Electrodeposition of Cu_2O on TiO_2 Nanotubes: enhanced penetration after plasma cleaning

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Solar energy is the only renewable energy resource that can meet the world's energy needs, and the ability to store solar energy in the form of hydrogen is needed to overcome the inherent intermittency of sunlight availability. Furthermore, the production of photoelectrochemical solar cells using low cost, low energy, and earth abundant materials is necessary to make this process economical. TiO_2 nanotubes exhibit a number of useful properties that make them useful for this photoelectrochemical splitting of water including 1D charge transport, high surface area, and stability in solution.[1] The formation of TiO_2 nanotubes from anodization of Ti and the modification of these nanotubes by electrodeposition of Cu_2O to sensitize TiO_2 to visible light are both routes that meet these requirements.

TiO_2 nanotubes were synthesized from anodization in 11 vol% H_2O / ethylene glycol with 0.5wt% NH_4F at 20V for 1 hour. N-type Cu_2O can be electrodeposited from a solution of 0.02M $Cu(CH_3COO)_2$ and 0.1M $NaCH_3COO$ (pH = 5.7) using a pulse plating technique with a deposition potential at -0.3V_{SCE}.[2]

We have successfully shown that TiO_2 nanotubes, known for their promising properties of high surface area and 1D charge transport, can be sensitized to visible light by the electrodeposition of Cu_2O, but that it was difficult to promote the penetration of the Cu_2O crystals into the nanotube interiors.[3] The anodization of TiO_2 in organic electrolytes may leave carbon species on the surface of the nanotubes, blocking possible sites for electrodeposition. We have applied a plasma treatment by exposing the TiO_2 nanotubes to an Ar and an O plasma sequentially. We show (Figure 1) that use of this plasma treatment facilitates the embedding of Cu_2O inside the nanotube. Enhancements in the visible range (Figure 2) are observed, with efficiencies at 500nm close to 1%. Optimization of deposition conditions including deposition time and pulse widths produced integrated quantum efficiencies as high as 3.5% over a 350-800 nm range.

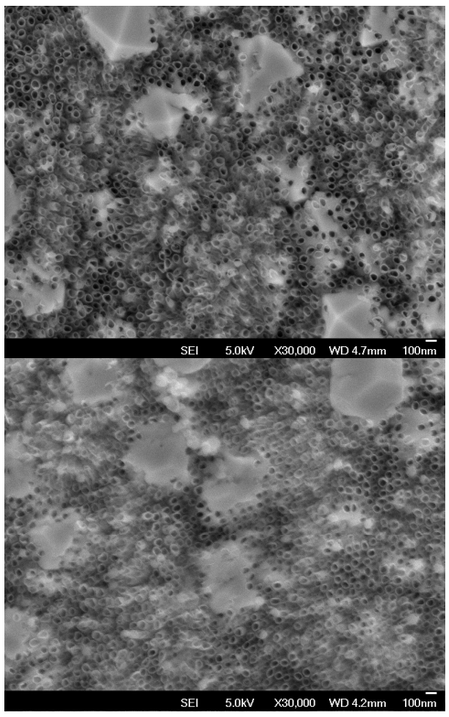

Figure 1. Morphology of n-Cu_2O electrodeposited on TiO_2 nanotubes (top) without plasma treatment and (bottom) with plasma treatment.

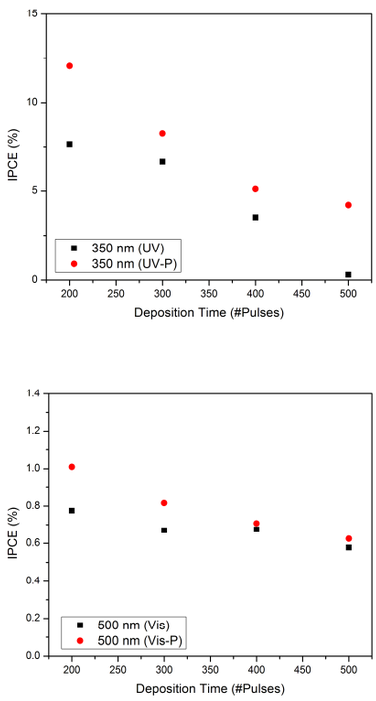

Figure 2. IPCE obtained on n-type Cu_2O modified TiO_2 nanotubes in both the (top) UV and (bottom) visible.

References

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