MONTE CARLO SIMULATION OF ENERGY REEMISSION BY A GOLD NANOPARTICLE UNDER PHOTON IRRADIATION

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A detailed Monte Carlo simulation of energy reemission processes upon irradiation of gold 2-14 nm nanoparticles by photons with energies near the 2*s*, $2p_{1/2}$, and $2p_{3/2}$ ionization thresholds is performed. The spectra of secondary electrons and photons emitted by the nanoparticle after photoionization of one of its atoms are calculated. At an incident photon energy of 12.0 to 14.5 keV, a nanoparticle with a diameter of 10 nm emits 5.0-6.9 electrons whose energies are sufficient for ionizing or exciting water molecules surrounding the nanoparticle. The number of such electrons slowly decreases with increasing nanoparticle diameter; simultaneously, the number of low-energy electrons emitted by the nanoparticle increases.

Keywords: gold nanoparticle; cascade relaxation; energy reemission; radiosensitization.

Introduction

The decay of a vacancy in the inner electron subshell of an ionized atom is usually a cascade of successive radiative and non-radiative transitions that is going on until a stable ionic state is reached. In heavy atoms, the cascade decay of deep vacancies can include a fairly large number of non-radiative transitions (Auger, Coster–Kronig, and super-Coster–Kronig processes) with electron emission. For example, during the decay of vacancies in the 2*s*, $2p_{1/2}$, and $2p_{3/2}$ subshells of the singly gold ion Au^+, the average number of emitted electrons is 10.2, 8.0, and 8.2, respectively [1, 2]. As shown in [3], most of the energy acquired by an atom in the act of primary photoionization is then reemitted into the surrounding medium with secondary cascade-produced electrons and photons. In particular, upon the decay of vacancies in the 2*s*, $2p_{1/2}$, and $2p_{3/2}$ subshells of Au^+, the cascade photons carry away 29.3%, 38.8%, and 30.4% of the energy of the primarily absorbed photon, and cascade electrons, 64.3%, 57.2%, and 65.1%. Only 4-6.5% of the energy remains stored in the final ions after cascade relaxation.

The electrons emitted during the cascade decay of inner vacancies of high-Z atoms usually have energies up to 15 keV. Their mean inelastic mean free paths in water is about 1-10 nm. Due to this, and to large photoionization cross section of inner subshells of heavy atoms, radiosensitizers based on metal nanoparticles (NPs), especially gold NP, are intensively studied in the radiotherapy of oncological diseases [4, 5]. Targeted delivery of radiosensitizer-NPs into cancer cells followed by hard X-ray irradiation leads to enhancement of absorbed dose inside the tumor tissue at a lower exposure, which allows minimizing radiation damage to healthy tissues.

In this work, Monte Carlo (MC) simulation of the irradiation of gold nanoparticles with diameters of 2 to 14 nm by photons with energies near the ionization thresholds of 2*s*, $2p_{1/2}$, and $2p_{3/2}$ Au subshell is performed. The spectra of photons and electrons emitted by nanoparticles, as well as the average energies re-emitted by nanoparticles, are calculated.

Method of calculation

A detailed description of the MC simulation method used in this work is given in [6], where energy re-emission by photon-irradiated iron nanoparticles has been studied. A brief description of this method is given below.

Each simulation consists of a great number of similar numerical experiments, or MC runs. Each MC run begins with the random choice of the site of initial ionization of the gold atom inside the NP and a random choice of the ionized subshell based on the calculated partial photoionization cross sections. Primary photoionization produces a photoelectron with a known energy and direction of motion, and a vacancy in the ionized atom, which is analyzed to see if its cascade decay is possible. If the decay of the vacancy is possible, then the procedure for simulation of vacancy cascade decay is initiated. As a result of the cascade relaxation, secondary photons and electrons are emitted, which, together with the photoelectron, are added to the list of secondary particles for further tracking of their propagation inside the NP and the inelastic processes they cause.

The interaction of photons and electrons with atoms of the NP is considered as a set of elementary acts of interaction of individual photons and electrons with individual atoms. The most probable processes in the considered energy range are taken into account: for photons, photoionization of atoms, and for electrons, elastic scattering by atoms and ionization of atoms by an electron impact. In the acts of secondary ionization, the ejected electrons are added to the monitoring list of secondary particles and the decays of vacancies (if they are possible) are simulated. The MC run ends when all secondary particles have left the NP and/or their energies have become less than the minimum ionization threshold. After all MC runs, the accumulated results are statistically processed.

Results and discussion

Fig. 1 shows the spectra of electrons emitted by the 10 nm gold NP after photoionization of one of its atoms by a photon with the energy $h\nu_0$ under and over ionization thresholds $I(nl_j)$ of $2s_{1/2}$ (bottom panel), $2p_{1/2}$ (middle panel), and $2p_{3/2}$ (top panel). It can be seen that most of the electrons emitted by the NP have energies up to 2.0-2.5 keV. For example, upon absorption of one photon with an energy of 14.5 keV (over $2s_{1/2}$ threshold), the NP emits on average 19.8 electrons, of which 18.8 have energies up to 2.5 keV.

