Green synthesis of nanoparticles and their applications to bio-environmental

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【論文審査】Review of the thesis

Synthesis of nanoparticles can be proceeded by physical, chemical and biological methods, but biological syntheses are advantageous in such a sense that it is cost effective and environmentally friendly, and furthermore there is no need for high pressure, high temperature and toxic chemicals. In the biological synthetic methods, either microorganisms or plant extracts are commonly used. It is supposed that using plants for synthesis of nanoparticles may be quite reasonable even compared to the other biological methods since several elaborate processes such as cell culture maintenance and specific handling procedures under aseptic conditions can be eliminated. The present doctoral thesis focuses on phyto syntheses of nanoparticles via bio-reduction of metal salt solution using aqueous leaf extracts of different plants.

The thesis entitled “Green synthesis of nanoparticles and their applications to bio-environmental fields” consists of 5 chapters; i.e., “Chapter 1: Introduction”, “Chapter 2: Synthesis of biocompatible silver-filling organic compounds nanoparticles via bio-

reduction using an extract from cherry leaves", "Chapter 3: Synthesis of nanoparticles composed of silver and silver chloride for a plasmonic photocatalyst using an extract from a weed *Solidago altissima* (golden rod)", "Chapter 4: Synthesis of nanoparticles composed of silver and silver chloride for a plasmonic photocatalyst using an extract from needles of *Pinus densiflora*" and "Chapter 5: Conclusion".

Chapter 1 Introduction

The chapter starts with some introductory explanation of phyto syntheses of nanoparticles and several advantages of phyto syntheses are summarised in comparison with the conventional physical and chemical methodologies. Some outstanding features of metal nanoparticles such as silver (Ag) and silver chloride (AgCl) are also discussed in detail. The present thesis focuses on the phyto syntheses of Ag and AgCl nanoparticles utilising leaf extracts from three types of plants; that is, Yoshino cherry, Golden rod and Japanese red pine.

Chapter 2 Synthesis of biocompatible silver-filling organic compounds nanoparticles via bio-reduction using an extract from cherry leaves

Multi-functional silver nanoparticles are in significant demand in both fundamental and practical studies thanks to their distinctive physicochemical properties. Silver nanoparticles can be synthesised by physical, chemical and biological methods, but biological syntheses are environmentally friendly, and furthermore there is no need for high pressure, high temperature and toxic chemicals. In the present study, silver nanoparticles (Ag NPs) covered with organic compounds (Ag@OC NPs) are synthesised by mixing a leaf extract from Yoshino cherry with aqueous solution of silver nitrate ($AgNO_3$). The synthetic procedure of Ag@OC NPs is explained in detail and the Ag@OC NPs are well characterised using state-of-the-art microscopy and spectroscopy such as transmission and scanning electron microscopy (TEM and SEM), X-ray diffractometry (XRD), Energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The Biocompatibility and antibacterial activities and surface enhanced Raman scattering (SERS) ability of the Ag@OC NPs are finally investigated.

The particles show their high mono-dispersibility in water and biocompatibility thanks to the compounds covering the core Ag NPs, and high antibacterial and SERS abilities owing

to the core Ag NPs. In other words, such significant features possessed by the present Ag@OC NPs are derived from the properties of both Ag NPs and organic compounds covering the core Ag NPs. It is supposed that the presently synthesised hybrid nanoparticles may well be actively utilised in the field of biomedicine; e.g., as nano agents for bio-imaging, nano media for photothermal therapy, nano vehicles for drug delivery and detectors of biomolecules and biomaterials.

Chapter 3 Synthesis of nanoparticles composed of silver and silver chloride for a plasmonic photocatalyst using an extract from a weed *Solidago altissima* (golden rod)

Weed species would in general cause hazardous situations on agricultural lands, which may eventually trigger loss of native biodiversity as well as serious economic damage. A terrestrial weed; *Solidago altissima*, belonging to the Asteraceae (Compositae) family, is commonly called golden rod. *S. altissima* is a native plant of North America and became a common alien plant in Japan several hundred years ago. It is well known that *S. altissima* can grow in agricultural fields under various conditions, and the growth of rice seedlings, for example, can be seriously inhibited by *S. altissima*.

In this chapter, nanoparticles composed of Ag and AgCl (Ag@AgCl NPs) are synthesised based on two-step procedure for the first time; i.e., (1) Production of AgCl NPs via the reduction of Ag^+ ($AgNO_3$) using an aqueous leaf extract of *S. altissima*, and (2) Production of Ag@AgCl NPs via the photo reduction of AgCl NPs. The structures and elements of the particles are well characterised and the photocatalytic activity of as-synthesised Ag@AgCl NPs is examined using rhodamine B (RhB). The SERS and anti-bacterial activities of Ag@AgCl NPs are also investigated.

Degradation of RhB is effectively achieved thanks to both surface plasmon resonance (SPR) and semiconductor properties of Ag@AgCl NPs. The particles also show high SERS and antibacterial activities. The present green approach to the synthesis of Ag@AgCl NPs using a weed may encourage the utilisation of hazardous plants for the creation of novel nanomaterials.

Chapter 4 Synthesis of nanoparticles composed of silver and silver chloride for a plasmonic photocatalyst using an extract from needles of *Pinus densiflora*

Ag@AgCl NPs are successfully synthesised as in the case of chapter 3 via the two-step

procedure; (i) The reduction of Ag^{+} ions using an aqueous extract from needles of *Pinus densiflora* to synthesise AgCl NPs, and (ii) The photo reduction of AgCl NPs to synthesise Ag@AgCl NPs. The chemical compounds present in the aqueous extract from the needles such as terpenoids, flavonoids, phenols, proanthocyanidin and components containing chlorine (Cl^{-}) are supposed to be responsible for the reduction reaction to synthesise AgCl NPs in the first procedure, noting that neither external chlorine components nor additional chemicals are supplied during the synthetic procedure. Ag NPs, which are formed in AgCl NPs via photo reduction, promote the photocatalytic activity induced by SPR in visible light.

