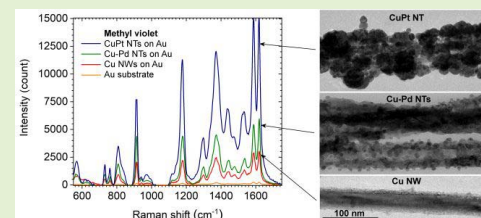


Cu-Pd Bimetal and CuPt Alloy Nanotubes Derived From Cu Nanowires: Novel Amplification Media for Surface-Enhanced Raman Spectroscopy

Eva Bozo, Aron Dombovari, Melinda Mohl, Vesa K. Virtanen, Simo Saarakkala^{ID}, Robert Vajtai^{ID}, and Krisztian Kordas

Abstract—Surface-plasmons of metals have been utilized to enhance the Raman spectra of various adsorbed moieties for over decades. While amplification of the spectral intensity takes place on most of the metals, due to their superb properties, Au, Ag and Cu surfaces represent the benchmark in surface-enhanced Raman spectroscopy. In this paper, we show that Cu-Pd bimetal and CuPt alloy nanotubes derived from Cu nanowires by simple galvanic exchange reactions are suitable for the efficient enhancement of Raman spectra when dispersed on Si surfaces. Amplification factors of 120 \times on Cu nanowires, 150 \times on Cu-Pd bimetal nanotubes and 250 \times on CuPt alloy nanotubes in reference to the substrate are measured for rhodamine 6G and methyl violet model compounds. We also show that the nanotubes dispersed on Au surfaces can contribute to a further intensity enhancement of the substrate and detect analytes adsorbed from 10⁻⁶ M analyte concentrations. Our results obtained using bimetallic and alloy nanomaterials shed light on a new strategy to synthesize and apply new types of metal nanostructures and compositions for surface-enhanced Raman spectroscopy in the future.

Index Terms—SERS, Cu nanowires, galvanic exchange reaction, CuPt alloy, Cu-Pd bimetal.



I. INTRODUCTION

SURFACE-ENHANCED Raman spectroscopy (SERS) is a powerful analytical tool to detect and quantify a broad

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E. Bozo is with the Microelectronics Research Unit, University of Oulu, 90570 Oulu, Finland (e-mail: eva.bozo@oulu.fi).

A. Dombovari and M. Mohl were with the Microelectronics Research Unit, University of Oulu, 90570 Oulu, Finland. They are now with Silicon Austria Labs GmbH, High Tech Campus Villach, 9524 Villach, Austria (e-mail: mohlmelinda@gmail.com; aron.dombovari@gmail.com).

V. K. Virtanen and S. Saarakkala are with the Research Unit of Medical Imaging, Physics and Technology, University of Oulu, 90570 Oulu, Finland (e-mail: vesa.k.virtanen@oulu.fi; simo.saarakkala@oulu.fi).

R. Vajtai is with the Department of Material Science and Nano-Engineering, Rice University, Houston, TX 77005 USA (e-mail: robert.vajtai@rice.edu).

K. Kordas is with the Microelectronics Research Unit, University of Oulu, 90570 Oulu, Finland (e-mail: krisztian.kordas@oulu.fi).

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range of chemicals even in trace quantities, and thus it has been widely employed in analytical chemistry [1], environmental monitoring [2], [3], biomedical diagnostics [4]–[7], food security [8], and even in forensic investigations [9], [10].

Enhancement of the Raman spectra are due to two primary reasons. On the one hand, the electric field in the proximity of resonant surface plasmons is amplified, which then enhances polarization of the adsorbate and increase Raman intensity (electromagnetic effect). On the other, (partial) charge transfer between adsorbed molecules on metal surfaces can result in the change of polarizability thus contributing to an enhanced polarization in the electric field (chemical or charge-transfer effect) [11].

