorption occurred at higher frequencies for the small particles; this blue shift is consistent with another study of the UV absorption for CeO_{2-x} nanoparticles [16]. The HNTs/CeO₂ nanomaterials clearly absorbed more UV radiation and in a wider range than the HNTs support. The blue shift for the CeO₂ nanoparticles could possibly have been

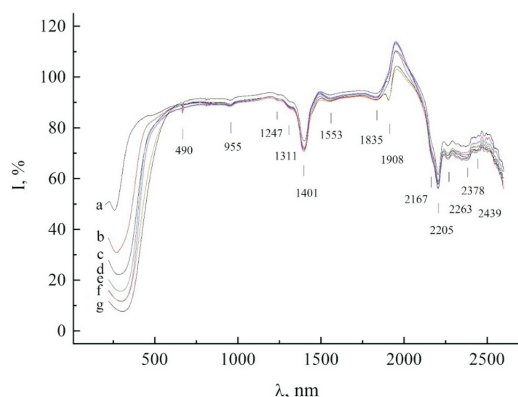


Fig. 2. Spectra of halloysite samples modified with cerium oxide: initial HNTs – a, 0.5 – b, 1 – c, 2 – d, 3 – e, 4 – f, and 5 – g%

ascribed to a quantum confinement effect but for CeO_2 , this explanation is not the normal one. Instead one would ascribe the blue shift to local atomic phenomena occurring in the small particles. Here, Ce^{III} defects are introduced into the crystal structure of CeO_2 , and the $\text{O}^{2-}(2p) \rightarrow \text{Ce}^{\text{III}}(4f)$ transition is observed spectrally at shorter wavelengths close to 250 nm. The contribution of the charge transition $\text{O}^{2-}(2p) \rightarrow \text{Ce}^{\text{IV}}(4f)$ to the signals is attributed to longer wavelength at maxima around 400 nm. Then it is presumed that the Ce^{III} defect density is higher in the small particles than in the large ones. The blank clay based support material (the halloysite nanotube clay) also absorbed UV radiation in the range 250–400 nm with a maximum at 258 nm. The clay contains some iron. Fe^{3+} has an electronic transition from the 3d to 4s orbital, and it has been shown that the UV protection ability is affected by impurities in the mineral in which the layer is formed [17].

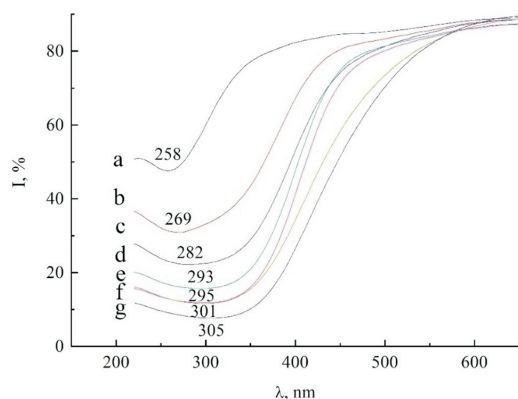


Fig. 3. UV-spectra of halloysite samples modified with cerium oxide: initial HNTs – a, 0.5 – b, 1 – c, 2 – d, 3 – e, 4 – f, and 5 – g%

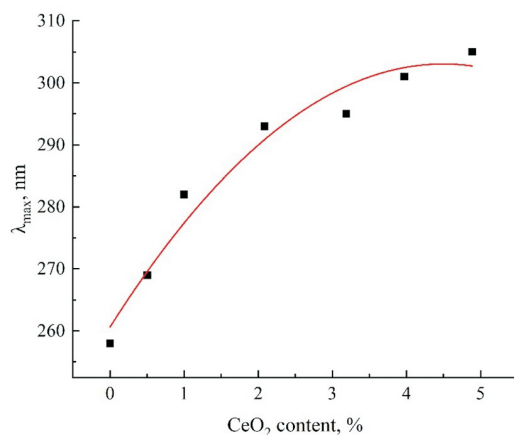


Fig. 4. Dependence of wavelength maxima on the content of cerium oxide in nanocomposites

A dependence of the absorption maximum on the content of CeO₂ was complex (Fig. 4). Note that the content of CeO₂ scaled linearly with the particle size but the absorption maxima scaled non-linearly with the cerium content $\lambda^{\max} = 260.60 + 18.88C - 2.10C^2$, $R^2 = 0.97$. It is clear that the particles size of the CeO₂ is important for the UV absorption maximum and that there was a defined blue shift. For the synthesized nanomaterials, the values of the band gap were $E_g = 3.28\text{--}3.41$ eV (SI). The typical band gap values are in good agreement with the literature data [18].

A cream was prepared with a mixture of nanomaterial with an organic base ethylhexyl methoxycinnamate, cetostearyl alcohol and dibutyl adipate and does of 2 mg/cm² of the cream was used in testing experiments. By its photoprotective action the cream exceeds the reference one with titanium dioxide due to lower degree of the erythema intensity – lower number of ulcers and deep lesions of the skin. The cream with CeO₂ nanoparticles revealed the wound healing action. There was a complete epithelization of the skin of guinea pigs within 6 days of the experiment compared to the group of animals with the untreated photodynamic injury, for which the value was 11 days [19].

Conclusions. In this study, HNTs modified with CeO₂ nanoparticles were studied for their action of UV protection. According to mapping elemental analysis of the samples, cerium was evenly distributed on the carrier surface. The CeO₂ enhanced the UV absorption and the absorption intensity was found to be correlated with the amount of CeO₂ in the samples. It was also observed that the nanoparticles of CeO₂ had a blue shift, which was consistent with findings in the literature. The blue shift was related to the associated UV absorption for $O^{2-}(2p) \rightarrow Ce^{III}(4f)$ and $O^{2-}(2p) \rightarrow Ce^{IV}(4f)$ transitions, and that the small particles have comparably more Ce^{III}.

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