Ag/TiO_2 Composite Ultra-fine Particle Studied with FE-SAM

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We have prepared the silver adhered titania fine particle of the size in several nanometer. Composite fine particle are produced with the intention of using as an inorganic antibacterial agent. Composition of them are analyzed by using FE-SAM and TEM. Optimum analytical conditions are discussed on the beam diameter and the electron scattering range as a function of the accelerating voltage. In order to achieve the higher spatial resolution, lower beam voltage is recommended for the SAM analysis.

1. Introduction

Reliable antimicrobial product is demanded by a social consciousness in order to attain the microbiological clean environment. Recently, photocatalyst or inorganic antibacterial agent have been widely used for this purpose. Photocatalytic activity of the anatase titania is higher than that of the rutile, moreover the activity may be improved by the adhesion of the transition metal. It is believed silver ion itself actually have the antibacterial properties.

Inorganic antibacterial agent have a structure resemble to the fine particle chemical catalyst. Particle size of the inorganic antibacterial agent is in several nanometer order, therefore the high spatial resolution of the electron spectroscopy is required to evaluate the composition of its surface.

2. Experimental

Composite fine particles of the silver adhered titania were synthesized with the intention of using as the inorganic antibacterial agent. Concentrations of silver in the inorganic antibacterial agent were varied from 1 % to 50 % in weight ratio. Efficiency of the antimicrobial activity of the composite inorganic antibacterial agent were tested by a minimum inhibitory concentration (MIC) method, using MRSA (Staphylococcus aureus IID 1677) and bacillus coli (Eschrichia coli IFO 3972) as the test bacteria.

Structure and the composition of the inorganic antibacterial agents were analyzed by using FE-SAM and TEM. SAM analysis had been performed by using PHI-SAM 670xi equipped with field emission electron gun. The diameter of the primary electron beam was measured as a function of the accelerating voltage. Monte Carlo calculation were carried out, in order to estimate the scattering range of the primary electron beam in the solid.

Typical conditions of SAM analysis for the composite fine particle of 200 nm in average diameter were accelerating voltage of the primary electron beam 10 kV, the probe current 1 nA and the incident angle 90 degrees with respect to the sample holder. Measured Auger peaks were Ag-MNN, Ti-LMM and O-KLL. TEM observation for the composite fine particle of 20 nm in average diameter had been performed by using JEOL JEM-2000FXII with 200kV accelerating voltage.

3. Results and discussion

Silver adhered inorganic antibacterial agent showed remarkable antimicrobial activity against bacillus coli (gram-negative bacteria) and moderate activity against MRSA (gram-positive bacteria). Inorganic antibacterial agent containing 5 % silver showed effective MIC value of 800 μ g/mL against bacillus coli and containing 50 % silver showed same value against MRSA

There are a number of problems on the observation of the ultra fine particle by using electron beam in SAM analysis. First of all, the diameter of the primary electron beam is one of the most important factor. Figure 1 shows the measured primary electron beam diameters as a function of the accelerating voltage. Diameter of the primary electron beam was measured by knife edge method using beam diameter measurement tool made of gold mesh of the size 0.01 mm, which is supplied from PHI. Definition of the transition width of 80%-20% intersection was adapted as the electron beam diameter. The primary electron beam diameter under the condition of 2 kV, 10 nA was 190 nm and 25 kV, 1 nA was 12 nm. Diameter of the primary electron beam decreased at the higher accelerating voltage and at the lower current. However the reduction rate of the beam diameter above 10 kV was not remarkable.