Although SERS was discovered in the 1970s [12], there is still an immense interest in finding newer and affordable materials as amplification media other than the traditional gold or silver surfaces. Platinum group metals, although also very expensive, are particularly interesting because their catalytic and electrocatalytic properties make the follow up of chemical reactions possible by observing adsorbed reactants and intermediates [13], [14]. As demonstrated experimentally [14]–[16] and confirmed theoretically [22], common metals

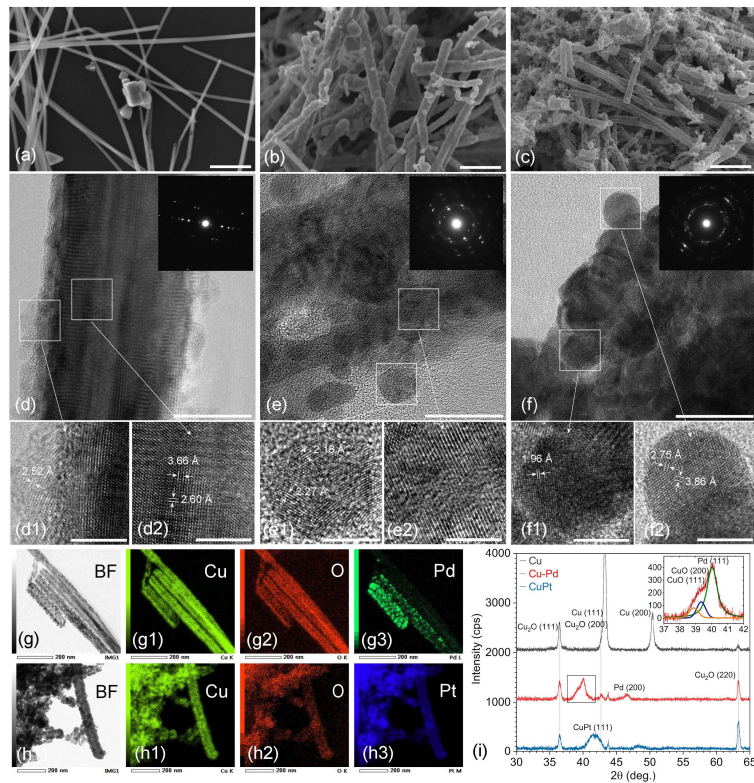


Fig. 1. SEM images of (a) Cu nanowires as well as (b) Cu-Pd and (c) CuPt nanotubes. Scale bars are 500 nm. TEM images and corresponding electron diffraction patterns (insets) of (d) Cu nanowires, (e) Cu-Pd and (f) CuPt nanotubes. The sub-panels (d1-f2) are magnified parts of the respective samples indicated by the white rectangular areas. (d1) Cu_2O crystals covering the surface of the Cu NWs. (d2) Cu crystal and its (100) and (110) planes. (e1) Polycrystalline Pd nanoparticle on the surface of the Cu-Pd nanotube identified by the (111) planes of Pd. (e2) Wall of the Cu-Pd nanotube. (f1) and (f2) Pt nanoparticles and their identified (200), (110) and (100) planes. Scale bars are 5 nm. Panels (g) and (h) show bright-field scanning TEM images of Cu-Pd and CuPt nanotubes, and their corresponding EDX elemental maps in the sub-panels. Scale bars are 200 nm. (i) XRD patterns of the nanostructures. Inset: resolved reflections of Pd and CuO.

(e.g. Fe, Co, Ni, Al, Sn) show reasonable Raman enhancement although less efficient than the noble metals. Furthermore, not only pure metals but their various alloys, bi- and tri-metallic compositions [18], [19] and multi-layered structures [20], [21] and hybrids with semiconductors [5], [7], [22] have been reported to improve SERS efficiency of less active metals because of multiple effects. One is based on the extended range of increased electric field on the surface of a metal or semiconductor near a highly SERS active particle or film (borrowed SERS activity) [23]. The other effect is associated with plasmonic hot electron injection from the metal to the semiconductor [24], which inherently results in different local fields and can alter the metal-molecule complex thus influencing both electromagnetic and chemical sensing mechanisms. In addition to the above processes, also the geometry, morphology, and size of particles influence SERS, as the local field is a function of surface curvature [25]–[29].

