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Review

Plasmonic-based nanomaterials for environmental remediation

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ABSTRACT

Technologies based on nanomaterials are gaining increased attention as a promising method for the removal of contaminants and inactivation/killing of pathogenic microorganisms. Plasmonic nanomaterials prove to be promising in this field due to their tailored properties, including optical, photothermal, conducive, and catalytic properties. These properties have been widely used for the design of efficient materials for the environmental applications by improving the light absorption efficiency, redox reaction kinetic rates, and charge separation efficiency. In the current review, the tailored properties of plasmonic nanomaterials and how they are employed for the design of efficient environment-functional materials are discussed in detail. A number of examples for the development of composite plasmonic nanostructures such as metal/semiconductor, metal/insulator/semiconductor, and metal/semiconductor/semiconductor are provided.

In addition, the recent achievements in plasmonic nanomaterials for the removal of contaminants (in both liquid and gaseous media) and the inactivation of pathogenic microorganisms are described with a number of examples. The major challenges in employing plasmonic nanomaterials for environmental applications are identified as: (1) complete mineralization of contaminants must be achieved in some cases due to the potential risks of intermediates; (2) the cost of plasmonic nanomaterials and the associated treatment processes need to be significantly decreased; (3) the stability of plasmonic nanomaterials in real environmental matrices is urgently needed to be improved; (4) the ecological safety of these nanomaterials should be investigated extensively. However, it is expected that with continuous progress of this field, plasmonic nanotechnology can be used for environmental applications more widely, not only for the examples shown in the current review, but also for soil remediation, resource recovery during waste treatment processes, and detection of contaminants. Finally, the toxicity of engineered plasmonic nanomaterials, the possibility of their release, fate, and transformation, in the environment and subsequent impact on the health of ecosystem are also addressed in detail.

1. Introduction

Environmental pollution due to the population growth and rapid industrialization of the developing regions has become a critical issue in recent times. The development of civilization has caused pollution of air, soil and water, which significantly poses threats to both human health and ecological safety. For example, water pollution causes approximately 14,000 deaths per day in developing countries, mostly because of drinking water contamination [1,2]. Some emerging contaminants which cannot be removed by traditional water treatment processes are now causing serious concerns [3,4]. Numerous scientific and technological efforts have been made to resolve these problems [5,6]. Among all the approaches, technologies based on nanomaterials are playing an increasingly important role. Early efforts on developing nanomaterials for contaminant removal mainly focused on photocatalysis for the degradation of industrial dyes [7,8]. More recently, several emerging organic contaminants such as endocrine disrupting chemicals and pharmaceutical effluents and personal care products have also been chosen to be the target contaminants since they are not effectively treated by conventional water treatment processes [9,10]. So far, technologies based on nanomaterials have also been used to address environmental issues of aqueous contaminants [11,12], oil spills [13] and air pollutants [14]. Some practical applications have been developed, such as the fabrication of TiO_2-coated glass, which is

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antifogging and self-cleaning [15]. In addition, the environmental applications of photocatalysis have expanded to a wider scope, including self-cleaning of buildings, inactivation and detection of microorganisms, and detection of pollutants [16]. It is also reasonable to believe that this scope will continue to expand since increasingly more severe environmental problems are emerging worldwide.

About two decades ago, “plasmonics”, was coined for a promising new technology that enables active manipulation of light by metallic nanomaterials [17]. Currently, plasmonics, an emerging interdisciplinary science and technology field, is being considered as a silver bullet for its potential applications in many sectors including environmental engineering [18]. The principles that drive plasmonics have been introduced most comprehensively in some recent review papers [18–20]. Since many classical review papers have summarized the achievement of plasmonic nanomaterials in terms of synthesis and applications, the current review discusses the progress of this field with a specific focus on what kind of environmental concerns plasmonic materials can help address.

Surface plasmon resonance (SPR) is related to the collective oscillations of conduction electrons in metals and it can be classified into two modes: propagating surface plasmons and localized surface plasmons [18]. Nanostructures that support surface plasmons experience a uniform electromagnetic field when excited by light as their dimensions are much smaller than the wavelength [21]. On the other hand, for nanostructures that possess at least one dimension close to the excitation wavelength, electromagnetic field is not uniform and surface plasmons propagate back and forth between the ends of the structures [22]. Thus, by tailoring the dimension, morphology and ambient environment of a metal, the latter can exhibit many fantastic optical properties [23,24], which offers new opportunities to the application of plasmonics in environmental sector [25]. The principle motivation for the current review is to explore the plasmonic applications in environmental remediation and their undergoing mechanisms (Fig. 1). We start from the properties of plasmonic nanomaterials (Section 2), such as optical, photothermal, conductive, and catalytic properties. Then we introduce how these properties are employed to design highly efficient nanomaterials for removal of contaminants (Section 3), and inactivation of bacteria (Section 4). Furthermore, the relevant physics and chemistry, recent achievements, and significant challenges in this field are be reviewed.

