

Supporting Information for:

Interfacial Cu/ZnO Contact by Selective Photodeposition of Copper onto the Surface of Small ZnO Nanoparticles in Non Aqueous Colloidal Solution.

Mahmoud A. Sliem,^a Todor Hikov,^a Zi-An Li,^c Marina Spasova,^c Michael Farle,^c Diedrich A. Schmidt,^b Martina Havenith-Newen^b and Roland A. Fischer^{*a}

^a Lehrstuhl für Anorganische Chemie II, Ruhr Universität Bochum, Universitätstrasse 150, 44801 Bochum, Germany.

^b Lehrstuhl für Physikalische Chemie II, Ruhr-Universität Bochum, Universitätstrasse 150, 44780 Bochum, Germany.

^cAG Farle, Fachbereich Physik Experimentalphysik, Universität Duisburg-Essen, Lotharstr. 1, 47048Duisburg, Germany.

Corresponding author email address: Roland.Fischer@rub.de

Corresponding Author: Prof. Dr. Roland A. Fischer, Ruhr-Universität Bochum, NC 2, Universitätsstr. 150, 44801 Bochum, Tel: +49 (0)234 32-24174, Fax: +49 (0)234 32-14174.

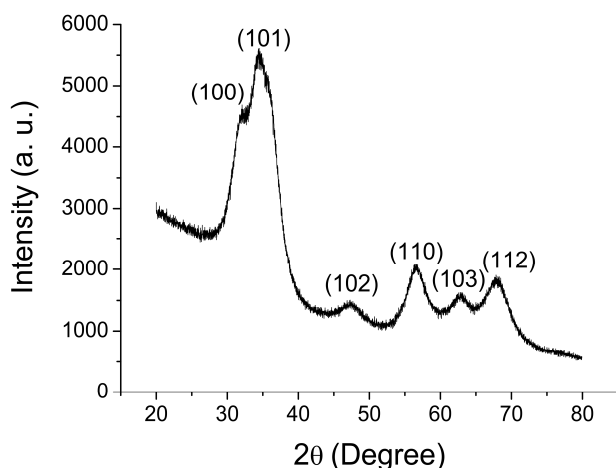


Figure S1. PXRD pattern of the HDA stabilized hexagonal, wurtzite ZnO phase [ZnO: PDF: 00-036-1451]. The peaks appear to be very broad and with low relative intensity against the background. Such behavior is to be expected from a sample containing nanocrystalline material with coherence lengths (crystalline domains) well below 10 nm.

XRD diffractograms were taken on a D8-Advance Bruker AXS diffractometer: Cu K α radiation ($\lambda = 1.54178$; Göbel mirror; θ - 2θ scan; $2\theta = 20 - 80^\circ$; step size = $0.0142 (2\theta)$; scan speed = 10 second/step; position sensitive detector; room temperature; α -Al₂O₃ was used as a external standard. The sample was filled under inert gas (glove-box) into standard capillaries (0.7-mm diameter) and measured in Debye–Scherer geometry. The reference data for the hexagonal wurtzite structure of ZnO was taken from the International Centre for Diffraction Data (ICDD, PDF-2 Release 2004) database.

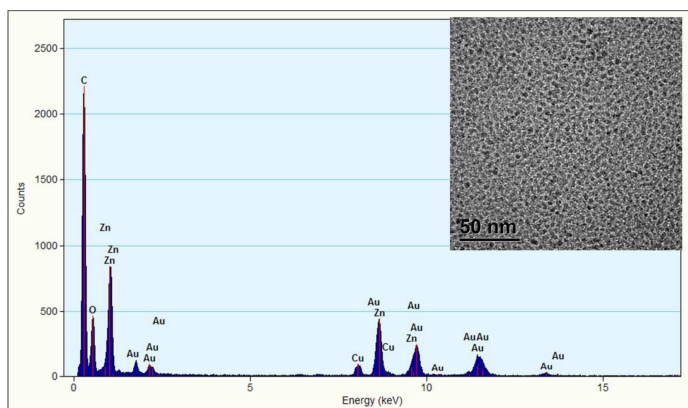


Figure S2. X-ray energy dispersive spectroscopy (XEDS) of HAD@Cu/ZnO nanocomposite particles of 15 wt. % Cu. Inset shows the TEM image of HAD@Cu/ZnO, 15 wt. % Cu.

