

Low temperature plasma in contact with liquids: a tool for modification and synthesis of new materials

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Abstract. In this work, the synthesis and modification of nanostructures was successfully carried out using the method of low-temperature plasma in contact with liquids. New photochromic composites based on TiO₂, W₁₈O₄₉, Mo₄O₁₁, have been obtained and characterized. To improve the photochromic properties, oxide sols were treated by an underwater diaphragm discharge for obtaining the binary structures of the MoO_x/WO_x and WO_x/MoO_x types ($2 < x < 3$) and doped TiO₂. The formation of such oxides was confirmed by TEM, XPS, XRD and Raman spectroscopy data. Plasma treatment increases color intensity and reversibility.

Keywords: plasma, low-temperature plasma, diaphragm discharge, binary structures, photochromic materials.

1. Introduction

Recent studies have shown that low-temperature gas-discharge plasma can be used to improve the properties of compounds obtained from sols [1]. The more promising type of discharge is an underwater diaphragm discharge, which is excited by an alternating current source. When voltage is applied to the electrodes, electrolysis begins, and a vapor-gas bubble is formed in the area of the small opening of the diaphragm (Fig. 1A). As the voltage increases further, the bubble collapses and a discharge occurs inside it (Fig. 1B), creating shock and sound waves, and the process repeats (Fig. 1C).

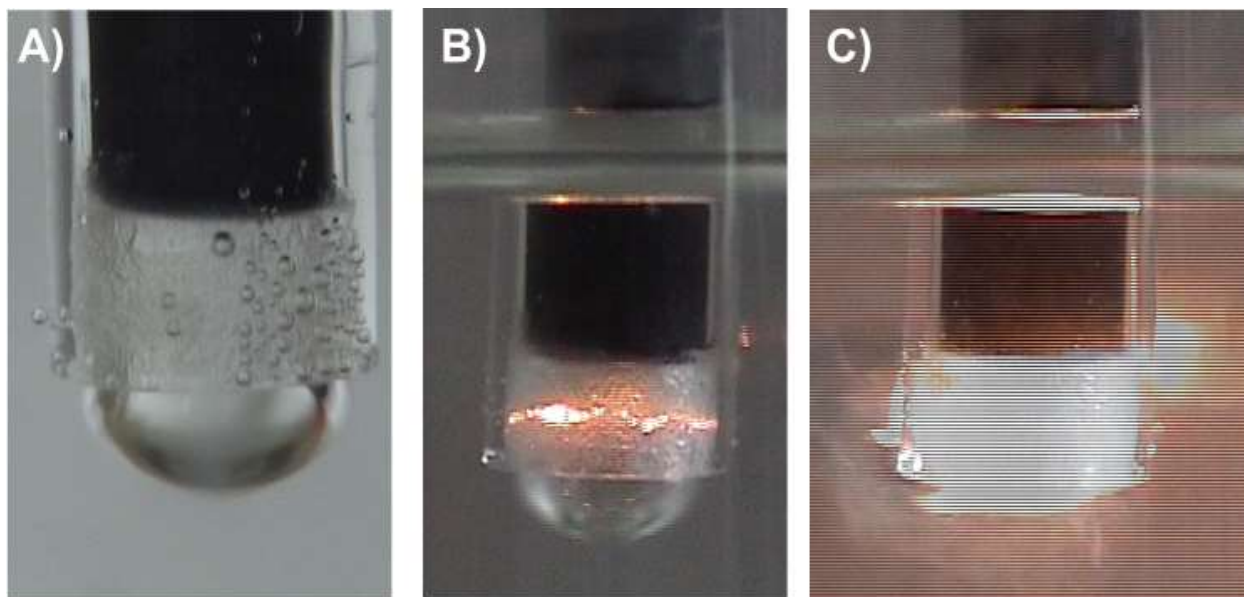


Fig. 1. Images of underwater emission: A) formation of a vapor-gas bubble; B) collapse of the bubble and discharge inside it; C) creation of a shock and sound wave.

The products of plasmolysis enter the main volume. The shock wave is induced the electrode's sputtering. This is confirmed by data on the loss of electrode mass and the appearance of metal atomic lines in the emission spectra of discharge. The sputtered material can be included in the structure of the treated material or oxidized, forming structures of binary compounds.