2. Plasmonic properties

2.1. Optical properties

One of the most attractive properties of plasmonic nanostructures is their strong light absorption efficiency, as reflected in their intense

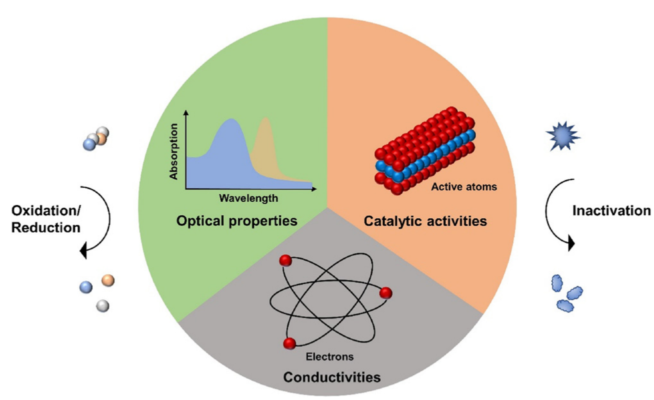

Fig. 1. Schematic illustration of the properties of plasmonic nanomaterials and their applications in the photocatalytic oxidation/reduction of pollutants and inactivation of bacteria.

color. When plasmonic nanoparticles are irradiated with light, the oscillating electromagnetic field induces a collective coherent oscillation of the free electrons (from conduction band) [18]. The specific wavelength where amplitude of oscillation reaches at maximum usually varies with metal types, shapes, and dimensions. Thanks to the marvelous achievements in the material science, morphologies of gold or silver nanoparticles can be controlled efficiently [26]. The varying morphologies, including spheres, rods, plates, and other geometries, as shown in Fig. 2, have helped the tuning of absorption wavelength across the visible range.

Generally, there are four methods to tune the optical properties of plasmonic nanostructures. Increase of size usually results in the red shift of absorption peak (Fig. 3a). For example, the increase in the diameters of gold nanoparticles could result in red-shift of SPR wavelength [43]. By tuning the aspect ratio of gold nanorods, a shift of absorption wavelength can be expected [44].

The second way is to fabricate composite structure, such as core/shell and Janus nanostructures, to manipulate the dielectric constants of the surrounding environment of plasmonic nanoparticles (Fig. 3b). For example, Wang et al. tuned the optical properties of Au@Cu_2O core/shell nanoparticles systematically by varying the thickness of Cu_2O shell [45]. They found that the plasmonic peaks red-shift continuously with the increase of Cu_2O shell thickness. This red-shift comes with the increase of shell thickness, which is further ascribed to the change of the refractive index of the surrounding medium. Similar effect was also observed for Au or Ag NPs coated with SiO_2 nanoshell, SiO_2 shell led to the red-shift of several tens of nanometers due to the increase refractive index of SiO_2 (1.43) in comparison to that of H_2O (1.33) [46]. In contrast, a blue-shift was observed by them when they progressively increased the voids between Au NPs and Cu_2O shell, which can be attributed to the decrease of the refractive index of the medium surrounding the Au NPs. Similar change of optical properties is also observed for Janus nanostructures [47].

The third way is to tune the morphology of plasmonic nanoparticles (Fig. 3c). For example, the absorption peak of isolated Au nanospheres usually lies around 520 nm, varying with its size. However, for isolated Au nanorods, besides the peak near 520 nm, a coupling peak at longer wavelength is also observed. Other morphologies as shown in Fig. 2. all demonstrate essentially different optical properties compared to spheres.

The forth way is to assemble isolated nanoparticles into secondary nanostructures (Fig. 3d). The differences between the optical properties of assembled nanostructures from that of their individual counterparts are caused by the different resonance modes. In assembled plasmonic nanostructures, individual plasmonic oscillations on nearby particles can couple via their near-field interaction and generate coupled plasmonic resonance modes [51]. Of particulate interest is the reversible assembly of such plasmonic nanostructures, which is expected to enable the dynamic tuning of the coupling peaks of SPR by external stimuli, and therefore benefit applications for detection [52]. In the case of the self-assembly of gold nanoparticles, one can observe a color change from red to blue, suggesting the formation of a linear chain structure. The formation of the chain structure is due to the balance between van der Waals attraction and electrostatic interaction among Au nanoparticles [27]. Meanwhile, gold nanorods are able to assemble in the forms of side-to-side and end-to-end, inducing variable optical changes [53].

In terms of plasmonic optical properties, silver offers more advantages over gold. Silver is able to support a strong surface plasmon across from 300 to 1200 nm, wider than gold is [18]. The well-controlled synthesis of silver nanostructures has achieved the full tuning of adsorption wavelength across visible-spectrum. By synthesizing silver with different morphologies including nanodiscs and nanoprisms, Yin et al. observed a shift of absorption wavelength from 450 nm to 871 nm [54]. However, the susceptibility of elemental Ag to oxidation often leads to the unexpected changes of their morphologies and thus of their