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Editorial

Machine Learning Methods and Sustainable Development: Metal Oxides and Multilayer Metal Oxides

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1. Introduction

The development of nanotechnologies and new methods of machine learning are responsible for the significant attention and demand for metal oxides and multilayer metal-oxide nanostructures. Metal oxides are a class of materials that are considered extremely important from both a scientific and a technological viewpoint. The physicochemical properties of metal oxides are governed by their growth process mechanisms, both chemical and physical.

The control of film properties, the process of film nanostructuring, and the use of different oxides in composites and multilayer systems are key parameters for tailoring materials' properties to selected applications. Metal oxides can become strategic critical resources because they are implemented in many high-tech products, such as computers, batteries for electric vehicles, magnets, scintillators, and aviation and medical devices. The secured supply of metal oxides is crucial to the continued production and exportation of technologies. Moreover, the specific properties of some metal oxides make them essential and difficult to substitute in several demanding applications.

The modern researchers aim to gather recent advances in the fields of machine learning methods; process synthesis; and the sustainable development of metal oxides, multilayer metal oxides, and metal oxide nanostructures for the global industry. These challenges are not only related to technology, but also environmental, societal, economic, and financial tools, as well as process management.

2. A Short Review of the Contributions in This Issue

As far as energy efficiency is concerned, one article addresses appropriate integrated technologies.

Petrucci et al. [1] show that the development of mixed-oxide electrodes is being intensively investigated to reduce the high cost associated with the use of noble metals and to obtain versatile and long-lasting devices. To evaluate their use for charge storage or anodic oxidation, in this paper, thin-film electrodes coated with ruthenium (RuO_x) and copper oxide (CuO_x) are fabricated by thermal decomposition of organic solutions containing the precursors by drop-casting on titanium (Ti) foils. The coating consisted of four layers of metal oxide. To investigate the effect of copper (Cu) on electrochemical performances, different approaches are adopted by varying the ratios of precursors' concentration, including a RuO_x interlayer. A comparison with samples obtained by only RuO_x has also been performed. The electrodes are characterized using scanning electron microscopy (SEM), cyclic (CV) and linear sweep (LSV) voltammetry, electrochemical impedance spectroscopy (EIS), and corrosion tests. The addition of Cu enhances the capacitive response of the materials and promotes the reversibility of electron transfer. The coatings obtained by the highest

Ru:Cu ratio (95:5) exhibit a more uniform surface distribution and increased corrosion resistance. The interlayer is beneficial to further reduce the corrosion susceptibility and to promote the oxygen evolution, but is detrimental to the charge storage power. The results suggest the possibility of enhancing the electrochemical performance of expensive RuO_x through a combination with a low amount of cheaper and more abundant CuO_x.

Ryu et al. [2] characterize resistive switching and neuromorphic simulation of Pt/HfO_2/TaN stack as an artificial synaptic device. A stable bipolar resistive switching operation is performed by repetitive DC sweep cycles. Furthermore, endurance (DC 100 cycles) and retention (5000 s) are demonstrated for reliable resistive operation. Low-resistance and high-resistance states follow the Ohmic conduction and Poole–Frenkel emission, respectively, which is verified through the fitting process. For practical operation, the set and reset processes are performed through pulses. Further, potentiation and depression are demonstrated for neuromorphic application. Finally, neuromorphic system simulation is performed through a neural network for pattern recognition accuracy of the Fashion-Modified National Institute of Standards and Technology dataset.

Ryu and Kim [3] study the threshold switching and short-term memory plasticity of a Pt/HfO_2/TaO_x/TiN resistive memory device for a neuromorphic system. First, we verify the thickness and elemental characterization of the device stack through transmission electron microscopy (TEM) and an energy-dispersive X-ray spectroscopy (EDS) line scan. Volatile resistive switching with low compliance current is observed under the DC sweep in a positive bias. Uniform cell-to-cell and cycle-to-cycle DC I-V curves are achieved by means of a repetitive sweep. The mechanism of volatile switching is explained by the temporal generation of traps. Authors conduct a neuromorphic simulation to calculate the pattern recognition accuracy. Results can be applicable to short-term memory applications, such as temporal learning in a neuromorphic system.

