PLASMA-ASSISTED METHODS FOR ENHANCEMENT THE PHOTOCATALYTIC PERFORMANCE OF TiO_2

ПОВЫШЕНИЕ ФОТОКАТАЛИТИЧЕСКОЙ АКТИВНОСТИ TiO_2 ПЛАЗМЕННЫМИ МЕТОДАМИ

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Plasma-assisted methods were applied to enhance the activity of TiO_2-based photocatalysts. . A radio frequency (RF)-plasma was applied to treat the bare and Ru dye-sensitised TiO_2 nanopowders (anatase) to enhance their photocatalytic activity. Plasma treatment was performed either in inert or in reactive atmosphere. In latter case, the plasma treatment resulted in covering the catalysts with a polymer layer. The photocatalytic activities of catalysts were evaluated by measuring the photodegradation of methyl orange (MO) in aqueous solution exposed to ultraviolet (UV) light. The MO concentration in solution was measured spectrophotometrically (UV-Vis spectrophotometry). The photocatalytic activity expressed in term of rate constant was 2.6 times higher for TiO_2 covered with a polymer layer than that for bare titania. A decrease in activity was observed after RF-plasma treatment of bareTiO_2.

Для усиления фотокаталитической активности катализаторов на основе TiO_2 были использованы плазменные методы. Плазма высокочастотного разряда использовалась для отбработки наноразмерного порошка TiO_2 (анатаз) до и после сенситизации красителем на основе Ru. Плазменная обработка проводилась как в инертной, так и в реакционной атмосфере. В последнем случае в результате плазменной обработки на поверхность катализатора наносились полимерные пленки. Фотокаталитическую активность исследовали в реакции фотодеградации метилового оранжевого (МО) в водном растворе при облучении ультрафиолетовым (УФ) излучением. Концентрацию МО определяли спетрофотометрически. Константа реакции фотодеградации МО в присутствии TiO_2, поктрытого полимерной пленкой, была в 2,6 раз выше константы реакции в присутствии необработанного оксида титана. Плазменная обработка TiO_2 снижала его активность.

Keywords: plasma, photocatalyst, TiO_2, photodegradation, methyl orange, radio-frequency discharge, plasma treatment, Ruthenium-based dyes.

Ключевые слова: плазма, фотокатализатор, TiO_2, фотодеградация, метиловый оранжевый, высокочастотный разряд, обработка в плазме, красители на основе Ru.

Plasma-assisted technologies can be considered as environmentally friendly energy saving processes. The use and disposal of hazard chemicals can be avoided. On the other hand, drying processes that require quiet a lot of energy are eliminated, since the entire plasma treatment processes are carried out under dry conditions. During last decades, plasma treatment was successfully used as an alternative route for catalysts preparation [1]. Traditional way for supported catalysts preparation includes an activation by thermochemical processes. Thermochemical treatment includes heat treatment in either oxidizing or reducing atmosphere. As it is well known, the activities of supported catalysts are strongly dependent upon size, shape and dispersion of the active phase. On the other hand, heat treatment can cause the undesirable morphological changes on the surface of the catalyst, such as sintering, particle size growth etc. To overcome this problem, a plasma-assisted method has been proposed for catalyst preparation [1].

In this paper, plasma-assisted methods were applied to enhance the activity of TiO_2-based photocatalysts. To date, titanium oxide is the most widely researched photocatalyst. TiO_2 is a chemical and thermal stable, non-toxic semiconductor photocatalyst. Titanium oxide is considered to be the best catalyst for the photodegradation of organic pollutants, since it not only degrades organic compounds including organic dyes but also mineralizes them to CO_2, H_2O and mineral acids [2]. Despite the many known advantages of using TiO_2, it suffers from the shortcoming of having a low efficiency in visible range. The photosensitization is considered to be a promising method to extend the light absorption. In previous work [3], the performance of Ru dye sensitized TiO_2 nanopowders was tested for photocatalytic H_2 evolution. The performance of TiO_2 nanopowders impregnated with Ru dye was found to be unsufficient because of the weak bonding between the dye molecules and the surface of the titanium dioxide. The second reason for poor catalytic performance was the self-aggregation of the dye molecules. To overcome this problem, the Ru dye- TiO_2 assembly was encapsulated by a polyamine layer anchored to the surface of titania. In this study, untreated and plasma treated bare TiO_2 nanopowders, as well as

