p-Type Cu$_2$O colloids optimized for photoelectrochemistry and electronics

**Yury V. Kolen'ko**,[1] Xiao-Qing Bao,[1] and Pedro Alpuim[1,2]

1 – INL, Avenida Mestre José Veiga, 4715-330 Braga, Portugal
2 – Department of Physics, Universidade do Minho, 4715-057 Braga, Portugal
yury.kolenko@inl.int

Owing to appropriate direct band energy of ca. 2.1 eV, high absorption coefficient and high hole mobility, the cuprite Cu$_2$O now stands as a competitive candidate as a photocatalyst for solar-assisted photoelectrochemical (PEC) H$_2$ evolution from water. Cu$_2$O is also a promising material for *p*-type metal-oxide semiconducting inks for solution-based printing of thin film transistors (TFTs), key components for microelectronics. Many examples of the synthesis of Cu$_2$O micro- and nanocolloids, which allow control over the particle size and shape, are known. A major synthetic challenge, however, is up-scaling the preparation of Cu$_2$O.

We use an automated synthesis system as a basis for the controlled large-scale surfactant-assisted synthesis of photoactive Cu$_2$O submicroparticles (Figure 1). Structure, morphological peculiarities, as well as enhanced solar H$_2$ evolution performance will be discussed. In particular, as a photocathode for PEC H$_2$ evolution, bare Cu$_2$O submicrocubes have a high onset potential of ca. 0.9 V versus the RHE at pH 1, which is significantly higher than the difference (~0.54 V) between the Fermi-level (0.48 V vs. SHE) of Cu$_2$O and the H$^+$/H$_2$ redox potential (0.06 V vs. SHE). This indicates a fraction of the photocurrent is induced by the reduction of Cu$_2$O to Cu (0) according to the eq 1 [1]:

$$Cu_2O + 2e^- + 2H^+ \rightarrow Cu + H_2O \qquad (1)$$
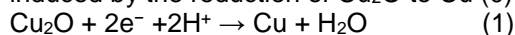
In addition, nearly monodisperse Cu$_2$O nanocolloids were prepared in high yields through thermal decomposition protocol (Figure 2). Cu$_2$O thin films were further fabricated by spin-coating of the nanocolloids on a 200-nm SiO$_2$@Si wafer. Room temperature dark conductivity, σ_d, of the films, measured between parallel coplanar contacts, is thermally activated (Figure 3). σ_d is in the range 2.1×10^{-5} Ω^{-1}cm^{-1} – 1.2×10^{-3} Ω^{-1}cm^{-1}, while the activation energy of σ_d, E_a, extracted from temperature-dependent σ_d measurements in the range 25 to 95 ºC, decreases from 0.44 eV to 0.25 eV, respectively.

References

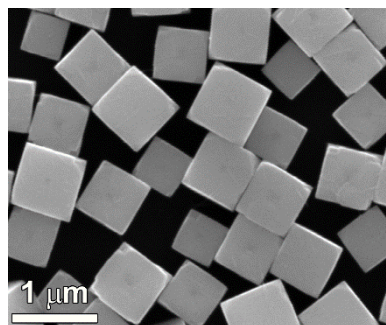[1] A. Paracchino, V. Laporte, K. Sivula, M. Gratzel, E. Thimsen. Nat. Mater., 10 (2011) 456.
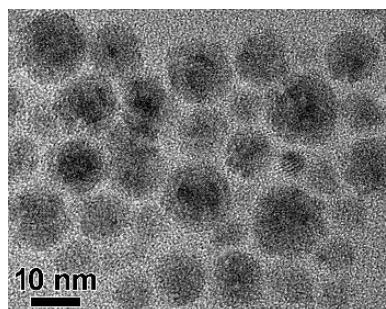
Figures

Figure 1

Figure 2

Figure 3