ScienceDirect

Environmental Research
Volume 195, April 2021, 110861

# Interactions between cerium dioxide nanoparticles and humic acid: Influence of light intensities and molecular weight fractions

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Received 25 December 2020, Revised 1 February 2021, Accepted 5 February 2021, Available online 15 February 2021, Version of Record 18 February 2021.

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## Abstract

Cerium dioxide nanoparticles ($CeO_2$ NPs) are ubiquitous in the water environment due to the extensive commercial applications. The complexity of heterogeneous humic acid (HA) plays a significant role in affecting the physicochemical properties of $CeO_2$ NPs in aqueous environments. However, the effects of light intensities and HA fractions on the interaction mechanism between $CeO_2$ NPs and HA are poorly understood. Here, we provided the evidence that both light intensities (>3 E $L^{-1}$ $s^{-1}$) and molecular weights (>10 kDa) can effectively affect the interactions between $CeO_2$ NPs and HA. The absolute content of reactive oxygen species (ROS) and quantum yield (Φ) of $^3$HA* were inhibited when HA (10 mg of C $L^{-1}$) interacts with $CeO_2$ NPs. However, they were positively correlated with the increasing irradiation time and simulated sunlight intensities. High molecular weights of HA fraction (>100 kDa) restrained the ROS generation and Φ of $^3$HA* due to surface adsorption between HA and $CeO_2$ NPs blocking reactive sites, competitive absorption for simulated sunlight. Fourier transform infrared and three-dimensional excitation-emission matrix fluorescence spectroscopy confirmed that the carboxylic groups of HA have high complexation capacity with $CeO_2$ NPs. These findings are essential for us to improve the understanding of the impacts of HA on $CeO_2$ NPs under different conditions in natural waters.

## Introduction

Nanotechnology is one of the fastest developing technologies in recent decades, leading to increasing use of engineered nanoparticles (ENPs) in many industrial applications including commercial products and water treatment (Abbas et al., 2020; Zhang et al., 2020). ENPs have been extensively applied in many sectors including electronic (Yue et al., 2018), pharmaceutical (Shan et al., 2018), environmental remediation (Li et al., 2019), and energy (Wang et al., 2017) due to their large surface area (Metreveli et al., 2020), structural diversity (Falcaro et al., 2016), and excellent electron transfer ability (Chen et al., 2019). It has been reported that the global production of $CeO_2$ NPs was 101–1000 t in 2010, and production is expected to be 1800–57,000 t by 2020 (Auta et al., 2017; Piccinno et al., 2012). Consequently, more concerns have been paid to the nanomaterials due to its unintentional release into the environment in growing production and use, which can cause adverse potential risks (Adam et al., 2016; Waghmode et al., 2019).

$CeO_2$ NPs are one of the most widely used metal oxide-based NPs in the 21st century (Song et al., 2020). It has been extensively used in the glass manufacturing, energy storage, pigments, biomedicine, and foods as well (Celardo et al., 2011; Sendra et al., 2017). Therefore, $CeO_2$ NPs are easy to enter the aquatic environment, leading to a potential risk to aquatic organisms (Vakondios et al., 2014). $CeO_2$ NPs, in aquatic environments, inevitably generated reactive oxygen species (ROS) once radiated by natural sunlight, and the oxidative stress induced by ROS generation is the most essential biotoxicity mechanisms of $CeO_2$ NPs (Celardo et al., 2011; Dai et al., 2020). However, many of the previous studies that explored ROS generation by $CeO_2$ NPs did not quantify the irradiation intensities of light (Ma, 2012; Ma et al., 2014).