Accelerated electron beam travels straight in the vacuum. But it should be diffused by the effect of elastic and/or inelastic scattering in the solid, then losses it's original kinetic energy. Monte Carlo simulation for titania and silver were carried out as a function of the beam voltage using commercially available

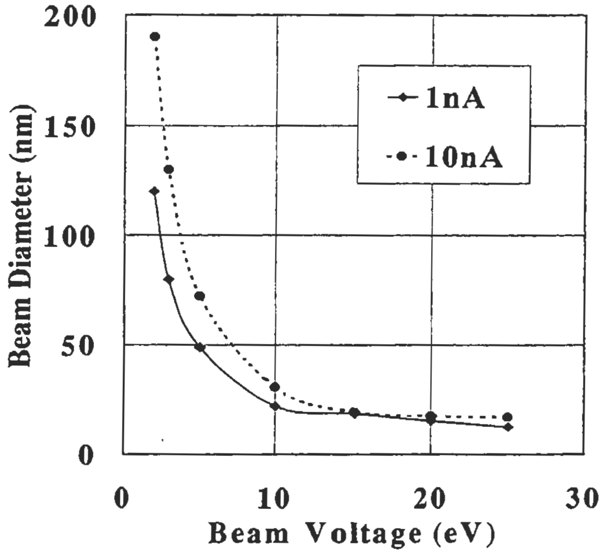


Figure 1. Measured primary electron beam diameter of SAM-670xi equipped with field emission electron gun.

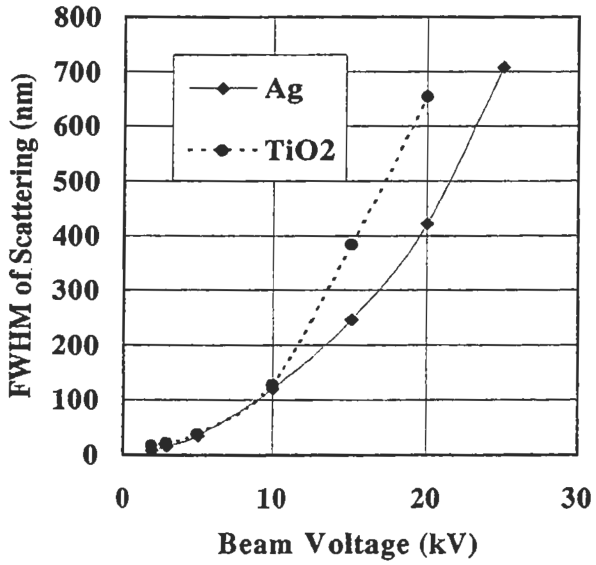


Figure 2. FWHM of the lateral scattering range calculated by Monte Carlo simulation.