The Ag@OC NPs are well characterised using TEM, SEM, XRD, EDX and XPS. The photocatalytic activity of as-synthesised Ag@AgCl NPs is examined using RhB. The SERS and anti-bacterial activities of Ag@AgCl NPs are also investigated.

The photocatalytic activity is evaluated by an ultraviolet-visible (UV-Vis) light absorption. Approximately 90 % of the RhB is degraded after 90 min. The high photocatalytic performance of Ag@AgCl NPs owes to the SPR of Ag NPs and the semiconductor features of AgCl NPs. It is clearly shown that the degradation of RhB is encouraged by the present Ag@AgCl NPs.

Chapter 5 Conclusion

Several innovative methodologies for synthesising high quality silver nanoparticles covered with organic compounds (Ag@OC NPs) and hybrid particles composed of silver and silver chloride nanoparticles (Ag@AgCl NPs) are developed. The major contributions of the present work to scientific and technological societies are summarised below:

(a) Ag NPs are successfully synthesised by mixing a leaf extract from *Prunus yedoensis* with aqueous solution of $AgNO_3$. The particles showed their high dispersibility in water, biocompatibility, surface enhanced Raman scattering activity and antibacterial activity. The significant features possessed by the present Ag@OC NPs are derived from the properties of both organic compounds capping the particles and core particles.

(b) The present Ag NPs may well be actively utilised in the field of biomedicine; e.g., as nano agents for bio-imaging, nano media for photothermal therapy, nano vehicles for

drug delivery and detectors of biomolecules and biomaterials.

(c) It is also inferred from the previous and present studies that metal-filling organic compounds nanoparticles may commonly be synthesised via bio-reduction using plants' extracts.

(d) A green method for synthesising hybrid particles composed of Ag and AgCl NPs (Ag@AgCl NPs) is developed using an aqueous leaf extract of *Solidago altissima* and *Pinus densiflora*. First, AgCl NPs are produced via the reduction of Ag^+ by *Solidago altissima* and *Pinus densiflora*.

(e) Ag@AgCl NPs show their effective plasmonic photocatalytic activity thanks to both surface plasmon resonance and semiconductor properties of Ag@AgCl NPs. The particles also show high surface-enhanced Raman scattering and anti-bacterial activities.

(f) Knowing that leaf extracts possess astonishing, supreme medicinal properties for healing various diseases and that the chemical components of leaves possess amazingly useful properties such as anti-cancerous ones, nanoparticles synthesised using plant leaf extracts may well be used as novel nanomedicine. It is highly possible that a variety of nanomedicine possessing excellent properties will be developed in a greener and more efficient way in the near future, designing various biocompatible medicinal composite nanomaterials based on some significant protocols shown by the present research.

【審査結果】Summary and decision

The thesis entitled "Green synthesis of nanoparticles and their applications to bio-environmental fields" focuses on the synthesis of (a) silver nanoparticles covered with organic compound (Ag@OC NPs) via bio-reduction of silver nitride ($AgNO_3$) solution using an aqueous leaf extract of Yoshino cherry and (b) nanoparticles, which are composed of silver (Ag) and silver chloride (AgCl); (Ag@AgCl NPs), via bio-reduction of $AgNO_3$ using aqueous leaf extracts of golden rod and Japanese red pine and then via the photo reduction of AgCl NPs. The results shown in the thesis are outstanding from an international point of view and the significant points in the present study are summarised below;

(1) Ag@OC NPs can be synthesised using an aqueous solution of Yoshino cherry. The synthetic procedure is extremely simple; i.e., the operational temperature is low and the pressure is atmospheric.

(2) Ag@OC NPs possess excellent properties such as high dispersibility in water, biocompatibility, surface enhanced Raman scattering (SERS) activity and antibacterial activity, which are attributed to both the core Ag NPs and the organic compound layers covering the core particles.

(3) Ag@AgCl NPs can be synthesised by extremely simple two-step procedure; that is, (a) the reduction of Ag^+ ions using aqueous extracts from plant leaves to synthesise AgCl NPs, and (b) the photo reduction of AgCl NPs to synthesise Ag@AgCl NPs. The nanoparticles can be synthesised at low temperature and atmospheric pressure.

(4) Ag@AgCl NPs also possess superb properties; that is, high photocatalytic, SERS and antibacterial activities.

(5) The presently synthesised hybrid nanoparticles may well be actively utilised in various fields. Particularly, the application of the nanoparticles in the field of biomedicine is highly probable; e.g., the particles can be used as nano agents for bio-imaging, nano media for photothermal therapy, nano vehicles for drug delivery and detectors of biomolecules and biomaterials.

(6) Phyto syntheses of nanoparticles using aqueous extracts from plants are of great interest and importance considering the reduction of the destruction of the environment. Syntheses of useful nanoparticles using weeds are, in particular, important to solve hazardous biological and agricultural problems.

The results obtained by the present doctoral study have been highly appreciated by some academic societies; two first-authoring papers have been published by international journals (Institute of Physics and Elsevier).

Judging by the results shown in the thesis and the number of international papers published so far, the level of the present research results is definitely high by international standards and the present results may well make a great contribution to the development of new eco-friendly methodologies for synthesising novel nanoparticles and nanostructures. The present results may also contribute to the development of advanced high precision biomedical devices and sensors. In conclusion, the thesis is considered to be a high quality, high standard one by international standards.