Recently, we have shown that Cu nanowires are suitable for SERS, in particular, when dispersed on Au thin films [30]. Although rapid oxidation of common metals may influence the local field and thus spectral amplification, in the case of Cu, the native surface oxides [31] do not seem to degrade SERS quality [30], [32]. In this paper, our aim is to extend our SERS studies on Pt and Pd derivatives of Cu nanowires. Our strategy follows the idea of combining highly and less SERS

active metals into a synergistic system by using very simple and easy-to-scale synthesis routes, which include hydrothermal growth of Cu nanowires [30], [31], [33] followed by a partial exchange of Cu with Pd and Pt in galvanic replacement reactions [34]. We show that the as-made hybrid nanostructures are having superior Raman enhancement as compared to Cu nanowires making them promising new candidates for SERS applications.

II. MATERIALS AND METHODS

Cu nanowires were synthesized by a hydrothermal route, [30], [31], [33] whereas their Pd and Pt modified derivatives were obtained by galvanic replacement reactions [34] similar to those as we reported earlier.

A. Synthesis of Cu Nanowires

1.4 g of $\text{CuCl}_2 \times \text{H}_2\text{O}$ and 3.2 g of D-glucose were dissolved in 640 mL distilled water, then while stirring, 11.5 g hexadecylamine was slowly added to the solution. After 4 hours of stirring, the light blue solution was inserted into a Teflon lined autoclave (Parr Instrument) to facilitate hydrothermal synthesis in 120 °C at autogenic pressure (~ 1.2 bar) for 24 hours (stirring at 35 rpm). After the reaction, the products were collected, and washed with distilled water, hexane and ethanol

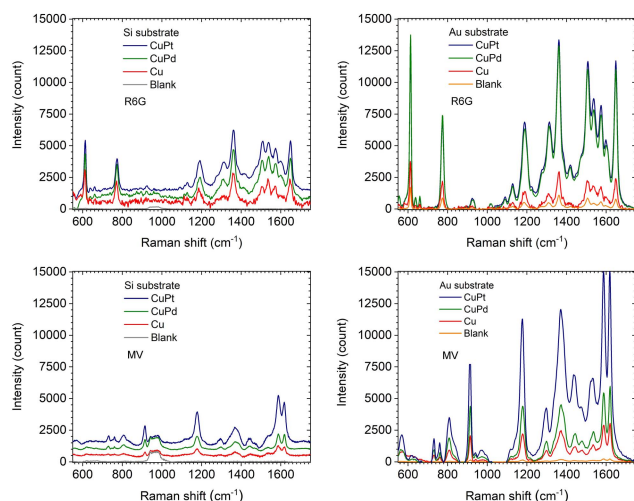


Fig. 2. Raman spectra of R6G and MV on Cu NWs, Cu-Pd and CuPt NTs dispersed on (a) and (c) Si and (b) and (d) Au surfaces. The dyes were cast from 10^{-4} M aqueous solutions. Each spectrum correspond to the best performing surface areas covered by networks of nanowires or nanotubes. The reference spectra correspond to Si and Au substrates coated only with either of the dyes. (Instrument: ThermoFisher DXR2xi Raman Imaging Microscope, $100\times$ objective, $\lambda = 532$ nm, $P = 2$ mW, $\tau = 0.02$ s, $1000\times$ scans, slit aperture: $50\ \mu\text{m}$ and laser spot: $0.6\ \mu\text{m}$.)

(each repeated three times). The purified product was kept in ethanol until further use.

B. Synthesis of Bimetallic Cu-Pd and Alloy CuPt Nanotubes

1 mL of Cu nanowire suspension was first diluted in ethanol (1 mg/mL) and then sonicated for at least half an hour then centrifuged at 3200 rpm and washed with dimethyl sulfoxide (DMSO). The copper nanowires were then dispersed in DMSO (5 mL) under N_2 atmosphere in a 50 mL flask. Aliquots of noble metal salt solutions (1 mM of potassium tetrachloropalladate or potassium tetrachloroplatinate in DMSO) were then added slowly to the copper nanowire dispersions (at $189\ ^\circ\text{C}$) and kept under reflux until its color became stable (typically 10 min). Thereafter the product was centrifuged and washed with ethanol and kept in ethanol.