The energy cost per atom in the oxides obtained by this method turned out to be promising compared to other typical plasma synthesis methods. It was found that the phase composition and size of the obtained structures are depended by the plasma parameters (current, time of treatment, material of electrodes).

Previous studies have shown that oxides of tungsten, molybdenum, and vanadium have improved photochromic properties [2–4]. The creation of a binary system based on such oxides can improve photochromic characteristics such as high color contrast, fast response to light irradiation and high bleaching rate [4]. In the case of titanium dioxide, its optical properties can be improved by doping or creating heterostructures.

In this work, the photochromic properties of molybdenum, titanium and tungsten oxides sols were investigated both without modification and after plasma treatment. The underwater AC diaphragm discharge was used as the tool of modification.

2. Preparation and modification of sols using plasma

To prepare tungsten oxide sol, we used the following procedure: sodium tungstate and 4 g of polyvinylpyrrolidone (PVP) with different molecular weights were added to 100 ml of distilled water. Then, the mixture was heated to 80°C under vigorous stirring at 1500 rpm using a magnetic stirrer. After that, 0.1 M hydrochloric acid was added dropwise to the mixture until pH 3 was reached to precipitate tungsten oxide. Then, the solution was stirred for 4 hours.

A new method was developed for the synthesis of molybdenum oxide in a similar manner. 12.36 g of ammonium heptamolybdate and 4 g of PVP with different molecular weights were used as a reagent. The stabilizer was added to 100 ml of distilled water at room temperature with vigorous stirring at 1500 rpm. Then 0.1 M hydrochloric acid was added dropwise to the mixture until pH 3 was reached to precipitate molybdenum oxide. After that, the solution was stirred for 4 hours.

To obtain titanium dioxide sol, it was necessary to dissolve 4 g of polyvinylpyrrolidone, 6 g of citric acid and 6 g of PVP in 50 ml of distilled water. Then the solution was heated to 80 °C and a solution of titanium isopropoxide was slowly added until a precipitate formed. After that, the solution was stirred until the precipitate was completely dissolved and the color changed to yellow.

All prepared sols were treated with an underwater diaphragm discharge of alternating current. Two electrodes were immersed in the sol volume. One of the electrodes was immersed in a quartz ampoule with a 2 mm diameter diaphragm. Mo, Nb, and W wires with a diameter of 1 mm were used as electrodes. The plasma treatment time was 1 minute. Current and voltage oscillograms were recorded using an ADS-2072 digital oscilloscope with the ability to record on a computer. The emission spectra of the diaphragm discharge were recorded using an AvaSpec ULS3648 spectrometer in the range from 200 to 900 nm.

3. Results and discussion

Electrical characteristics estimations showed that the number of discharge pulses is 3–8 per second. The discharge power is 23–24 W. At the same time, the electrode material sputtering rate is 0.035 g/h

In the case of molybdenum and tungsten oxides sols, XRD patterns (Fig. 2) and TEM data (Fig. 3) showed the revealed new structures. This is associated with the formation of binary oxide structures. The X-ray diffraction patterns of the tungsten oxide sol (Fig. 2A) show peaks associated with Mo_4O_{11} . And the XRD patterns of the molybdenum oxide sol (Fig. 2B) show peaks associated with $\text{W}_{18}\text{O}_{49}$ [5–8]. This is confirmed by the TEM analysis data (Fig. 3). The image shows domains of different sizes (polyhedral structure).