TiO_2 nanopowders impregnated with a Ru dye were employed for photocatalytic degradation of methyl orange (MO) in aqueous solution exposed to ultraviolet (UV) light. The kinetic of the photodegradation of methyl orange was modelled using Langmuir–Hinshelwood rate equation.The kinetic of the photodegradation of methyl orange was modelled using Langmuir–Hinshelwood rate equation.

TiO_2 anatase nanopowder (Aldrich, < 25 nm, 99.7 %) was used as the photocatalyst powder. A Ru dye solution (0.3 mM) was prepared by dissolving commercially available N3 ($C_{26}H_{16}N_6O_8RuS_2$, Aldrich) in absolute ethanol with stirring overnight at room temperature to ensure the complete dissolution of all solids. Fig.1 present the structural formula of the N 3.

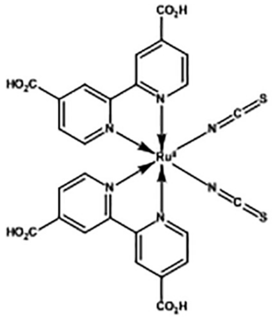

Figure 1 – Structural formula of Ruthenium-based N3 ($C_{26}H_{16}N_6O_8RuS_2$) dye

The dye solution was then adsorbed onto the surface of the anatase nanopowder with stirring at room temperature for 24 h. Finally, the solvent was evaporated and the sample was dried at 60 °C.

Plasma treatment and plasma polymer coatings of TiO_2 – based photocatalysts were performed in radio frequency (13.56 MHz) plasma generated in a rotating drum reactor "Piccolo" (Plasma Electronic GmbH, Neuenburg, Germany). The reactor is illustrated in fig.2 and describe in details in [4].

The plasma treatment was performed at a power of 300 W in inert (argon, Ar) atmosphere for 15 min. The treatment was performed under gas flow conditions (20 sccm) at atotal pressure of 15 Pa. The plasma polymer coatings were deposited using a low-pressure RF plasma polymerization process with allyl alcohol as precursor and argon as carrier gas. The deposition was also performed in the rotating drum reactor. The following process parameters have been set: RF plasma power 300 W, deposition time 15 min, gas composition 20 sccm Ar and approx.1,5 sccm allyl alcohol, pressure 15 Pa. The plasma polymer coatings were deposited onto both bare and N 3 impregnated TiO_2 anatase nanopowder. Whereas the plasma treatment was applied to only bare TiO2 anatase nanopowder. The samples undergone plasma treatment and plasma polymer coating are summarized in table 1.

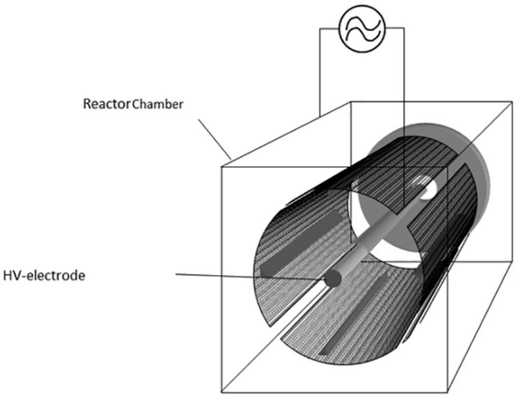

Figure 2 – Rotating drum reactor "Piccolo" (Plasma Electronic GmbH, Neuenburg, Germany)

Table 1 –Summary of plasma treatment conditions

Preparation route number	Sample	Plasma treatment	Impregnation with a Ru dye	Plasma polymer coating
1	TiO_2	–	–	–
2	TiO_2-RF	RF-plasma, Ar, 300 W, 15 Pa, 20 sccm, 15 min	–	–
3	TiO_2-N3	–	+	–
4	TiO_2-pp1	–	–	RF-plasma, Ar : allyl alcohol (as precursor), 300 W, 15 Pa, 20 sccm:1.5 sccm 15 min
5	TiO_2-N3-pp2	–	+	RF-plasma, Ar : allyl alcohol (as precursor), 300 W, 15 Pa, 20 sccm:1.5 sccm 15 min

