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Transparent Inorganic Metal Oxide Solar Cells in Chemistry Class

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Abstract

Due to the increasing challenges related to climate crisis and energy supply, the development of renewable energy sources is a major field of research and important for sustainable developments. In this context, solar cells play an important role and are already widely applied based on silicon. Nevertheless, silicon solar cells exhibit disadvantages such as a high energy demand in production and the requirement of highly pure raw material [1]. For these reasons, the working principle of silicon solar cells can only be discussed theoretically in chemistry classes, but their production under school conditions is not possible. Because of the disadvantages related to silicon solar cells, alternative solar cells like Grätzel cells [2] and perovskite solar cells [3] have already been subject in scientific research and can - in contrast to silicon solar cells - be easily built within a school lesson [4-5]. Furthermore, pure inorganic solar cells based on combined thin films of p- and n-semiconducting oxides of titanium and nickel have come into interest of researchers [6]. Being optically transparent and durable, their future integration as a photovoltaic active layer in windows is discussed, deposited by physical techniques like sputtering. For educational purposes, we developed a process to replace sputtering by facile sol-gel-syntheses which can be easily implemented in schools: After preparing a particle dispersion, thin films of two semiconducting metal oxides creating a heterojunction are applied on conductively coated glasses (FTO) with a self-built spin-coater assembled using low-cost components. In our contribution, we present experiments as well as teaching and learning materials covering topics from chemistry (sol-gel-synthesis) and physics (semiconductors) for upper secondary classes.

Keywords: *solar cells, sol-gel-chemistry, renewable energies, education for sustainable development, curricular innovations*

1. Introduction

An annual world energy consumption of approx. 630 EJ [7] and the challenges of climate crisis underline the need of renewable energy sources. Regarding the energy amount, most renewable energy can be obtained from solar radiation on earth, which is approx. 725000 EJ [7] per year. Hence, solar energy can make an important contribution to the reduction of fossil energies and carbon dioxide emission. The large amount of space occupied by conventional solar cells and the high energy requirements during production necessitate research into new types of solar cells which can be used on areas that previously seemed unsuitable for solar cells. In this context, UV-light-harvesting transparent solar cells which have the potential to be applied as windows have been investigated [6]. Large cities have more window areas than roof areas, which makes the use of solar cells in windows appear interesting. The topic offers points of reference for education for sustainable development (ESD), and the consideration of real-life feasibility also has the potential to be used for discussion scenarios in lessons.

Transparent solar cells can be fabricated from *p*- and *n*-semiconducting metal oxides, for example titanium(IV)-oxide and nickel(II)-oxide. Creating a *pn*-heterojunction between two intrinsically doped semiconductive metal oxides, these solar cells are similar to silicon solar cells which consist of *p*- and *n*-doped silicon and can serve as a illustrative model. For school purposes, the technique of sputtering applied in [6] is replaced by sol-gel-process. After describing basic principles of metal oxide solar cells and sol-gel-chemistry, the fabrication and investigation of a solar cell made of titanium(IV)-oxide and nickel(II)-oxide as well as educational perspectives are presented in this paper.

2. Theoretical Background

2.1 Working Principle of a Metal Oxide Solar Cell (MOSC)

Conventional silicon solar cells generally contain silicon doped with heteroatoms like boron (3 valence electrons, *p*-type semiconductor) or phosphorus (5 valence electrons, *n*-type semiconductor). In MOSCs, two different metal oxides are combined, e.g., titanium(IV)-oxide and nickel(II)-oxide. Titanium(IV)-oxide (TiO_2) mainly contains titanium atoms with the oxidation state of +IV, but is a non-stochiometric oxide with small amounts of titanium atoms having the oxidation state of +III. Taking this fact into account, the chemical formula of TiO_2 can also be written as TiO_{2-x}.[8] The resulting excess of electrons leads to *n*-doping. Nickel(II)-oxide (NiO) also contains nickel atoms with an oxidation state of +III leading to an intrinsic *p*-doping (NiO_x).