Ryu and Kim [4] present conductance modulation in a Pt/TiO_2/$HfAlO_x$/TiN resistive memory device in the compliance region for neuromorphic system applications. First, the chemical and material characteristics of the atomic-layer-deposited films were verified by X-ray photoelectron spectroscopy depth profiling. The low-resistance state was effectively controlled by the compliance current, and the high-resistance state was adjusted by the reset stop voltage. Stable endurance and retention in bipolar resistive switching were achieved. When a compliance current of 1 mA was imposed, only gradual switching was observed in the reset process. Self-compliance was used after an abrupt set transition to achieve a gradual set process. Finally, 10 cycles of long-term potentiation and depression were obtained in the compliance current region for neuromorphic system applications.

Ryu and Kim [5] examine the irregular resistive switching behaviors of a complementary metal-oxide semiconductor (CMOS)-compatible Cu/Al_2O_3/Si resistor device. X-ray photoelectron spectroscopy (XPS) analysis confirmed the chemical and material compositions of a Al_2O_3 thin film layer and Si substrate. Bipolar resistive switching occurred in a more stable manner than the unipolar resistive switching in the device did. Five cells were verified over 50 endurance cycles in terms of bipolar resistive switching, and a good retention was confirmed for 10,000 s in the high-resistance state (HRS) and the low-resistance state (LRS). Both the high reset current (~10 mA) and low reset current (<100 μA) coexisted in the bipolar resistive switching. The authors investigated non-ideal resistive switching behaviors, such as negative-set and current overshoot, which could lead to resistive switching failure.

Kim et al. [6] demonstrate the synaptic properties of the alloy-type resistive random-access memory (RRAM). They fabricated the $HfAlO_x$-based RRAM for a synaptic device in a neuromorphic system. The deposition of the $HfAlO_x$ film on the silicon substrate was verified by X-ray photoelectron spectroscopy (XPS) analysis. It was found that both abrupt and gradual resistive switching could be implemented, depending on the reset stop voltage. In the reset process, the current gradually decreased at weak voltage, and at strong voltage, it tended to decrease rapidly by Joule heating. The type of switching determined by the first reset process was subsequently demonstrated to be stable switching by successive set and reset processes. A gradual switching type has a much smaller on–off window than abrupt switching. In addition, retention maintained stability up to 2000 s in both switching cases. Next, the multiple current states were tested in the gradual switching case by identical pulses. Finally, the potentiation and depression of the Cu/$HfAlO_x$/Si device as a synapse in an artificial neural network was demonstrated and confirmed that gradual resistive switching was suitable for artificial synapses using neuromorphic system simulation.

In [7], Ryu and Kim investigated the resistive switching and synaptic behaviors of a TiO_2/Al_2O_3 bilayer device. The deposition of Pt/Ti/TiO_2/Al_2O_3/TiN stack was confirmed by transmission electron microscopy (TEM) and energy X-ray dispersive spectroscopy (EDS). The initial state before the forming process followed Fowler–Nordheim (FN) tunneling. A strong electric field was applied to Al_2O_3 with a large energy bandgap for FN tunneling, which was confirmed by the I–V fitting process. Bipolar resistive switching was conducted by the set process in a positive bias and the reset process in a negative bias. High-resistance state (HRS) followed the trap-assisted tunneling (TAT) model, while low-resistance state (LRS) followed the Ohmic conduction model. Set and reset operations were verified by pulse. Moreover, potentiation and depression in the biological synapse were verified by repetitive set pulses and reset pulses.