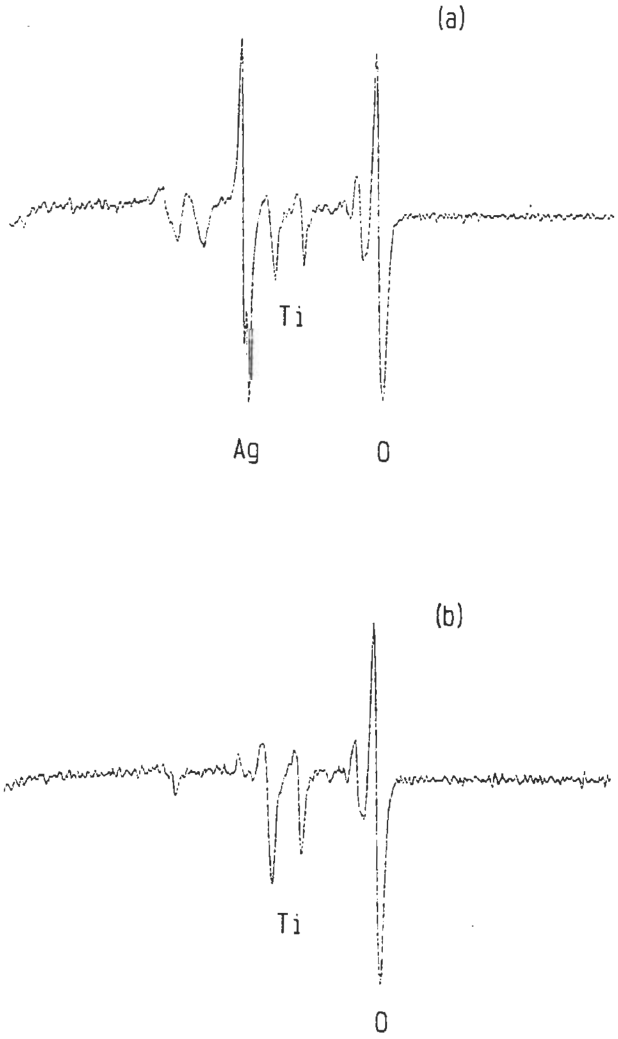


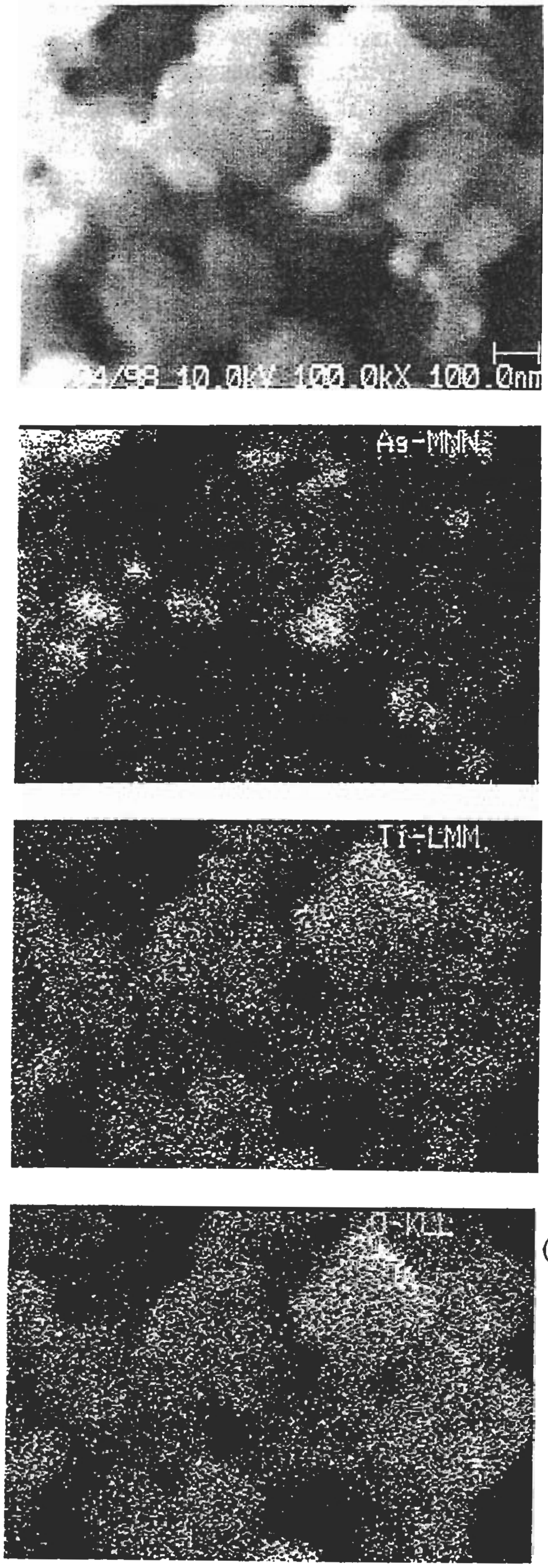
Figure 3. Auger spectra for (a) the ultra fine particle of silver and (b) titania fine particle.

calculation software supplied from JEOL. Figure 2 shows the diameters of the lateral scattering range defined by FWHM. Scattering range of the primary electron increased at the higher accelerating voltage. Generally, electron scattering range is lager in the low density solid than in the high density solid. It is clearly seen that the scattering range for titania is larger than that of silver above 10 kV, whereas approximately equivalent range under 10 kV. Incidentally, it is desirable that the scattering range restrict smaller than the fine particle size by the analytical condition at lower beam voltage.

For the reasons stated above, take both problems into considerations, an instrument with small beam diameter at low voltage is required for the fine particle analysis[1]-[3].