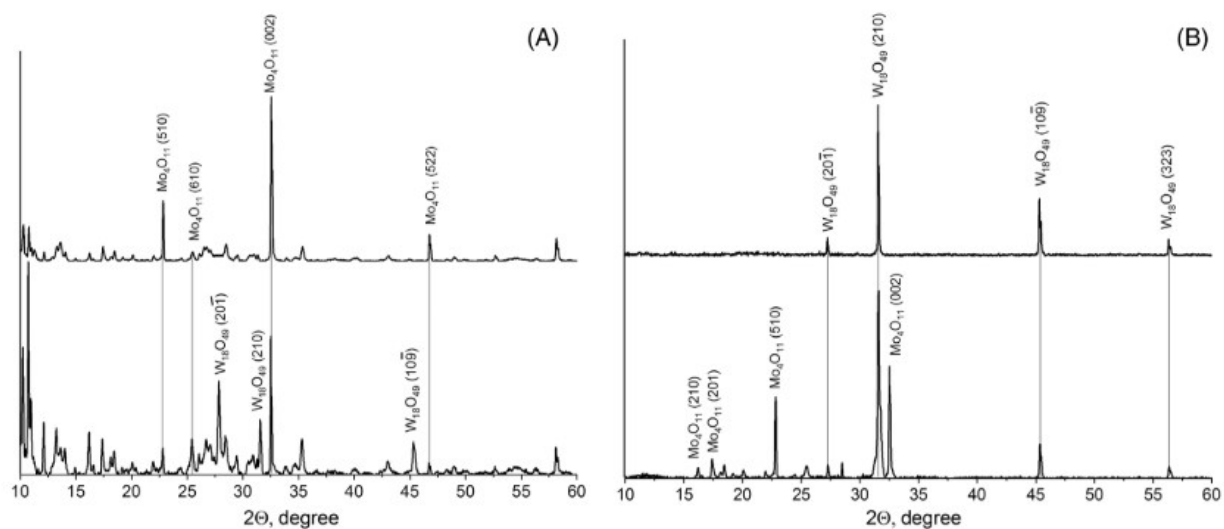


Fig. 2. X-ray diffraction patterns of molybdenum (A) and tungsten (B) oxide sols before (upper curves) and after (lower curves) diaphragm discharge treatment.

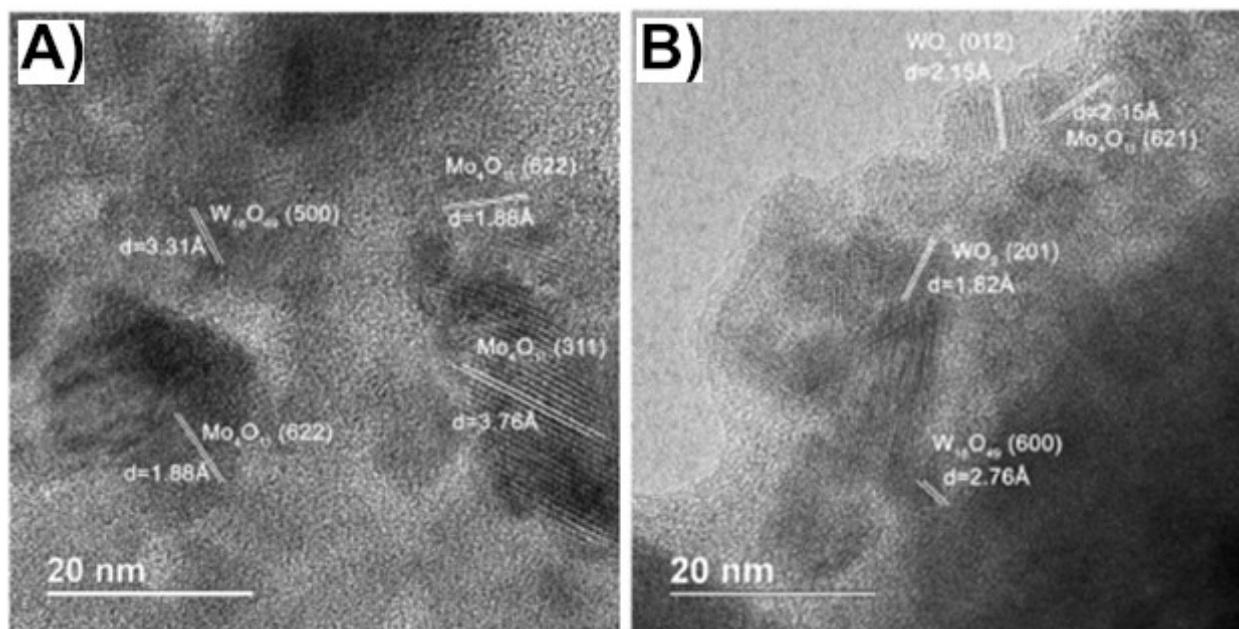


Fig. 3. TEM images of Mo_4O_{11} (A) and $\text{W}_{18}\text{O}_{49}$ (B) sols.

In the case of TiO_2 , plasma treatment leads to deformation of the crystal lattice. This indicates doping of the structure.