C. Materials Characterization

The morphology, microstructure and composition of the products were characterized by field-emission scanning electron microscopy (FESEM, Zeiss Ultra Plus, 15 kV, samples were drop cast on chips of a Si wafer), transmission electron microscopy and electron diffraction (EFTEM, Jeol FS 2200, 200 kV, samples were drop cast on Ni grids) and energy dispersive X-ray spectroscopy (EDX installed in both SEM and TEM). For crystal structure analysis we used powder X-ray diffraction (XRD, Bruker D8 Discovery, Cu $K\alpha$, with 2θ scans between 5° and 90° at a rate of $0.01\ ^\circ/\text{s}$) of each sample drop cast on the surface of glass slides.

D. Surface-Plasmon Enhanced Raman Spectroscopy Analysis

Surface-plasmon enhanced Raman spectroscopy (SERS) measurements of rhodamine 6G (R6G) and methyl violet

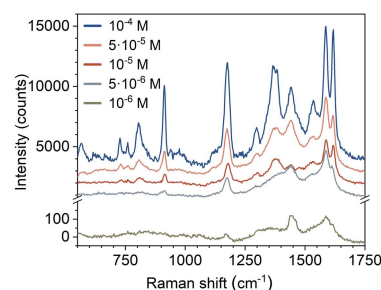


Fig. 3. Raman spectra of methyl violet adsorbed on CuPt NTs (dispersed on Au surface) from solutions of different concentrations (from 10^{-4} M to 10^{-6} M).

(MV) model compounds were carried out on random networks of the nanomaterials. The NWs of Cu and NTs of Cu-Pd or CuPt were drop cast from their corresponding dispersions in ethanol on pristine Si and Au coated chips (laser cut to $10\times 10\ \text{mm}^2$ size from the corresponding wafers). After drying, aqueous R6G or MV (both 10^{-4} M) were drop cast on the NW and NT coated chips and dried in air before analysis using Raman microscopy (ThermoFisher DXR2xi Raman Imaging Microscope) with the following parameters: $100\times$ objective, $\lambda = 532$ nm, laser power 2 mW, exposure time 0.02 s, number of scans $1000\times$, full range resolution grid, slit aperture $50\ \mu\text{m}$ and laser spot size $0.6\ \mu\text{m}$. (Representative SEM images of Cu NWs and Cu-Pd NTs on Si and Au surfaces are shown in Supplementary information, Fig. S1.)

III. RESULTS AND DISCUSSION

According to scanning electron microscopy (SEM) analysis, the hydrothermally grown Cu nanowires have a length between 10 and $50\ \mu\text{m}$, and an average diameter of ~ 50 nm. The nanowires are straight, and only some kinks may be seen in their structure due to crystal twinning (Fig. 1a). After the partial galvanic replacement with Pd or Pt, the overall nanowire structure changed for tubular due to the consumption of Cu and simultaneous deposition of Pd or Pt, respectively (Fig. 1b,c). In addition, the originally smooth surface of the nanowires turned rough and highly nanostructured. About half of the Cu atoms are replaced with either Pt or Pd as measured by energy dispersive X-ray spectroscopy (EDX).

The surfaces of the nanotubes are polycrystalline and have a grain size of 5 to 10 nm of the corresponding noble metal. Under these metal nanoparticles, the crystal structure of the nanotubes is different as suggested by high-resolution transmission electron microscopy (TEM) (Fig. 1d-f), EDX (Fig. 1g,h) and X-ray diffraction (XRD) (Fig. 1i). The Pt replaced Cu seems to be a bimetallic alloy rather than a mixture of individual Cu and Pt crystals hence the notation CuPt. On the other hand, for Cu replaced by Pd, we find X-ray reflections from separate crystals of the two metals in the corresponding pattern thus the material is noted as Cu-Pd.