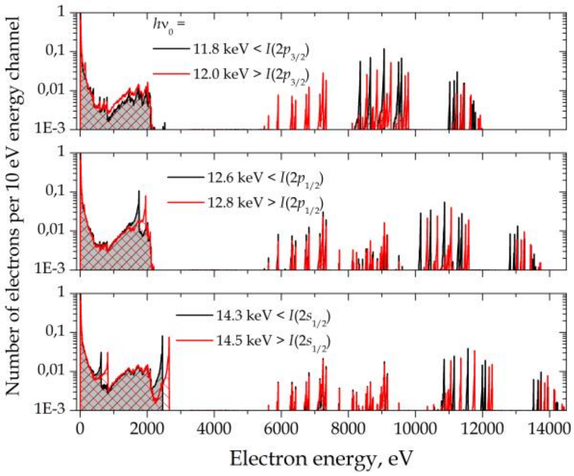

Fig. 1. Spectra of electrons emitted by 10 nm gold NP after photoionization of one of its atoms by photon with energy $h\nu_0$

Fig. 2 shows the energies emitted by a 10 nm gold NP after photoionization of one of its atoms at various incident photon energies.

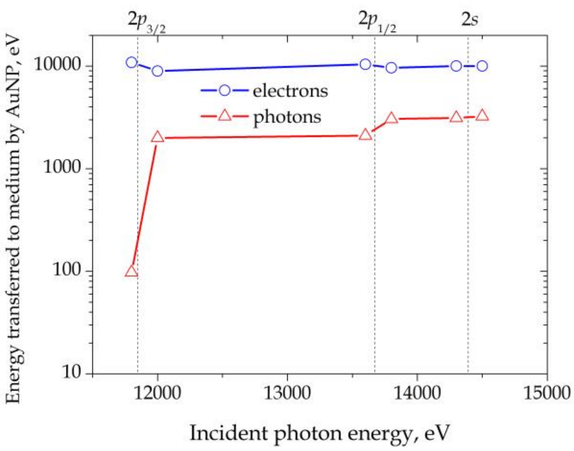

Fig. 2. Energy reemitted to the medium by 10 nm gold NP with all escaping electrons and photons

Fig. 3 shows calculated average number of electrons emitted by gold NPs of different sizes upon absorption of one photon with the energy of 14.5 keV. Up triangles represent the numbers of high-energy electrons (energy > 7.3 eV) that are able to ionize or excite water molecules surrounding the nanoparticle. The number of such electrons slowly decreases from 6.4 to 5.6 as the nanoparticle diameter increases from 2 to 14 nm. The reason for this is an increase in the average number of secondary electron-impact ionization events in which high-energy electron lose their energy while travelling from the volume of the NP to its surface. For the same reason, the number of low-energy electrons emitted by the NP with energies less than 7.3 eV (down triangles in Fig. 3) increases with NP diameter. A large number of low-energy electrons emitted by the NP is due to asymmetric energy sharing by two final state electrons in electron impact ionization events. One of them, usually called the knocked out, carries away only a small part of the shared energy, and the other, the scattered one, a larger part.

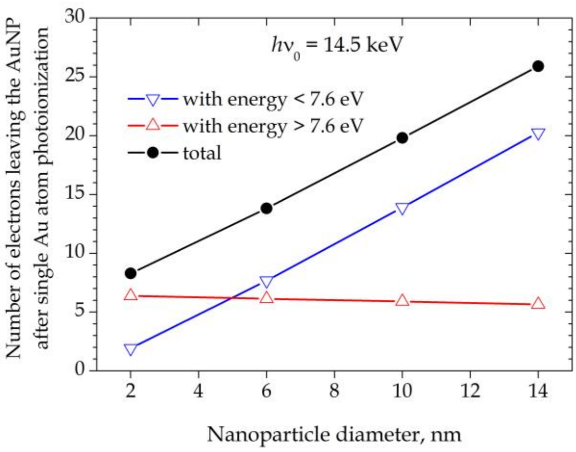

Fig. 3. Average number of electrons emitted by the gold NP after its photoionization by a photon with energy $h\nu_0$ = 14.5 keV (over Au2*s* threshold) at various nanoparticle diameters. Up triangles are high-energy electrons that can ionize or excite water molecules surrounding the nanoparticle, down triangles are low-energy electrons that are unable to cause ionization, circles are all electrons

It should be noted that low-energy electrons produced in large quantities may play a significant role in radiotherapy causing the DNA strand breaks through a dissociative electron attachment mechanism [7, 8].

Conclusion

A detailed MC simulation of the processes occurring in the gold NP nanoparticle under irradiation with photons with energies near the Au2s, Au2$p_{1/2}$, and Au2$p_{3/2}$ thresholds is performed. The spectra of electrons and photons emitted by the nanoparticle are calculated. It is shown that the NPs reemit most of the acquired energy into the environment with secondary electrons and photons. The results of this study are relevant for the development of strategies in radiotherapy when using gold NPs as radiosensitizers.

Acknowledgement

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