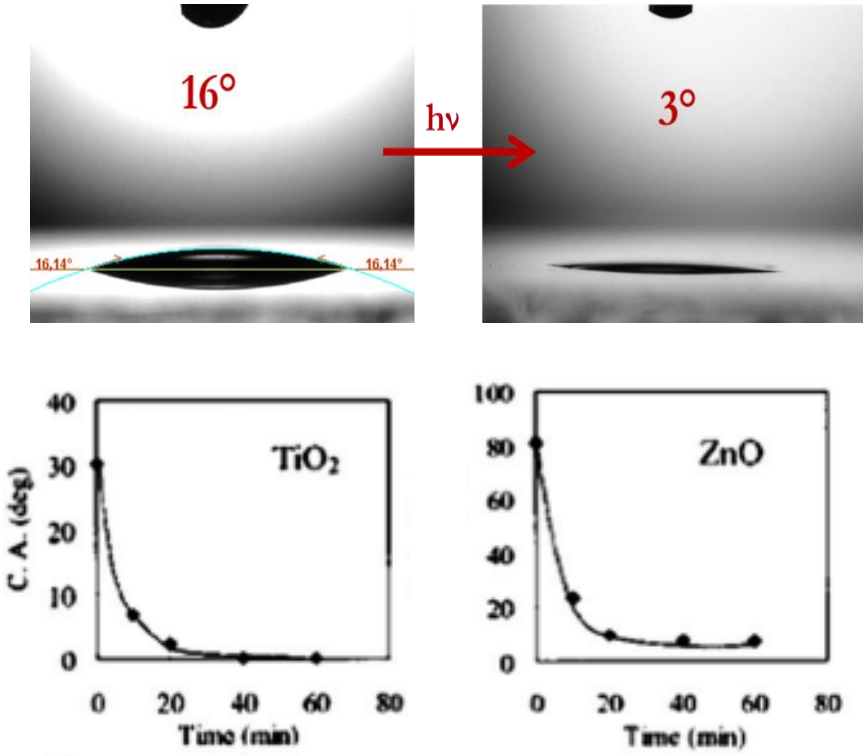
Photoinduced hydrophilicity of layered heterostructures Cu_2/TiO_2 and Cu_2O/ZnO

Maria V. Maevskaya[1*], AidaV. Rudakova,[1] Alexei V. Emeline[1], Detlef W. Bahnemann[1,2]

[1] Laboratory "Photoactive Nanocomposite Materials", Saint-Petersburg State University, Ulianovskaia str. 1, Peterhof, Saint-Petersburg, 198504, Russia
[2] Institut fuer Technische Chemie, Gottfried Wilhelm Leibniz Universitaet Hannover, Callinstrasse 3, D-30167 Hannover, Germany
*maevskaya.mv@gmail.com

Photoinduced hydrophilicity of ZnO and TiO_2nanocoatings



Photoinduced hydrophilic state of nanocoatings under action UV irradiation .[1]
(Copyright 2002 American Chemical Society.)

ZnO and TiO_2 are well-known oxides that exhibit a transition to a superhydrophilic state under the action of ultraviolet radiation.
The first stage in this phenomenon is the generation of charge carriers and their subsequent interaction with the hydroxyl-hydrated cover.
However, at the moment, the role of each type of charge carriers in this phenomenon is not known.

[1] M. Miyauchi, A. Nakajima, T. Watanabe and K. Hashimoto, Chem. Mater., 2002, 14, 2812.

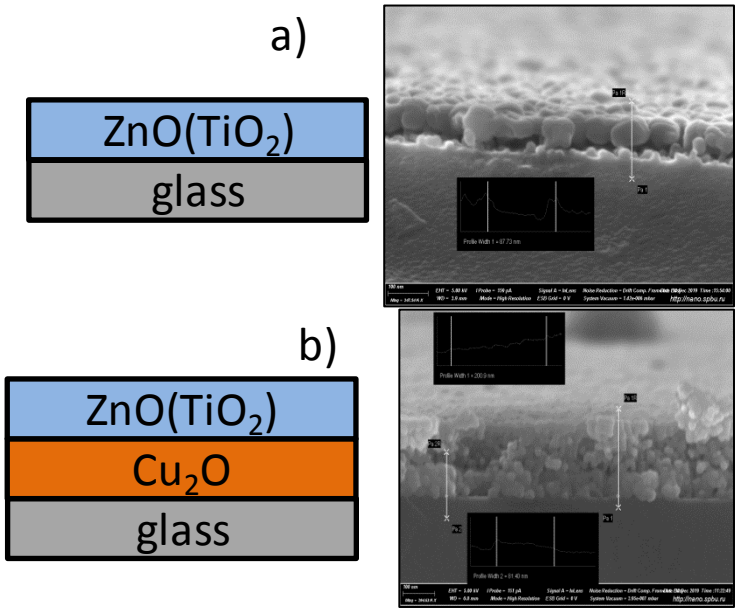
Synthesis and characterization of heterostructures

Synthesis: The heterostructures were formed layer-by-layer.