In Shaikh et al.'s paper [8], a novel Co_3O_4@TiO_2 composite was synthesized by applying two-step methods. ZIF-67 was synthesized and used as a template for the synthesis of the composite. The composite was designed by using the effective photocatalytic properties of Co_3O_4 and TiO_2. The resulting synthesized composite was supposed to offer superior properties compared to their counterparts. The synthesized Co_3O_4@TiO_2 composite was characterized by powder X-ray diffraction (PXRD), Brunauer–Emmet–Teller (BET), atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Electrochemical water splitting, including hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) studies on the Co_3O_4@TiO_2 composite, was evaluated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) analysis in a 2M aqueous KOH electrolyte. The current generation stability of these samples was deliberated by chronoamperometric measurements. It was observed, from LSV results at a 1 mV/s scan rate, that metal oxides incorporated on other metal oxides have a higher current density and lower onset potential as compared to pure metal oxides. From the obtained results, it has become evident that synthesized studies on the Co_3O_4@TiO_2 composite possess significant potential for electrochemical water splitting with the lowest onset potential, highest current density, better OER, and HER activity.

Danish et al. [9] found that, along with industrialization and rapid urbanization, environmental remediation is globally a perpetual concept to deliver a sustainable environment. Various organic and inorganic wastes from industries and domestic homes are released into water systems. These wastes carry contaminants with detrimental effects on the environment. Consequently, there is an urgent need for an appropriate wastewater treatment technology for the effective decontamination of our water systems. One promising approach is employing nanoparticles of metal oxides as photocatalysts for the degradation of these water pollutants. Transition metal oxides and their composites exhibit excellent photocatalytic activities and show favorable characteristics, including non-toxicity and stability, which also make them useful in a wide range of applications.

Danish et al. [10] found that decarbonization strategies have become an important factor in industrial expansion, along with the invention of new catalytic methods for carrying out non-thermal reactions, energy storage methods and environmental remediation through the removal or breakdown of harmful chemicals released during manufacturing processes. Moreover, the practical applicability of these materials is also discussed, as well as the transition of production to an industrial scale.

In [11], Danish et al. review the fabrication of silver oxide nanoparticles (Ag_2O-NPs) via plant-mediated and microbe-mediated green synthesis, describing the green synthesis of Ag_2O-NPs which can employ extracts of different plants and microbial sources. The performances of the biosynthesized Ag_2O-NPs are also reviewed, highlighting their potential use in photocatalysis and biomedical applications. The green chemistry approach for the preparation of nanoparticles is becoming more attractive as it uses non-toxic chemicals and reagents. It also offers a cost-effective synthesis process given the readily available plant sources and microbe as redox mediators used to convert metallic cations to metal or metal-oxide nanoparticles. The extracts of these plants and microbe sources contain phytochemicals and metabolites in variable quantities, which serve as redox mediators and capping agents that stabilize the biosynthesized nanoparticles. The present article reviews the recent studies on the fabrication of silver oxide nanoparticles (Ag_2O-NPs) via plant-mediated and microbe-mediated green synthesis, which offers a concise discussion on the green preparation of Ag_2O-NPs by employing extracts of different plants and microbial sources. The performances of the biosynthesized Ag_2O-NPs are also reviewed, thus highlighting their potential use in photocatalysis and biomedical applications.

The present article discusses the structural features and photocatalytic applications of a variety of metal-oxide-based materials. The practical and economical applicability of these materials is also discussed by exploring the footprint analysis as well [12–14].

3. Conclusions

This Special Issue contains miscellaneous papers on the synthesis and application of metal oxides, metal oxide nanoparticles, and multilayer systems. Some studies focus on metal oxides such as TiO_2, ZnO, WO_3, CuO, and Cu_2O, which are the most common and recognized to be cost-effective, stable, efficient, and above all, environmentally friendly for a sustainable approach for environmental remediation and energy applications. A review reports on the green synthesis of silver oxide nanoparticles for photocalaysis and biomedical application. Another work focuses on synthesis and characterization of RuO_x and CuO_x for potential applications in electrochemical energy storage systems. The Special Issue also reports on multilayer systems such as $Pt/HfO_2/TaN$, $Pt/HfO_2/TaO_x/TiN$, $Pt/TiO_2/HfAlO_x/TiN$, etc., for application in resistive switching devices and neuromorphic systems.