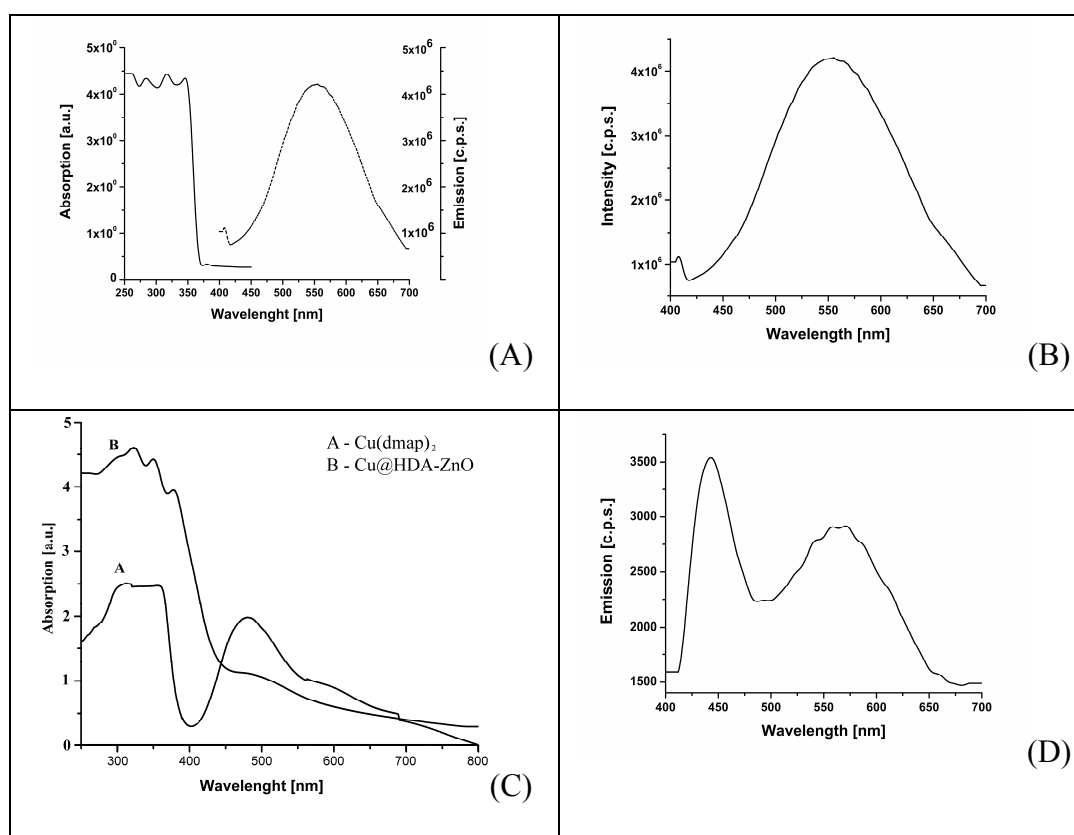
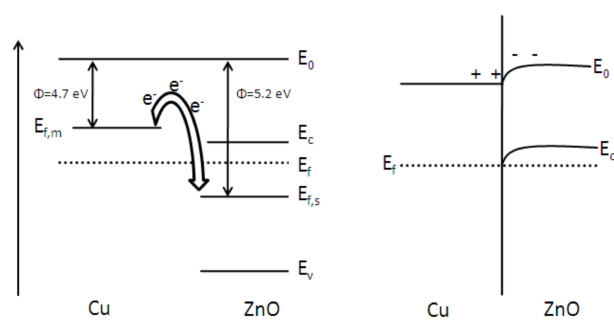


Figure S3. Optical properties of ZnO NPs and colloidal Cu/ZnO NPs with 15 % wt.% Cu with respect to ZnO. (A) represents the UV-VIS and PL spectra of ZnO. (B) illustrates the PL spectrum of ZnO. (C) shows the UV-VIS spectra of [Cu{(OCH(CH₃)CH₂N(CH₃)₂)₂}₂] (line A) and Cu/ZnO (line B) and (D) shows the PL spectrum of Cu/ZnO with 15 % wt.% Cu with respect to ZnO.



Scheme S4. Conceptual band gap structure of Cu and ZnO before and after interfacial contact.

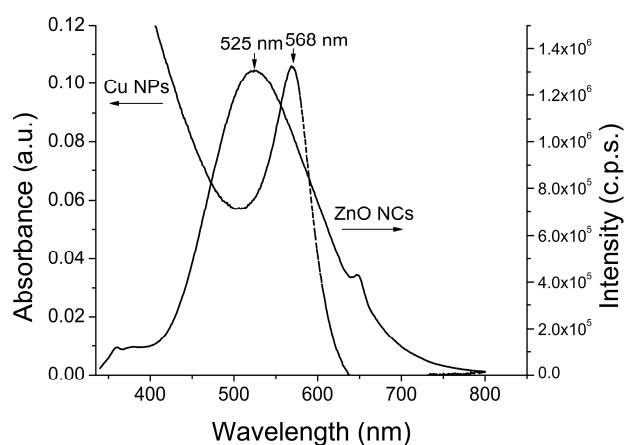


Figure S5. Photoluminescence spectrum of HDA@ZnO NCs ($\lambda_{\text{ex}} = 325 \text{ nm}$) and plasmon absorption band of HDA@Cu NCs in n-hexane.

