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Review

Chemical transformation of silver nanoparticles in aquatic environments: Mechanism, morphology and toxicity

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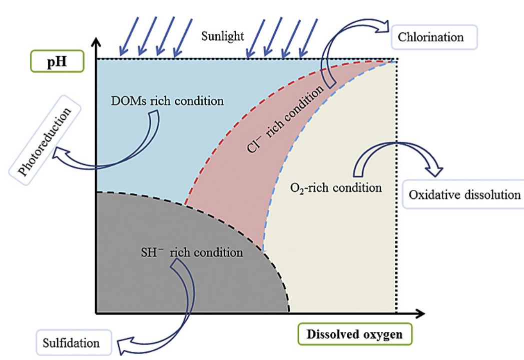
HIGHLIGHTS

- Importance of morphology and toxicity changes of Ag NPs in whole water environment is highlighted.
- Correlations between water environmental factors and these four chemical transformations of Ag NPs are discussed.
- Various environmental transformations of Ag NPs should be accounted for in a full picture to understand their human health and environmental risk assessment.

GRAPHICAL ABSTRACT



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ABSTRACT

Silver nanoparticles (Ag NPs) have been inevitably introduced into ecological environment during their extensive applications in daily human life. Thermodynamically, Ag NPs are unstable and transform into other species under various aqueous conditions. Ag NPs and their transformation products pose potential threats to environment and humans. However, the complex environmental conditions and transformations of Ag NPs complicate their human health and environmental risk assessment. To bridge the knowledge gap, four essential environmental transformations, oxidative dissolution, sulfidation, chlorination and photoreduction, of Ag NPs are reviewed herein. The mechanism, morphology and size change, as well as the toxicity of Ag NPs during these transformations under certain aqueous conditions are detailed. In particular, these environmental transformations have shown strong correlations that are discussed. The transformation, fate, bioavailability, morphology and toxicity of Ag NPs are critical factors and should be considered in a complete human health and environmental risk assessment of Ag NPs. The fluctuation of these factors in the realistic environment is also vital and should be considered.

Contents

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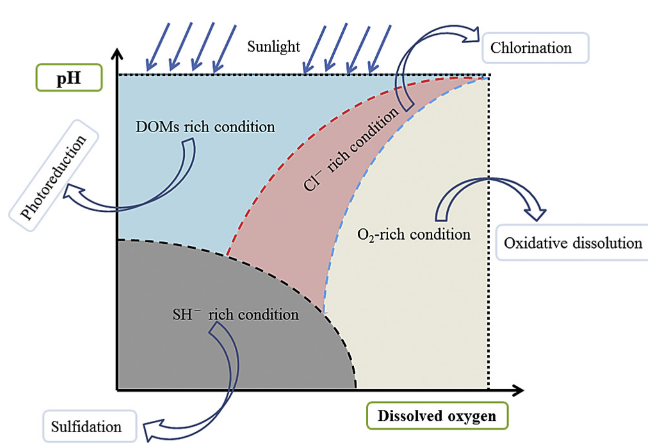
1. Introduction

Silver nanoparticles (Ag NPs) are known for their antibacterial capability and are one of the most widely produced and commercially applied nanoparticles (Tolaymat et al., 2010). Ag NPs have garnered public attention in environmental safety and toxicity domains, because they have been introduced into the aquatic environment during production, storage, and application, and most of Ag NPs (>50%) could be released from productions (such as clothes) during their first wash (Benn and Westerhoff, 2008; Geranio et al., 2009; Kittler et al., 2010). Hoque and him colleagues collected Ag NPs existing information from a Canada wastewater treatment plants (WWTPs). The amounts of Ag NPs (9.3 nm) could up to 1.90 mg/L in wastewater (Hoque et al., 2012). The potential threats of Ag NPs have been shown in a range of organisms, such as bacteria, algae, fungi, invertebrates, plants and fish (Marambio-Jones and Hoek, 2010; Fabrega et al., 2011; Sharifi et al., 2012; Bondarenko et al., 2013; Le Ouay and Stellacci, 2015; Soenen et al., 2015). Many excellent studies had previously reviewed the toxicity (Johnston et al., 2010; Marambio-Jones and Hoek, 2010; Fabrega et al., 2011; Levard et al., 2012; Sharifi et al., 2012; Bondarenko et al., 2013; Le Ouay and Stellacci, 2015; Soenen et al., 2015), physical, biological and chemical transformations (Marambio-Jones and Hoek, 2010; Fabrega et al., 2011; Levard et al., 2012; Lowry et al., 2012b; Virender, 2013; Yu et al., 2013; Dwivedi et al., 2015; Zhang et al., 2016a), and biouptake (Rai et al., 2009; Johnston et al., 2010; Mahmoudi et al., 2011; Sharifi et al., 2012) of Ag NPs. However, a knowledge gap remains in the health and environmental risk assessment of Ag NPs. Predicting or assessing environmental risks of Ag NPs remain difficultly because they present distinct toxicity to particular organisms (Garner et al., 2015) and Ag NPs trend to transfer to diverse species in different aquatic environments. Importantly, Ag NPs and their chemical transformation products normally coexist in aquatic environment and jointly influence environment and human health. Thus, the risk and toxicity of Ag NPs to aqueous environments could not solely explained by their nano properties, such as size and surface activity, but greatly depend on their chemical transformation products. In addition to their fate, toxicity and bioavailability, the environmental transformation processes and products of Ag NPs are primarily and critically important for determination of the human health and environmental risks posed by Ag NPs.

Ag NPs have various transformation pathways, as shown in Scheme 1, and various transformation products under certain aqueous conditions. Generally, Ag NPs are unstable under oxygen-rich aqueous conditions, part of the Ag NPs tend to dissolve to Ag^+. Therefore, Ag NPs and Ag^+ usually coexist under oxygen-rich aqueous conditions, and they cooperate to produce hazardous effects to aquatic organisms. Interestingly, many investigations had found toxicities of Ag NPs are primarily contributable to released Ag^+ that only account for less than 10% of total Ag NPs mass (Fabrega et al., 2009; Peretyazhko et al., 2014). The Ag^+ can be photoreduced to small Ag NPs by sunlight with dissolved organic matters (DOMs). This process will alter the equilibrium between Ag NPs and Ag^+, and impact fate and toxicity of Ag NPs. Notably, sunlight shows two different effects on release of Ag^+ from Ag NPs (Yu et al., 2016): it increases Ag^+ release by accelerating the oxidation of Ag NPs(Grillet et al., 2013) and decreases the Ag^+ release by promoting the aggregation of Ag NPs (Cheng et al., 2011; Shi et al., 2012, 2013). Both Ag NPs and Ag^+ have a high affinity toward sulfur that naturally exists in anaerobic environments to form Ag_2S solid. Due to low solubility, the newly formed Ag_2S is more stable and less toxic than Ag NPs or Ag^+; thus, the sulfidation processes of Ag NPs are considered a natural antidote for the



Scheme 1.