Due to the combination of different *n*-doped and a *p*-doped semiconductors, a depletion layer is formed (*pn*-heterojunction). UV irradiation with enough energy is able to overcome the band gap and causes the formation of electron-hole-pairs (excitons). Electric current flows if the electric circuit is closed (figure 1) [6].

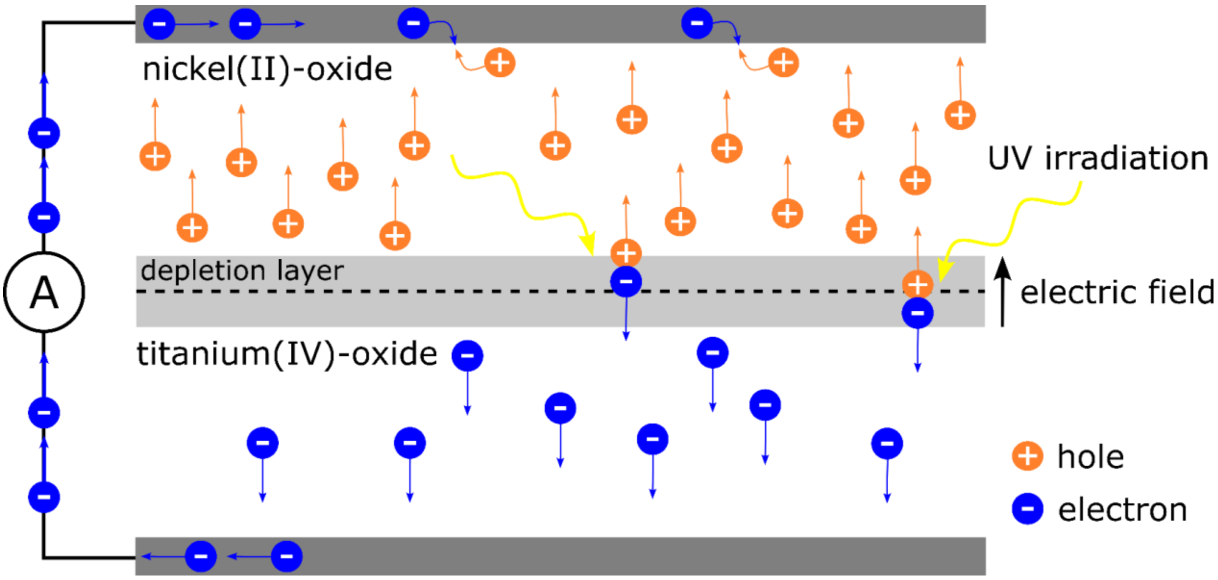

Figure 1: Working principle of a MOSC with titanium(IV)-oxide as *n*-type semiconductor and nickel(II)-oxide as *p*-type semiconductor.

2.2 Sol-Gel-Process

The sol-gel-process is a common method to synthesize thin films of metal oxides. The term “sol” refers to a dispersion of particles formed by small precursor molecules. In many cases, the sol is prepared by the hydrolysis of a metal alkoxide forming hydroxy groups. In the following, the precursor molecules condense forming dispersed sol particles [10]. To increase wettability and stability of the sol, additives such as ethylene glycol or 2-aminoethanol are sometimes added. Figure 2a shows the sol-gel-process using the example of titanium(IV)-oxide. After preparation, the sol is applied on a FTO glass. Various coating techniques can be used for this purpose. In spin coating, the rotation of a plate distributes the sol evenly and forms a gel layer which becomes solid during subsequent temperature treatment (figure 2b). In this paper, we use spin coaters assembled from PC fans and 3D-printed covers (figure 2c) [11].