Motivated by the promising SERS results we obtained lately using Cu nanowires to detect rhodamine 6G dye, it appeared to be a natural step to extend our research to its galvanic replaced Pt and Pd derivatives. The synthesized CuPt and Cu-Pd nanotubes as well as Cu nanowires were dispersed on

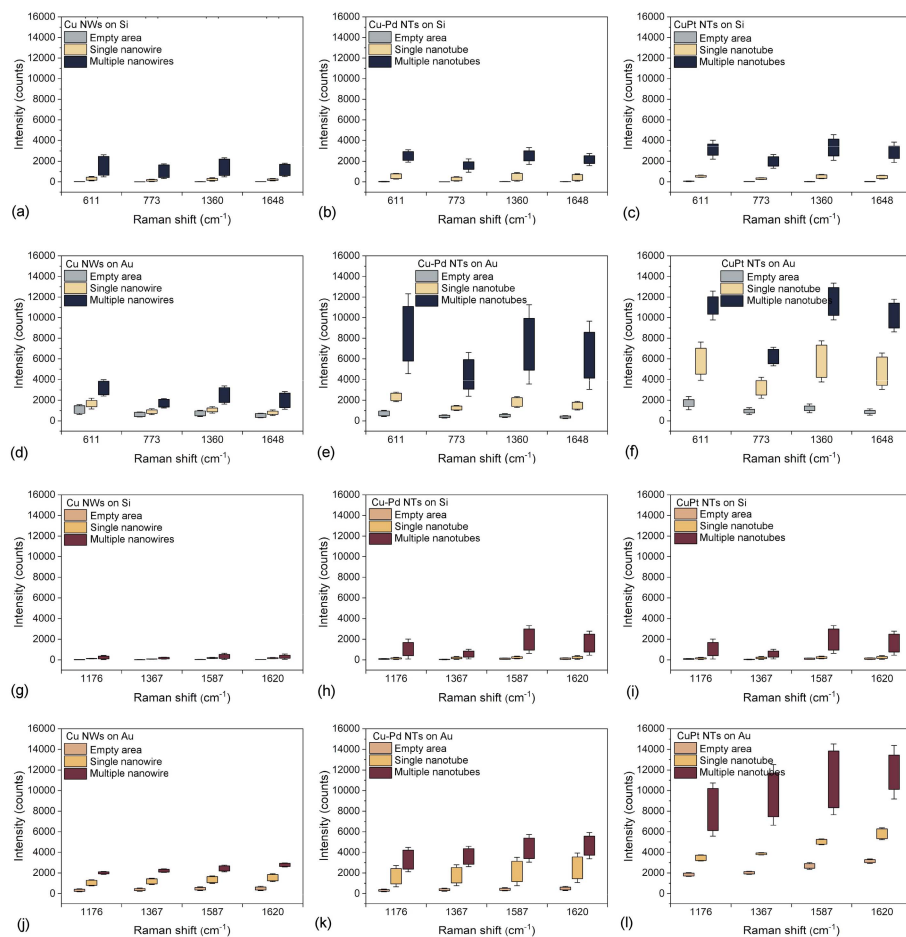


Fig. 4. Raman peak intensity statistics for (a-f) R6G and (g-l) MV on Cu NWs, Cu-Pd NTs and CuPt NTs dispersed on Si and Au surfaces. Each plot displays the intensities measured on networks of NWs or NTs as well as on individual particles. Empty area data correspond to peak intensities measured on locations in the proximity of NWs or NTs. The dyes were drop cast from 10^{-4} M aqueous solutions.

Si and Au surfaces, and then coated with solutions of rhodamine 6G (R6G) and methyl violet (MV) dyes. After drying, we collected Raman spectra of the dyes from several locations of each sample populated with large number of nanowires or nanotubes. For reference, we use Si and Au surfaces coated only with either of the dyes (Fig. 2). As expected, on Si surface (without any NWs or NTs), we can hardly observe the spectra of the dyes. On Au surface, we see the spectra of both dyes but the intensity of peaks is low and not resolved entirely. In the presence of Cu NWs, we find the spectra are well resolved but with moderate peak intensities. On the other hand, the intensity of peaks improves significantly on surfaces covered with CuPt or Cu-Pd NTs (Fig. 2). The overall amplification factors for both types of dyes as compared to the corresponding substrates are approximately $15\times$ (Cu), $30\times$ (Cu-Pd) and $60\times$ (CuPt) on Au and $120\times$ (Cu), $150\times$ (Cu-Pd) and $250\times$ (CuPt) on Si. The smaller substrate to NW (or NT) amplification on Au surface is due to the already ~ 10 -fold Raman intensities as compared to the Si surface.