Treatment of oxides with diaphragm discharge directly affects their photochromic properties: the intensity of coloration under the influence of UV light (Fig. 4A,B and Fig. 6A,B) and the rate of color change after the treatment is stopped (Fig. 4C and 5).

When sols are irradiated with ultraviolet light for 15 minutes, the color intensity increases in the following order: $\text{Nb}/\text{TiO}_2 > \text{Mo}/\text{TiO}_2 > \text{W}/\text{TiO}_2 > \text{TiO}_2$ (Fig. 4B). The maximum intensity of the solution is observed after 10 minutes of irradiation.

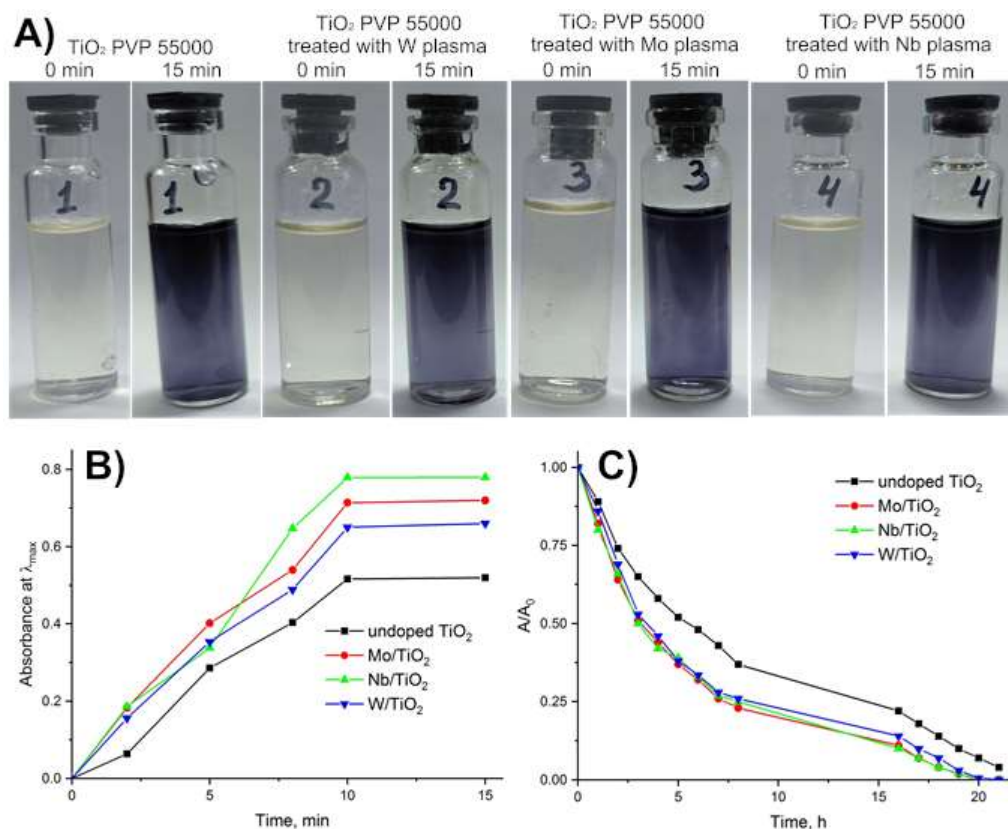


Fig. 4. Colour intensity upon exposure to UV radiation on TiO₂ sols before and after plasma treatment: A) and B) subsequent colour changes under UV light; C) colour changes after interruption of treatment.

In the case of the titanium dioxide-based sol, the solution was decolorized within 20 hours, whereas, according to literature data, the fastest decolorization achieved in another study was 24 to 26 hours (Fig. 5).

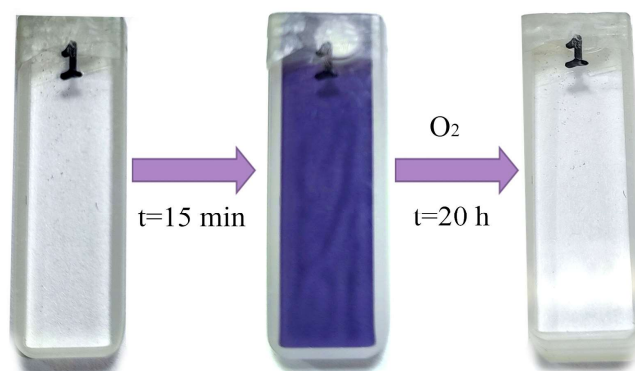


Fig. 5. Change in color of titanium oxide sol after cessation of UV radiation exposure.