HA is one of the main components of dissolved organic matter (DOM), and ubiquitous in aquatic environment (Kong et al., 2019; Li et al., 2015; Wang et al., 2015). Additionally, it is a complex mixture of molecules with different physical structures, chemical compositions and properties, including carboxyl, alcoholic, phenolic, and ketonic oxygen-containing moieties functional groups (Chen, 2002; Filella, 2008). Under irradiation with light, the individual HA molecule is excited to singlet state ($^1$HA*) followed by conversion to triplet state ($^3$HA*), which reacts directly with pollutants in aqueous environments through energy or electron transfer interactions (Wan et al., 2019). The process plays an important role in the attenuation of pollutants (al Housari et al., 2010; Mostafa and Rosario-Ortiz, 2013). However, metal oxide nanoparticles tend to form complexes with HA, thereby affecting its photoreactivity (Chandran et al., 2014). The fluorescence quenching of HA was caused by the complexation of metal oxide nanoparticles in the presence of ZnO NPs (Dai et al., 2020). HA has the ability to inhibit the generation of reactive oxygen species (ROS) under irradiation due to its adsorption onto NPs surface (Chandran et al., 2014). At the same time, the molecular weight distribution of HA can affect the characteristics of HA in water (Zha et al., 2018). Thus, it is necessary to consider environmental factors (i.e., exposure to sunlight, adsorption of HA with different molecular weights) when investigating the interactions between $CeO_2$ NPs and HA in the environment.

The research on the DOM/$CeO_2$ NPs interactions was so far limited to the physicochemical processes, such as dissolution, aggregation, and ROS generation (Li et al., 2020a, 2020b), the impacts of light intensities and HA fractions on the interaction mechanism between $CeO_2$ NPs and HA are rarely investigated. Hence, this study systematically reveals the details of interactions between $CeO_2$ NPs and HA under various conditions. The crystallinity and morphology of $CeO_2$ NPs was characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and atomic force microscope (AFM). Aggregation behavior of $CeO_2$ NPs was systematically studied under different pH by the measurements of zeta potential and particle size. In addition, chemical changes of HA under different light intensities were assessed by ATR-FTIR and Excitation-Emission Matrix (EEM) spectra in the presence of $CeO_2$ NPs. Change of ROS and $^3HA^*$ content under irradiation were monitored, which provides theoretical explanation and insight into the experimental results. At the same time, the interactions between HA with different molecular weights and $CeO_2$ NPs were determined.

## Section snippets

### Reagents and materials

$CeO_2$ NPs with purity >99.5%, purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China), have a primary particle size < 50 nm. HA and 2,4,6-trimethylphenol (TMP, > 98%) was purchased from Sigma-Aldrich. All reagents in the experiment were of at least analytical grade, and the experimental water was 18.2 MΩ/cm deionized (DI) water.…

### Nanoparticle characterization

The structure and morphology of $CeO_2$ NPs were characterized by several techniques including XRD, TEM, and AFM. Details are according to the…

### Characterization of $CeO_2$ NPs

The properties of $CeO_2$ NPs were characterized using XRD, TEM, and AFM, respectively. XRD image of $CeO_2$ NPs is presented in Fig. S4. The powder XRD analysis showed that the $CeO_2$ NPs exhibited a typical fluorite-like cubic structure indexed to the JCPDS card (JCPDS NO.34–0394). The TEM images illustrated that the $CeO_2$ NPs did not have good dispersion, and existed as aggregates. $CeO_2$ NPs were nearly polygon and the particle size varied in the range of 200–600 nm, which was larger than the primary…

## Conclusions

Under natural solar irradiation, the interactions between $CeO_2$ NPs and HA may generate ROS and $^3HA^*$ to different extents, which adds uncertainties with regard to biotoxicity, and affects the attenuation of organic pollutants during wastewater treatment. This study demonstrated that the interactions between $CeO_2$ NPs and HA were affected by the integrated effects of variations in light time, simulated sunlight intensities, and HA fractions. The increase of light time and incident light intensity…

## Credit author statement

Hongliang Dai: Writing – review & editing Methodology, Project administration. Tongshuai Sun: Methodology, Writing – original draft. Ting Han: Writing – review & editing. Xiang Li: Methodology, Writing - review. Zechong Guo: Methodology, Writing – review. Xingang Wang: Writing – review & editing Methodology, Project administration. Yong Chen: Writing – review & editing Methodology, Project administration All authors read and approved the final manuscript.…

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

## Acknowledgements

This research has been supported by the National Natural Science Foundation of China (No. 51908252, 21876056), the China Postdoctoral Science Foundation (No. 2019M652274), and the Postdoctoral Preferred Funding Project of Jiangxi (No. 2019KY17). The English in this document has been checked by a company that provides professional English language editing services. The authors wish to thank the anonymous reviewers for their constructive comments that improved the manuscript.…

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