Cu2O film was formed from sol-gel(diethanolamine (Fluka, 99%), isopropanol (99.8%, Ecos-1), $Cu(OAc)_2 \cdot H_2O$ (99.0%, Vekton))by dip-coating method and annealed in N2 atmosphere.

TiO2 layer was synthesized on SiO_2-coated glass and Cu2O substrates by ALD method at 200˚C from $TiCl_4$.

ZnO layer was synthesized from sol-gel(ethylene glycol (99.5%, LenReactiv) ,zinc acetate dihydrate $Zn(OAc)_2 \cdot 2H_2O$ (99.0%, Vekton), isopropanol (99.8%, Ecos-1) , triethylamine(99.5%, PanReac AppliChem))by dip-coating and annealed at 280˚C.



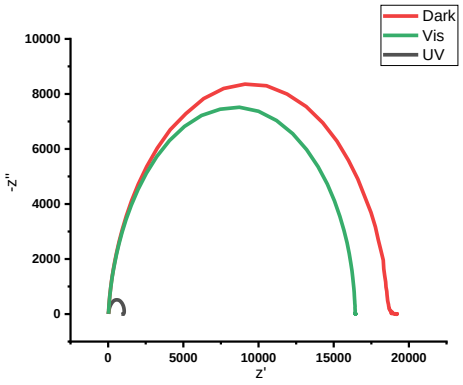
a) Cross-section ZnO nanocoating, b)cross-section ZnO/Cu_2O heterostruture

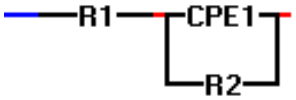
Table1. Characterization data

Sample	Crystalline phase	Thickness, nm	Particle diameter, nm	Smoothness, nm
TiO_2	Anatase	55	50	3
TiO_2/Cu_2O	Anatase/Cuprite	45/85	40	3
ZnO	Zincite	100	15	4
ZnO/Cu_2O	Zincite /Cuprite	120/80	15	5

Impedance spectroscopy

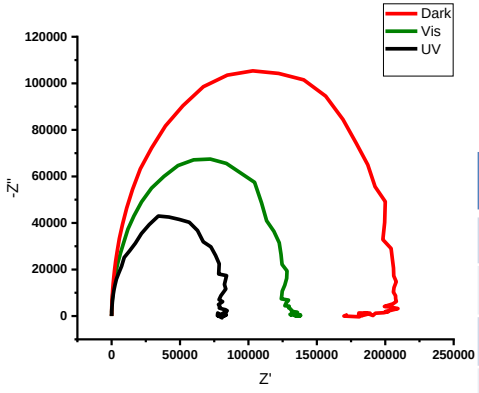
Data impedance spectroscopy for TiO2 nanocoatings

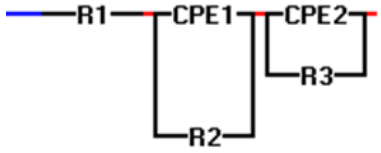




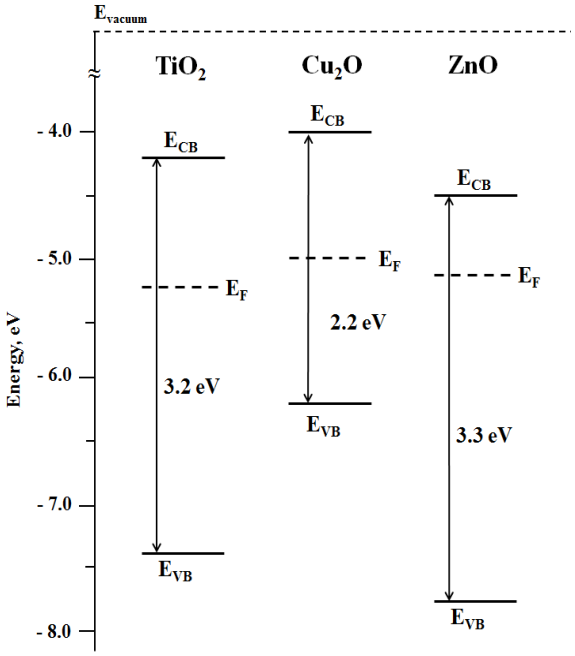
Tio2	dark	Vis	UV
R1	22.153	22.153	22.153
R2	18 581	16 445	1 125
P1	1.16E-09	1.23E-09	1.35E-09
n1	0.93	0.93	0.93