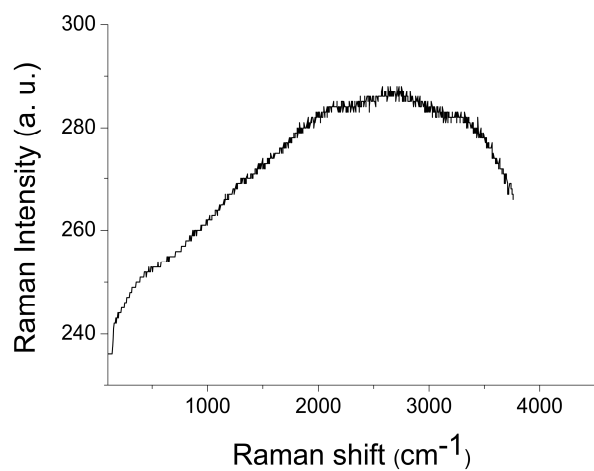


Figure S6. The huge green photoluminescence that is observed for ZnO NCs after annealing (i.e. without any ligand) using Nd-YAG laser ($\lambda_{\text{ex}} = 532$ nm). Laser power is 1 mW.

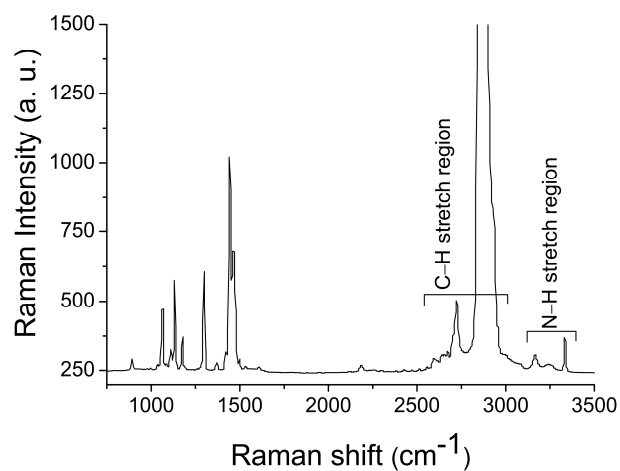


Figure S7. Raman spectrum of HDA upon excitation at $\lambda_{\text{ex}} = 532$ nm using Nd-YAG laser. Laser power is 43 mW.

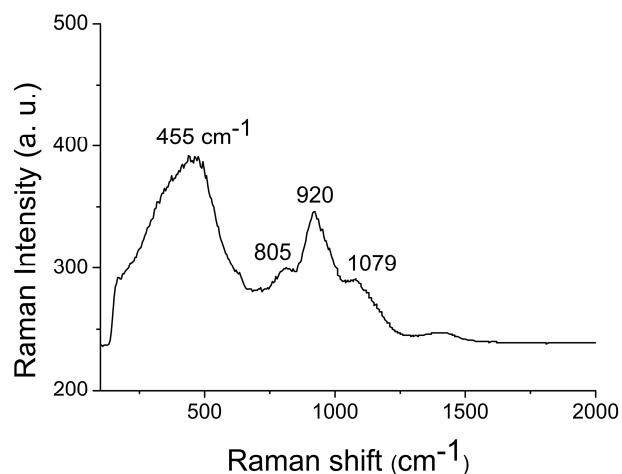


Figure S8. Raman spectrum of glass slide (150 μM thick) upon excitation at $\lambda_{\text{ex}} = 532 \text{ nm}$ using Nd-YAG laser. Laser power is 43 mW.

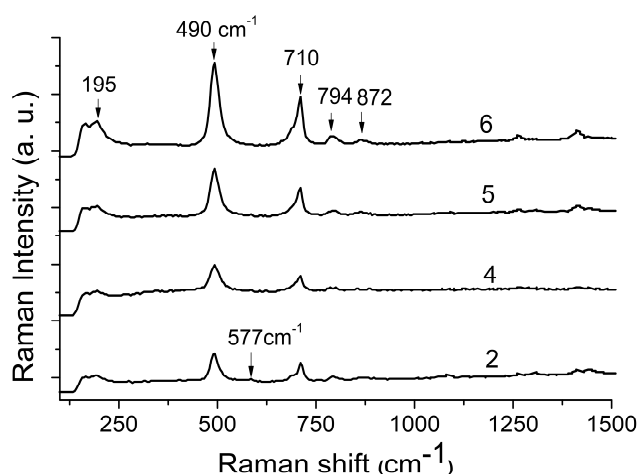


Figure S9. Nonresonant Raman scattering spectra of 2-5 nm size ZnO NPs (**2**) reference sample and the samples Cu/ZnO NPs with (**4**) 30 %, (**5**) 50 %, and (**6**) 70 % wt. % of Cu using a Nd-YAG laser ($\lambda_{\text{ex}} = 532 \text{ nm}$). Laser power is 5 mW.