The Raman intensities show proportionality to the concentration of the analytes (Fig. 3). The spectrum of MV can be resolved well for 10^{-5} M, and we observe reasonable peak intensities even at 10^{-6} M comparable to that obtained using Ag NWs with a detection limit of 10^{-7} M for MV [35].

It is important to point out here, that significant improvement (5 to 40-fold) of the Ag NWs enhanced spectrum of 4-mercaptobenzoic acid was shown on Ag-Au nanowires [36], and as reported very lately. Also, Ni templated Ag-Au nanocages [18] helped detection of R6G at 10^{-10} M limit of analyte concentration. Furthermore, as Ag nanoparticles grown on semiconducting NWs of Si [37] and GaN [38] showed even better detection limits (10^{-14} M and 10^{-12} M, respectively) for R6G, These results suggest that implementing Ag or Au on Cu NWs instead of Pd or Pt; or combination with semiconducting nanoparticles/surfaces could probably provide better spectral amplifications and thus shall be assessed in detail in the future.

To demonstrate the robustness of the measurements, we collect spectra at several locations of NW or NT coated surfaces and calculate the intensity statistics for the characteristic Raman peaks (Fig. 4). The results show some minor scattering of the peak intensity data measured in different locations; however, the typical amplification factors show a consistent trend. It is worth pointing out, that even individual NWs or NTs induce reasonable Raman amplification. Furthermore, it is also interesting to note, that the Raman peak intensities measured on Au surfaces in the proximity of NWs or NTs (blank areas) show rather high values for both types of dyes. We do not observe such high intensities on Au wafers without

NWs or NTs, and we do not see either a similar effect on blank areas of Si wafers otherwise coated with NWs or NTs. Such a phenomenon fits well the “borrowed SERS activity” model.

IV. CONCLUSION

In closing, we studied surface-plasmon enhanced Raman spectroscopy using Cu-Pd bimetal and CuPt alloy nanotubes synthesized by a partial galvanic exchange of Cu nanowires. Significant amplification of the Raman spectra of rhodamine 6G and methyl violet was demonstrated on Si or Au surfaces with a detection limit of 10^{-6} M. The improved Raman intensity enhancement of nanostructured CuPt and Cu-Pd nanotubes in reference to smooth Cu nanowires suggests that their corrugated surfaces facilitate local field enhancement (shape effect) and the presence of Pd and Pt nanoparticles on the surface extend the range of increased electric field adjacent to the particles (borrowed SERS activity).

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Eva Bozo was born in Hungary in 1993. She received the B.Sc. degree in chemistry from the University of Szeged in 2018. She was a Research Assistant with the Microelectronics Research Unit, University of Oulu, Finland. Her research mainly focuses on synthesis and characterization of nanomaterials.

Aron Dombovari was born in Hungary in 1984. He received the degree in chemistry and physics from the University of Szeged, Hungary, in 2009. He performed his internship at the University of Cagliari, Italy, and the University of Oulu, Finland, from 2008 to 2009. After his studies, he spent almost 2 years at a spin-off company as a Chemist and a Product Developer. From 2011 to 2018, he was a Research Assistant with the Microelectronics Research Unit, University of Oulu, Finland. Since 2018, he has been a Senior Research Engineer with the Silicon Austria Labs GmbH, where he works on advanced packaging solutions for sensors, ICs, MEMS, and integration for smart systems. His research has been focused on the synthesis of various nanomaterials, including their chemical, structural and electrical characterization for electronic, sensor, energy storage, and other applications.

Melinda Mohl received the Ph.D. degree in the synthesis and application of one-dimensional metal nanostructures from the University of Szeged, Hungary, in 2011. She performed research visits at the University of Namur, Belgium, and at Rice University, USA. From 2011 to 2018, she was a Post-Doctoral Researcher and a Project Manager with the Microelectronics Research Unit, University of Oulu, Finland, where she worked on the development of various nanomaterials for catalytic, sensing, and energy storage applications. She is currently a Senior Scientist with the Sensor System Division, Silicon Austria Labs GmbH. Her research interest is focused on printed electronic sensors and on the development of quality control systems for inorganic solar cell production.

