Single Ag nanowire photoluminescence and spectroelectrochemistry in alkaline solution

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Silver nanowires (NWs) have interesting electrical and optical properties that can be used in a variety of applications including transparent electrode, gas sensor, biomolecular sensing, photonic structure to launch an optical signal at a scale beyond the optical refraction limit, plasmonic antenna for surface-enhanced Raman scattering (SERS) and fluorescence. It is also known that electronically excited silver clusters can emit photoluminescence (PL) under visible light irradiation. The strong fluorescence is from excited Ag atoms, dimers and trimers and other aggregation states of Ag atoms. Such interesting photoluminescence can be used to unravel many mysteries underlying the complex characteristics of a biological system because silver clusters show strong, size dependent emission and they are easy to make. We present the PL and spectroelectrochemistry of single Ag NWs by using combined optical and electrochemical methods. PL intensity and blinking behavior from a single Ag NW is found to be highly dependent on excitation intensity, polarization direction, illumination time and electrode potential.

Experimental

Single nanowire spectroelectrochemistry setup comprised of a homebuilt confocal fluorescence microscopy, a potentiostat and sensitive photodetectors.

Photoluminescence collected from a single silver nanowire in air. A: laser intensity dependence of the photoluminescence collected per 10 msec. B: zoom-in PL intensity trajectory of a single nanowire at a laser intensity of 50 µW. C: statistic results of burst frequency of the data in B at certain peak height in counts.

Photoluminescence/Raman spectrum collected from a single silver nanowire in air (A) and time evolution (B) of the spectrum under continuous laser irradiation at 488 nm (0.5 mW). 1 sec collection time per spectrum was used.

Spectroelectrochemistry of single of Ag NWs

Cyclic voltammetry of silver nanowires and PL from a single silver nanowire in 0.1 M NaOH. Red curve is the second complete cycle of the potential and the blue one is the third one from the second cycle. The PL spectra of the first cycle is not shown. Scan rate: 0.01 V/sec. Reference electrode: Ag/AgCl.

Polarization dependence of the PL from two crossed silver nanowires in 0.1 M NaOH at rest potential.

Conclusion

1. The stochastic changes in the photoluminescence of one site on a single nanowire in air are attributed to the fluorescence photoactivated silver clusters not from Raman of adsorbed surfactant.
2. The PL of single silver nanowires in alkaline solution is highly dependent on the electrode potential and polarization direction of the incident light, providing a new way to study single Ag NW electrochemistry.
3. Strong PL intensity can be obtained when two wires cross and activated by laser irradiation at open circuit potential.