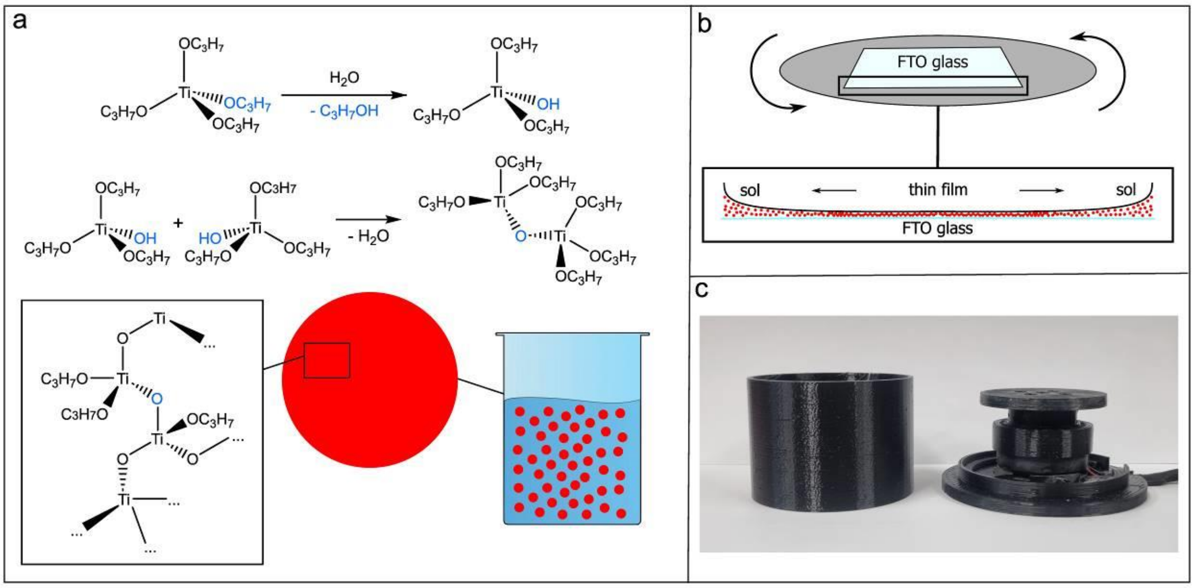

Figure 2: Elements of the sol-gel-process forming titanium(IV)-oxide (a: hydrolysis of the precursor titanium(IV)-isopropoxide, condensation and formation of sol particles, b: spin-coating technique; c: low-cost spin coater assembled from a PC fan with 3D-printed cover).

3. Experimental Section

3.1 Preparation of Titanium and Nickel Oxides by Sol-Gel-Technique

Equipment: snap-cap vial, beaker (25 mL), Eppendorf pipette, pipette (10 mL), spatula, heating plate (ceramic, temperature range up to 500 °C), magnetic stirrer, double-sided adhesive tape, adhesive tape, FTO glass (e.g., Sigma Aldrich), spin-coater (see figure 2c), multimeter

Chemicals: water, ethanol (anhydrous, GHS 02/07), propan-2-ol (GHS 02/07), hydrochloric acid solution ($w = 37\%$, GHS 05/07), 2-aminoethanol (GHS 05/07), ethylene glycol (GHS 07/08), titanium(IV)-isopropoxide (GHS 02/07), nickel(II)-acetate tetrahydrate (GHS 07/08/09)

Safety Instruction: Work with nickel salts should be conducted under a fume hood wearing nitrile gloves.

Procedure: The **titanium(IV)-oxide sol** is prepared in a snap-cap vial. Anhydrous ethanol (250 µl) is mixed with hydrochloric acid solution (25 µl, $c = 0.1$ mol/L, ethanolic). Subsequently, titanium(IV)-isopropoxide (25 µl) is added, and the solution is stirred to mix the sol. The sol has to be used within 10 min.

The **nickel(II)-oxide sol** is prepared in a beaker (25 mL). A mixture of propan-2-ol (10 mL) and 2-aminoethanol (0.3 mL) is stirred with nickel(II)-acetate tetrahydrate (1.07 g). Afterwards, ethylene glycol (0.2 mL) is added. The sol is usable after a resting period of 24 h and is storable for up to 1 month.