Plasma-treated vanadium oxide and tungsten oxide sols showed brighter colors and were decolorized faster. For example, for tungsten oxide sol treated with Mo wire diaphragm discharge, the complete decolorization time was only 1 hour (Fig. 6A), while for molybdenum oxide sol it was

50 minutes (Fig. 6B). At the same time, for untreated sols it took 3 hours for $W_{18}O_{49}$ and 6 hours for Mo_4O_{11} .

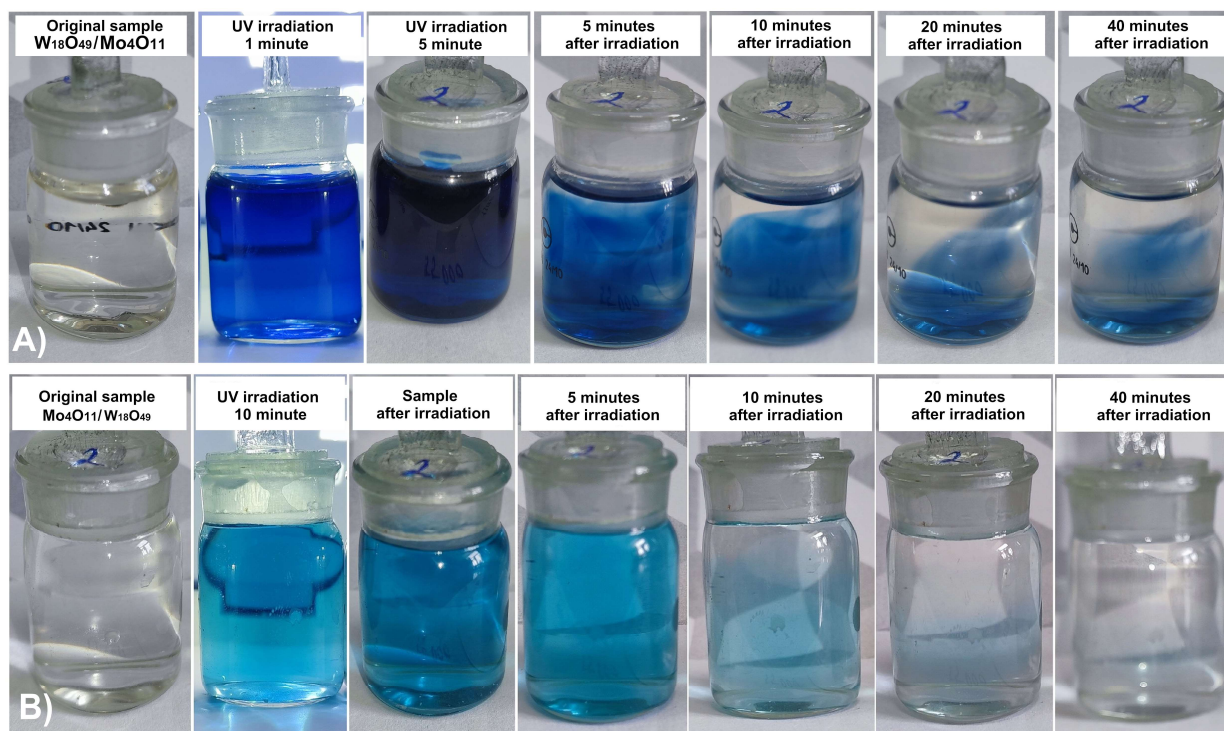


Fig. 6. Intensity of coloration when sols $W_{18}O_{49}$ (A) and Mo_4O_{11} (B) are exposed to UV light after plasma treatment.

In the case of vanadium oxide (V_2O_5) sols, exposure to a diaphragm discharge results in the formation of doped structures, as well as the appearance of vanadium oxides in intermediate oxidation states (non-stoichiometric oxides) V_3O_7 and $V_{10}O_{24}$.

4. Conclusion

Using different types of plasma for materials production and processing allows us to create new types of metal oxides with improved properties. The plasma modification enhances the photochromic and photoactive characteristics of the selected metal oxides, either by forming binary structures or through doping.

Acknowledgements

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5. References

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