As Guest Editors of this Special Issue, we hope that the studies reported here will be useful to researchers in order to advance their respective research fields.

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References

1. Petrucci, E.; Porcelli, F.; Orsini, M.; De Santis, S.; Sotgiu, G. Mixed oxide electrodes based on ruthenium and copper: Electrochemical properties as a function of the composition and method of manufacture. *Metals* **2022**, *12*, 316. [CrossRef]
2. Ryu, H.; Jung, H.; Lee, K.; Kim, S. Multi-level resistive switching of $Pt/HfO_2/TaN$ memory device. *Metals* **2021**, *11*, 1885. [CrossRef]
3. Ryu, H.; Kim, S. Volatile resistive switching characteristics of $Pt/HfO_2/TaO_x/TiN$ short-term memory device. *Metals* **2021**, *11*, 1207. [CrossRef]
4. Ryu, H.; Kim, S. Gradually modified conductance in the self-compliance region of an atomic-layer-deposited $Pt/TiO_2/HfAlO_x/TiN$ rram device. *Metals* **2021**, *11*, 1199. [CrossRef]
5. Ryu, H.; Kim, S. Irregular resistive switching behaviors of Al_2O_3-based resistor with Cu electrode. *Metals* **2021**, *11*, 653. [CrossRef]
6. Kim, S.; Kwon, O.; Ryu, H.; Kim, S. Improved synaptic device properties of $HfAlO_x$ dielectric on highly doped silicon substrate by partial reset process. *Metals* **2021**, *11*, 772. [CrossRef]
7. Ryu, H.; Kim, S. Gradually tunable conductance in TiO_2/Al_2O_3 bilayer resistors for synaptic device. *Metals* **2021**, *11*, 440. [CrossRef]
8. Shaikh, Z.A.; Laghari, A.A.; Litvishko, O.; Litvishko, V.; Kalmykova, T.; Meynkhard, A. Liquid-phase deposition synthesis of ZIF-67-derived synthesis of Co_3O_4@TiO_2 composite for efficient electrochemical water splitting. *Metals* **2021**, *11*, 420. [CrossRef]
9. Danish, M.S.S.; Estrella, L.L.; Alemaida, I.M.A.; Lisin, A.; Moiseev, N.; Ahmadi, M.; Nazari, M.; Wali, M.; Zaheb, H.; Senjyu, T. Photocatalytic applications of metal oxides for sustainable environmental remediation. *Metals* **2021**, *11*, 80. [CrossRef]

10. Danish, M.S.S.; Bhattacharya, A.; Stepanova, D.; Mikhaylov, A.; Grilli, M.L.; Khosravy, M.; Senjyu, T. A systematic review of metal oxide applications for energy and environmental sustainability. *Metals* **2020**, *10*, 1604. [CrossRef]
11. Danish, M.S.S.; Estrella-Pajulas, L.L.; Alemaida, I.M.A.; Grilli, M.L.; Mikhaylov, A.; Senjyu, T. Green synthesis of silver oxide nanoparticles for photocatalytic environmental remediation and biomedical applications. *Metals* **2022**, *12*, 769. [CrossRef]
12. Kranina, E.I. China on the way to achieving carbon neutrality. *Financ. J.* **2021**, *5*, 51–61. [CrossRef]
13. Sannikova, L. Legal Framework for Green Finance in the EU and Russia. *Financ. J.* **2021**, *5*, 29–43. [CrossRef]
14. Zhihua, F.; Yu, C. Promoting Green Development in China's New Development Stage Through Tax Reform. *Financ. J.* **2021**, *5*, 44–50. [CrossRef]