The metal oxide thin films are prepared according to the following steps:

1. A FTO-glass (3 cm x 3.5 cm) is cleaned with deionized water and ethanol. After drying, the conducting side is determined using a multimeter.
2. The FTO-glass is placed on the benchtop with the conductive side facing up. About 20% of the conducting surface is covered with adhesive tape. The titanium(IV)-oxide sol (100 µl) is applied on the surface and gently distributed evenly across the surface to receive a homogenous film.
3. The FTO-glass is attached in the middle of the spin-coater with double-sided adhesive tape and the spin-coating process is started (approx. 25 s)
4. After spin-coating, the FTO-glass is carefully removed from the spin-coater, and all adhesive tapes are removed. Subsequently, it is placed on the heating plate and heated at 500 °C for 20 min.

5. After cooling, the process is repeated with the nickel(II)-oxide sol, starting from step 2. The coated FTO glass is needed for the fabrication of the solar cell in 3.2.

Results: After applying the titanium(IV)-oxide sol and tempering on the heating plate, a thin film can be observed which appears slightly colored in the backlight (figure 3). This observation is repeated after the second layer has been applied.

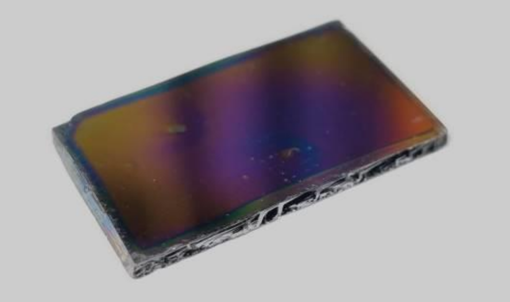

Figure 3: Interference effects of titanium(IV)-oxide layer (Note: To improve visibility, the titanium(IV)-layer was deposited on a silicon wafer).

Interpretation: Due to hydrolysis and condensation reactions and subsequent tempering, thin films of titanium(IV)-oxide and nickel(II)-oxide are formed. Interference effects on the thin layers are responsible for the color impression.

Characterization of layers: To investigate layer composition, small pieces of a silicon wafer were coated with the titanium(IV)-oxide sol and the nickel(II)-oxide sol. After spin-coating, they were tempered at 500 °C for 20 min.
Subsequently, X-ray diffraction (XRD) measurement was performed using a Bruker D8 Advance XRD with CuK$_\alpha$ radiation (λ = 154 pm). Figure 4 shows XRD reflexes compared to literature [12-13].
According to [14], thin films prepared by sol-gel-process have a thickness of several hundred nanometers, which we were able to confirm for titanium dioxide by means of SEM. In addition, the observed interference effects can be explained by a layer thickness in this range.