Data impedance spectroscopy for Cu2O/TiO2 heterostructure



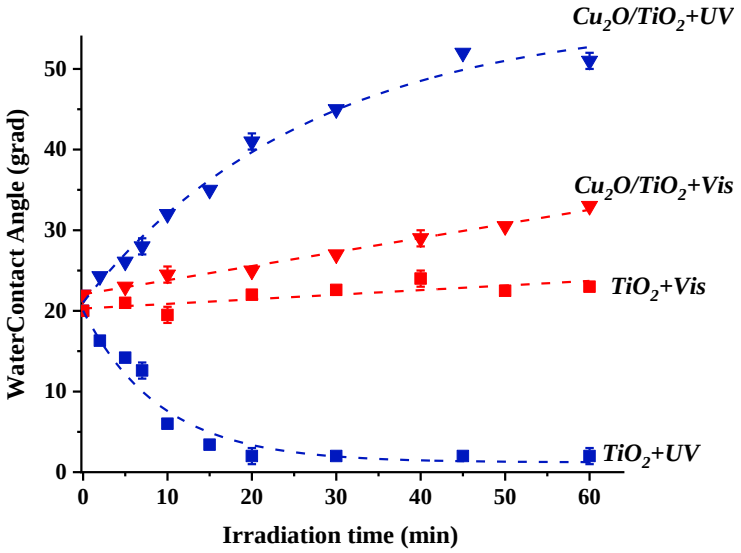


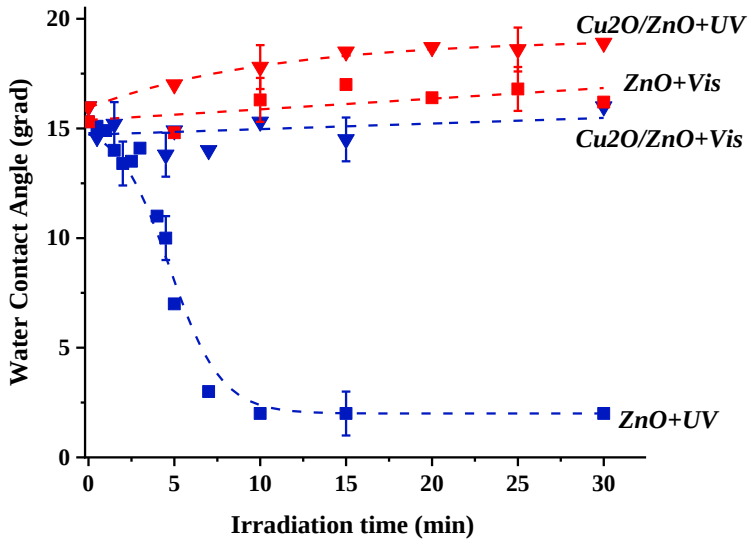
Cu_2O/TiO_2	dark	Vis	UV
R1 *fix*	16.042	16.042	16.042
R2	36 585	24 293	8.5E-13
R3	1.7358E05	1.0803E05	82208
P1	2.8313E-09	3.6902E-09	3.9678E-09
n1	1	0.887	0.599
P2	8.9831E-10	8.9831E-10	8.9831E-10
n2	0.98	0.98	0.98



Energy diagrams of individual components of heterostructured coatings

Hydrophilicity of heterostructures





Kinetics of contact angle with water under Visible Light(λ>420nm) and UV(320nm<λ<380nm)

The Cu_2O substrate affects the direction of the hydrophilic conversion. In contrast to single-component films, heterostructures transform into a more hydrophobic state in both cases under the influence of visible light, and under the influence of ultraviolet irradiation. This effect of the Cu_2O substrate is explained in terms of charge separation at corresponidng heterojunctions with electrons transferred from Cu_2O.

Acknowledgment

The reported study was funded by RFBR, project number 19-32-90111

Experimental studies were performed using equipment of laboratory “Photoactive nanocomposite materials”

We are thankful to the Resource Center (RC): “Nanophotonics”

RC “Centre for Innovative Technologies of Composite Nanomaterials”,

RC “X-ray Diffraction Studies”

RC “Centre for Physical Methods of Surface Investigation”
RC “Nanotechnology”.