Figure 3 (a) shows the Auger spectrum of the ultra fine particle of the adhered silver on the titania and (b) titania fine particle of the size 200 nm in average diameter. Analytical conditions are 10 kV, 1 nA and diameter of the primary electron beam 30 nm. The component element of respective analytical point were distinguished from others by the differences of Auger signal intensity, although the influence of the Auger excitation of Ag-MNN, Ti-LMM and O-KLL by the scattered primary electron could not eliminate completely. In order to minimize the influence of Auger excitation by scattered primary electron, analytical condition of lower accelerating voltage is recommended for SAM analysis on the composite fine particle

Figure 4 (a) shows the SEM image of the



(a)

(b)

(c)

(d)

Figure 4. Observation of the inorganic antibacterial agent of the size 200 nm in average diameter by (a) SEM, (b) Ag-MNN, (c) Ti-LMM and (d) O-KLL respectively.

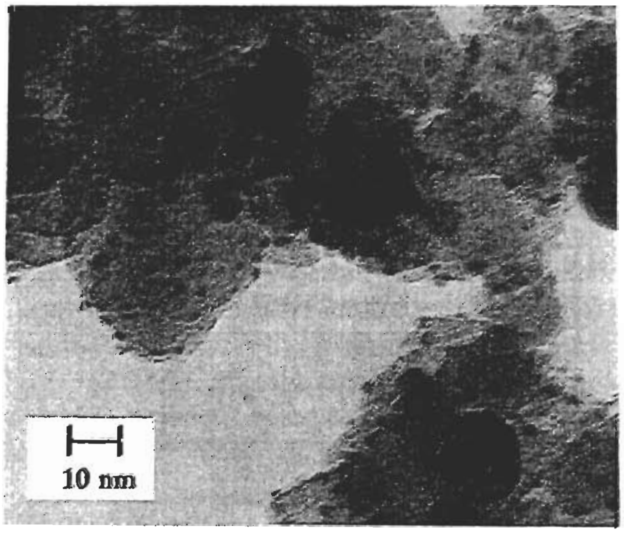


Figure 5. TEM image of the inorganic antibacterial agent of the size 20nm in average diameter.

inorganic antibacterial agent of the size 200 nm in average diameter. Figure 4 (b) shows the SAM image of Ag-MNN, (c) Ti-LMM and (d) O-KLL respectively. A lot of ultra-fine particle of the silver less than 50 nm in diameter on the surface of the titania fine particle could be observed quite clear from these Auger images. Analytical conditions of SAM observation are accelerating voltage 10 kV, beam current 1 nA, magnification 100,000 and the diameter of the primary electron beam 20 nm.

Figure 5 shows the TEM image of the inorganic antibacterial agent of the size 20 nm in average diameter. Magnification of this TEM image was 300,000. A large number of ultra-fine particle less than 2 nm in diameter adhered to the titania carrier fine particle. Former ultra fine particle was distinct from the later fine particle, although the lattice image of the composite fine particle was not quite clear. Silver and titanium were detected from respective fine particle by the fluorescent X-ray analysis using EDX.

4. Conclusion

Inorganic antimicrobial agent containing 5 % silver showed effective MIC value of 800 μ g/mL against bacillus coli. Effectiveness of antimicrobial activity increased with the composition of silver concentration.

Diameter of the primary electron beam was decreased at the higher accelerating voltage and at lower current. However the reduction rate of the beam diameter above 10 kV was not remarkable. Minimum primary electron beam diameter of 12 nm was obtained under the condition of 25 kV, 1 nA.

Scattering range of the incident electron beam was estimated by Monte Carlo calculation as a function of the beam voltage. Scattering range was increased at the higher accelerating voltage. In order to minimize the influence range of Auger excitation by the scattered electron, lower accelerating voltage condition was recommended for the analysis of the ultra fine particle.

Composite inorganic antibacterial agent was observed by using SAM and TEM. A large number of silver ultra fine particle adhered to the surface of the titania fine particle.

SAM instrument with small beam diameter at low voltage is required for more precise investigation on the analysis of ultra fine composite particle.

5. References

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