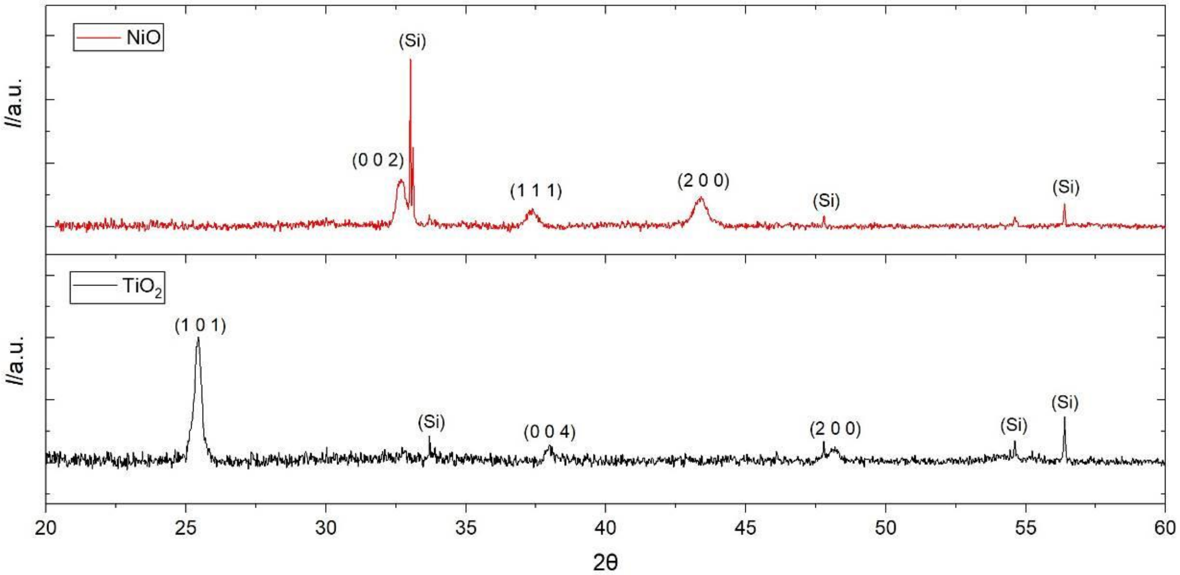

Figure 4: Characterization of metal oxide layers (XRD spectra of of titanium(IV)-oxide layer and nickel(II)-oxide layer).

3.2 Fabrication and Investigation of a Transparent Solar Cell

Equipment: coated FTO glass (see 3.1), FTO glass (approx. 3 cm x 3.5 cm), binder clips, transparent adhesive tape, UV LED (λ = 365 nm, e.g., LG Innotek UV SM-LED 3535), cables, crocodile clamps multimeter

Chemicals: water, ethanol (GHS 02/07)

Safety Instruction: Take care not to look into the UV LED. If necessary, special UV safety goggles can be worn.

Procedure: Another FTO-glass (3 cm x 3.5 cm) is cleaned with deionized water and ethanol. After drying, the conducting side is determined using a multimeter. The conductive side is placed on top of the coated FTO-glass and secured by wrapping with transparent adhesive tape. Binder clips are added to stabilize the solar cell. The solar cell is connected to a multimeter using cables and crocodile clamps and illuminated with the UV LED (distance approx. 1 cm). Open-circuit voltage (U_{OC}) and short-circuit current (I_{SC}) are measured, respectively. Figure 5 shows the assembly of the MOSC and the experimental setup.

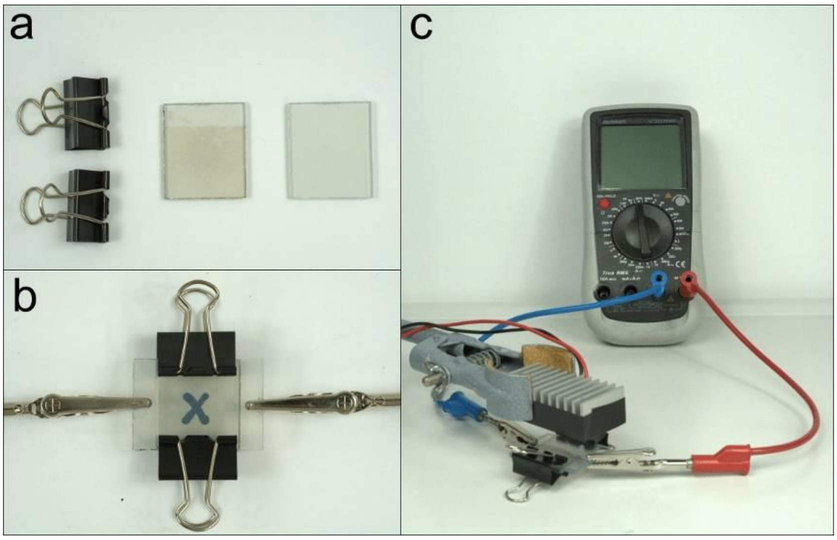

Figure 5: Assembly of the MOSC and experimental setup (a: parts of the solar cell [binder clips, coated FTO glass, uncoated FTO glass, from left to right], b: transparency of the solar cell, c: experimental setup).

Results: When illuminating the cell with the UV LED, an increase of open-circuit voltage U_{OC} and short-circuit current I_{SC} can be measured. The measured short-circuit current I_{SC} is approx. 20 µA and the open-circuit voltage U_{OC} is approx. 490 mV.

Interpretation: The photons emitted by the UV LED have enough energy to induce a photovoltaic effect in the solar cell, i.e., the formation of excitons. Due to the electric circuit closed in this setup, an electric current is able to flow.