Prior to photocatalytic experiments, direct photolysis of MO solution was studied by UV-irradiation in the absence of the photocatalyst for 1 h.. Dye adsorption on the surface of the photocatalyst was also studied. Aqueous solutions of MO mixed with photocatalysts were stirred in dark for 1 h to observe whether there was any color removal due to adsorption. It was found no observable color removal due to direct photolysis or due to the MO adsorption on the surface of the catalysts.

For photocatalytic activity studies, 10 mg of powder sample was dispersed in 5 ml of aqueous solution of methyl orange with a concentration of 50 mg/L. The dispersion was irradiated by UV-light using a 240 W high-pressure Hg lamp (DRT-240) with stirring. Aliquots were collected at various time intervals to monitor the photodegradation of dye. In the absorption spectra of methyl orange water solution, there are two main peaks, one is color peak at ~465 nm, and another is characteristic peak of benzyl at ~ 192 nm. The photocatalytic reaction was monitored spectrophotometrically by observing absorbance of methyl orange at the peak absorbance wavelength (λ_{max} = 465 nm). The spectra were taken with UV-Vis spectrophotometer (SOLAR PB 2200, Belarus). Prior to the experiments, the UV-Vis spectrophotometer was calibrated in order to determine the linear range of the absorbance-concentration relationship.

The rate of methyl orange decomposition (C_r) was calculated as

$$C_r = \frac{C}{C_0} = \frac{A_t^{465}}{A_o^{465}}, \qquad (1)$$

Where C_0 is initial concentration of dye solution, C is concentration of dye solution at any time t after photoirradiation, A_o^{465} and A_t^{465} are the initial absorption and absorption at photoirradiation time t at the λ_{max}= 465 nm.

The catalysts efficiency was expressed in terms of the rate constant of photodegradation. The rate constant for degradation k was obtained from a first order plot. It corresponds to the slope of the straight line of the curve $ln\frac{C}{C_o}$ vs time of irradiation

$$lnC_r = ln\frac{C}{C_o} = -kt. \qquad (2)$$

Prior to the photocatalytic experiments, the non-photocatalysis decolorization of MO solution due to photolysis or adsorption on the catalysts' surface was examined. Direct photolysis of MO solution was studied by UV-irradiation in the absence of the photocatalyst. The irradiated solution was analyzed by recording variations in the absorption in UV-visible spectra of MO. For the adsorption measurements, the suspension of catalyst and MO solution was magnetically stirred in dark. Adsorption capacity of the catalysts were also determined by analyzing the variation in MO spectra. The rate of non-photocatalysis decolorization was determined with respect to the change in intensity of absorption peak at 462 nm.

Fig. 3 shows the result from photodegradation of MO for various TiO_2-based catalysts. The order of photodegradation efficiency of various catalysts was TiO_2-pp1 > TiO_2 > TiO_2-RF> TiO_2-N- pp2 > TiO_2-N3. As can be seen in fig. 1, polymer capped Ru dye impregnated titania nanopowders (TiO_2-N3- pp2) is almost non-active. Approximately 86 % of MO was left after 10 min of irradiation. No further photodegradation of MO was observed. For Ru dye impregnated photoatalyst (TiO_2-N3), the value of A_t^{465} increased with time. It might be caused by the absorbtion of Ru dye that was deleted from the surface of the TiO_2 nanopowders. For bare TiO_2, approximatelly 99% of MO was degradeted after 20 min of irradiation. Covering of TiO_2 with polymer layer led to enhancement of catalyst perfromans. For TiO_2-pp1 catalyst, less then 0,1% of MO was left after 10 min of irradiation. Unexpected decrease in activity was observed after RF-plasma treatment of TiO_2.

Further work will be carried out to elucidate the origin of the catalytic activity of TiO_2 nanopowders covered with polymer layer.