Vesa K. Virtanen received the M.H.Sc. degree from the Medical and Wellness Technology Program, University of Oulu, in 2018. He is currently pursuing the Ph.D. degree with the Professor Simo Saarakkala's Diagnosis of Osteoarthritis Group (DIOS), Research Unit of Medical Imaging, Physics and Technology (MIPT), University of Oulu. His thesis is focused on the detection of articular cartilage degeneration with infrared spectroscopy and atomic force microscopy.

Simo Saarakkala was born in Finland in 1979. He received the M.Sc. and Ph.D. degrees in medical physics from the University of Kuopio, Finland, in 2005 and 2007, respectively. He received the Docent of medical physics in 2009 and biomedical physics in 2010 from the University of Oulu, Finland, where he is currently a Professor of Biomedical Engineering since 2018 and also the Scientific Director of the Infotech Oulu Focus Institute. He has been a Visiting Scientist with The Hong Kong Polytechnic University, Hong Kong, and The University of Auckland, New Zealand. He has published more than 150 peer-reviewed scientific articles. His research is focused on diagnostics and imaging of osteoarthritis at different levels, i.e., from tissue and cell level up to the clinical level, using various biomedical and medical modalities. He serves as an Editorial Board Member of 5 scientific journals. He acted as a reviewer for more than 25 international scientific journals, and is regularly reviewing international grant applications.

Robert Vajtai received the bachelor's and Ph.D. degrees in physics and the Ph.D. degree in solid-state physics from the University of Szeged (formerly Jozsef Attila University), Hungary, in 1986, 1991, and 1997, respectively. From 1987 to 2002, he was with the Faculty of the Department of Experimental Physics. He was a Research Fellow with the Ångström Laboratory, Swedish Institute, Uppsala, from 1998 to 1999; as an Eötvös Fellow with EPFL, Lausanne, Switzerland, from 1995 to 1996, and at the Max Planck Institute, Göttingen, Germany, in 1993. He spent eight years at the Rensselaer Polytechnic Institute. He was the Laboratory Manager of the Nanoparticle Generation and the Carbon Nanotechnology Laboratories, Rensselaer Nanotechnology Center. Since 2008, he has been a member of the Research Faculty with Rice University. He is currently a Research Professor with the Materials Science and NanoEngineering Department, Rice University.

His research interests include synthesis processing, characterization of nanometals and nanosized oxides, and different forms of nanocarbon: carbon nanotubes, graphene and macroscopic systems designed and built from these building blocks, especially the application of nanomaterials for building energy storage devices, multifunctional parts of vehicles, sensors and thermal management systems. In these topics, he has 23,000 citations for 365 papers, and he edited the *Springer Handbook of Nanomaterials*.

Krisztian Kordas was born in Hungary in 1975. He received the M.Sc. degree in physics and chemistry from the University of Szeged, Hungary, in 1998, and the Dr.Tech. degree in microelectronics from the University of Oulu, Finland, in 2002. He was a Research Fellow with the Academy of Finland from 2004 to 2009. He has been a Docent of Nanotechnology since 2005. Previously, he has been a Visiting Lecturer at the Rice University, Houston, US (2017), Research Professor (2012–2016) and Chief Assistant (2009–2012) at the University of Oulu; and Assistant Professor at the Department of Chemistry, Umeå University, Sweden (2011–2012). He is currently a Professor of Micro- and Nanoelectronic Materials and Components for ICT applications with the University of Oulu in 2016.

He authored more than 170 refereed scientific papers and 7 book chapters that received more than 5200 citations. He has been supervising 15 Ph.D. students and coordinating/participating in more than 20 national and international research projects. His research focuses on 1D and 2D materials, porous and hierarchical nanostructures, and their integration in devices for micro and nanoelectronics, sensors, photocatalysis and energy applications.