4. Educational Perspectives

4.1 General Aspects

The topic of MOSCs offers various opportunities to connect with K-12 chemistry and physics. In this context, metal oxide solar cells represent a new solar cell type accessible at schools and line up next to perovskite solar cells and Grätzel cells which have already been didactically developed.[2][3] One advantage of metal oxide solar cells is their similarity to conventional silicon solar cells having too large demands of energy and purity of materials for an assembly in a simple hands-on experiment. Hence, they only serve as a didactic black box. Characteristics of semiconductors and the general working principle of solar cells can be repeated and deepened using the example of metal oxide solar cells. As a possible link to chemical aspects, the topic of oxidation numbers taught in schools can be applied here because it is useful to explain how the metal oxides serve as *p*- and *n*-semiconductors. The similarities to *n*- and *p*-doped silicon described above then become clear. Possible changes of band gaps due to the formation of a heterojunction are disregarded, which can be interpreted as a educational reduction. The transparency of the solar cell can serve as proof for the students that only light in the UV range is absorbed.

As an outlook on further research, the application of other metal oxides for MOSCs is a possible topic. For example, zinc(II)-oxide is a *n*-type semiconductor and copper(II)-oxide a *p*-type semiconductor. In our tests, MOSCs with these metal oxides delivered a lower output in comparison to MOSCs with titanium(IV)-oxide and nickel(II)-oxide. In addition, it is also possible to coat two metal oxides onto several FTO glasses. In this scenario, students test different semiconductor combinations and experience that only a solar cell consisting of *p*-type and *n*-type semiconductor is functional. Otherwise, neither photovoltage nor photocurrent can be measured. In addition, a possible combination of e.g., titanium(IV)-oxide and copper(II)-oxide has the potential to minimize safety risks.

To enhance the performance of the MOSC described in 3.2, carbon powder can be distributed on the coated FTO glass before placing the second FTO glass. This significantly improves the performance of the cell, but leads to a loss of optical transparency. Due to its increased power, this solar cell is able to charge a small capacitor (e.g., $C = 0.1$ F, $t = 30$ min) that can be used to operate a wing motor for a few seconds.

Furthermore, MOSCs as a new type of solar cells can make an important contribution to education for sustainable development (ESD), which is subject of the following section.

4.2 ESD Aspects

ESD brings sustainability aspects into chemistry education and offers various opportunities to debate on transparent MOSCs. According to [15], ESD consists of three perspectives: economic, ecological and social perspective. Students assess MOSCs as a new technology and evaluate whether the application of MOSCs as photovoltaic windows makes sense in terms of economy, ecology and social aspects. One possible point is that transparent solar cells only absorb light in the UV range. Hence, they use a comparatively small proportion of the sunlight. To examine this, students compare the absorption spectrum of a transparent MOSC with the solar spectrum. Additionally, the solar cell can be irradiated with light of different wavelengths applying monochromator filters, which reveals that e.g., green and red light do not have enough energy to induce a photovoltaic effect. In contrast to this point, photovoltaic windows offer the potential to open up areas previously unsuitable for solar cells because large amount of space used by conventional silicon solar cells is already perceived as a problem by some people (social aspect). Especially in cities, photovoltaic windows can open up large areas for use. Furthermore, costs of production (economic aspect), recycling aspects and toxicity of MOSCs (ecological aspects) can be discussed. One possible scenario for a chemistry lesson dealing with photovoltaic windows is a panel discussion.

5. Conclusion

In conclusion, MOSCs emerge as a viable alternative to existing solar cells such as Grätzel cells or perovskite solar cells, especially for integration into chemistry classes. MOSCs can be built using the sol-gel-process and spin-coating technique, making the process straightforward and comprehensible for students. This approach requires minimal quantities of readily available chemicals and consumes only little time. From an educational perspective, it offers opportunities for comparing the functional principles with silicon solar cells in semiconductor physics, exploring oxidation states, evaluating the transparency and possible real-life feasibility of transparent solar cells connected to ESD aspects.

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