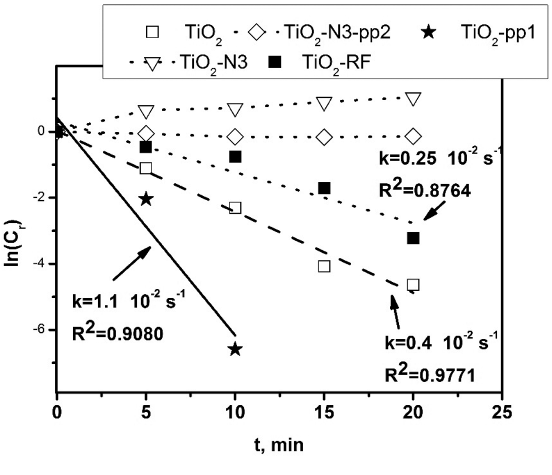

Figure 3 – Kinetics of the degradation of MO under UV-irradiation

The photocatalytic activity expressed in term of rate constant was 2.6 times higher for TiO_2 covered with a polymer layer (TiO_2-pp1) than that for bare titania. The rate constants (k) were found to be $1.1\cdot10^{-2}$ s^{-1}, $0.4\cdot10^{-2}$ s^{-1} and $0.25\cdot10^{-2}$ s^{-1} for TiO_2 covered with a polymer layer (TiO_2-pp1), bare TiO_2 (TiO_2) and RF-plasma treated TiO_2 (TiO_2 – RF), correspondently.

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РОЛЬ ЕДИНЫХ ИНФОРМАЦИОННЫХ СТАНДАРТОВ ДЛЯ ЭНЕРГЕТИЧЕСКОЙ СИСТЕМЫ SMART GRID

THE ROLE OF COMMON INFORMATION STANDARDS FOR THE ENERGY SYSTEM SMART GRID

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Энергетические системы состоят из множества энергетических предприятий и энергетических объектов, которые в процессе своей деятельности обмениваются данными как между собой, так и с внешними по отношению к энергосистеме субъектами-партнерами и промышленными объектами-потребителями. Но так как, для обмена используются данные от нескольких источников, возникает проблема совместимости данных.

Energy systems consist of a variety of energy enterprises and energy facilities, which in the course of their activities exchange data, both among themselves and with external entities in relation to the energy system-partners and industrial facilities-consumers. But since data from several sources is used for exchange, there is a problem of data compatibility.

Ключевые слова: энергосистема, семантическая сеть, онтология, электроэнергетика.

Keywords: energy system, semantic web, ontology, electricity.

Энергетические системы относятся к сложным производственным системам, состоящим из множества энергетических предприятий и энергетических объектов, способных в процессе своей деятельности вступать в различные виды отношений, как между собой, так и с внешними по отношению к энергосистеме субъектами-партнерами и промышленными объектами-потребителями. Управление в энергетике можно рассматривать как упорядочивание основных векторов деятельности энергопредприятий с целью их координации и регулирования отношений для сохранения целостности и устойчивости работы всей энергосистемы. Критериями управления энергосистем можно считать:

– снижение неопределенности в системе за счет обеспечения актуальной информацией о ее состоянии;

– достижение устойчивости функционирования энергосистемы на основе выработки своевременных и актуальных управленческих решений.

Технология Smart Grid позволяет обеспечить управление энергосистем, соответствующее вышеперечисленным критериям, используя интеллектуальные счетчики, регулирование спроса на электроенергию, динамическое управление электросетями [1].

Smart Grid (умные сети) – это система передачи электроэнергии от производителя к потребителю, которая самостоятельно отслеживает и распределяет потоки электричества для достижения максимальной эффективности использования энергии. Используя современные информационные и коммуникационные технологии, всё оборудование сетей Smart Grid взаимодействует друг с другом, образуя единую интеллектуальную систему энергоснабжения. Собранная с оборудования информация анализируется, а результаты анализа помогают оптимизировать использование электроэнергии, снизить затраты, увеличить надежность и эффективность энергосистем.

Безопасное, надежное и экономичное энергоснабжение тесно связано с быстрой, эффективной и надежной коммуникационной инфраструктурой. В контексте Smart Grid это означает эффективную интеграцию всех компо-