Development of TiO$_2$- and MWCNT based photocatalysts with Au and Cu clusters by electrophoretic deposition

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Abstract. This paper presents the features of electrophoretic deposition of TiO$_2$, TiO$_2$-MWCNT composites. The influence of various dispersant additives in the suspension on the electrophoretic mobility of TiO$_2$ particles and the morphology of the formed layer has been studied. The effect of modification by Au and Cu clusters on the photocatalytic activity was investigated.

1. Introduction

Today, photocatalytic reactions occurring in TiO$_2$-based materials are actively studied to solve various problems: energy fuel generation, air and water purification, and much more [1–4]. Especially actual area of research is the photocatalytic conversion of carbon dioxide into organic molecules such as methane (CH$_4$), methanol (CH$_3$OH), formic acid (HCOOH), carbon monoxide (CO), and others [5, 6]. Among the many different photocatalysts, TiO$_2$-based materials are the most relevant due its high oxidative efficiency, chemical stability, long durability, nontoxicity [7, 8]. The main disadvantage of the TiO$_2$ is its wide band gap (3.0–3.2 eV), which limits its absorption to UV light range (5% of the solar spectrum energy). Nanostructuring of titanium dioxide and modification with various elements is the main solution for improving photocatalytic activity. Carbon nanotubes are advanced one-dimensional nanomaterials used in photocatalysis, sensors, and solar cells [9, 10]. CNT-TiO$_2$ heterojunction promotes fast charge separation and reduces recombination probability. Also, carbon nanotubes act as impurities, forming Ti-O-C or Ti-C defect sites that enable visible light absorption [11].

One of the available and promising methods of forming photocatalytic composites is the electrophoretic deposition technology (EPD) based on the electrokinetic motion of particles under the influence of an electric field [12]. Electrophoretic deposition technology allows obtaining nanostructured materials of multi-component compositions without unique and expensive equipment. This paper presents the features of the formation of composites based on TiO$_2$ and multi-walled carbon nanotubes (MCNTs) by electrophoretic deposition followed by surface modification with Au and Cu particles by the vacuum-thermal method. Photocatalytic performance of the developed composites was investigated in the gas-phase CO$_2$ reduction.
2. Experimental details

2.1. Materials

In this work, TiO$_2$ nanopowder with an average particle size of 100 nm (anatase phase) hydroxypropyl cellulose (HPC), sodium lauryl sulfate (SLS), nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$•6H$_2$O) and multi-walled carbon nanotubes (MWCNTs) were used. Chemically pure isopropyl alcohol (99.8%) was used as a solvent.

The substrates of 100 μm thick stainless-steel foil used as electrodes. The stainless steel foil was etched in HF:HNO$_3$:H$_2$O solution (1% HF, 13% HNO$_3$) at a temperature of 50-60 °C for 15 minutes. Then the substrates were washed in deionized water and dried in vapor of isopropyl alcohol. MWCNTs were synthesized by aerosol chemical vapor deposition method [13]. The synthesized nanotubes were treated with hydrochloric acid for 24 hours followed by washing in deionized water until neutral pH. Then the nanotubes were annealed at 350°C for 4 hours to remove amorphous carbon and other inclusions. The diameter of nanotubes ranges from 56 to 140 nm, and their length is several tens of micrometers.

Gold and copper clusters were formed on TiO$_2$ and TiO$_2$-MWCNT samples by chemical vapor deposition. The distance between the evaporator and the substrate was 20 cm. The weights of Au and Cu for evaporation were 11.3 mg and 5.1 mg respectively. Method of metal nanoparticle formation is described in more detail in previous works [14–16].

2.2. Characterization

Mass of electrophoretically deposited layers was calculated by weighing the electrodes before and after deposition. Surface morphology, thickness, and composition of layers were studied by scanning electron microscopy and energy dispersive X-ray analysis.

The gas analysis was performed on a Hewlett Packard 5890 Series II 2-FID equipped with a flame ionization detector. The carrier gas is helium; the velocity of the carrier gas in the column is 1 ml/min. Qualitative analysis was performed based on the time of components passage of the gas mixture through the column. The peak area was used as the determining parameter. The relative measurement error did not exceed 10%.

To study the photocatalytic activity of CO$_2$ reduction, a special stand with 2 UV (300 W) lamps, a reaction chamber and a heating element was developed. The reaction chamber was a sealed cylindrical vessel with a quartz window equipped with two openings for the inlet and outlet of the gas mixture. The samples were placed parallel to the quartz window and were fixed with titanium clamps. The samples were studied in in-situ mode at 50 °C.

3. Results and discussion

3.1. TiO$_2$ electrophoretic deposition

The suspension based on TiO$_2$ powder without any additives quickly settled. The suspension was more stable with the addition of HPC as dispersing agent, but TiO$_2$ particles were not deposited on the electrode during EPD the process. When the surfactant SLS and HPC was added, the TiO$_2$ particles were deposited on the anode. The figure 1 shows images of layers formed from suspensions containing SLS and SLS/HPC at 70 V, 20 min.

A suspension based on SLS and HPC is the most stable, but the particle deposition rate on the electrode is much lower and the layer forms very dense. Since the porosity of the material is an essential parameter for the material photocatalytic activity [17]. SLS-based suspension more suitable for the photocatalytic material formation. Next, a series of experiments was carried out to study the SLS content effect on the TiO$_2$ particle electrophoretic mobility (figure 2).

The electrophoretic deposition rate rises with increasing SLS content. The ratio of 0.08 mg of SLS to 1 mg of TiO$_2$ was selected as optimal since it contributes to the highest deposition rate and stability of the suspension. To maintain suspension stability, the suspension was ultrasonically treated after each deposition cycle.
Figure 1. SEM images of samples deposited from suspensions of (a) TiO$_2$/SLS and (b) TiO$_2$/SLS/HPC.

Figure 2. Dependence of the SLS content effect on the TiO$_2$ particle electrophoretic mobility at the mode: 70 V, 1 cycle, 20 min (a). Dependence of the deposited layer mass on the applied electric field strength for a 5 minutes deposition process at composition of 0.08 mg/ml SLS (b).

Figure 2 (b) shows the dependence of the deposited layer mass on the applied potential to the cell for a 5 minutes deposition process at composition of 0.08 mg SLS to 1 mg of TiO$_2$. The graph shows that the electrophoretic deposition rate changes linearly with increasing electric field strength. The electric field strength of 70 V/cm and a deposition time of 12 min were chosen like optimum, which promotes a homogeneous porous layer formation. The mass of the deposited layer in this mode on average 0.7 mg/cm$^2$.

3.2. TiO$_2$-MWCNT electrophoretic deposition
Electrophoretic deposition of carbon nanotubes occurs in the presence of charging agents in the suspension. To form the TiO$_2$-MWCNT layer, a suspension was prepared with the addition of SLS, HPC and Ni(NO$_3$)$_2$•6H$_2$O according to the reference of work [18]. Modified suspension composition was of 80 mg of TiO$_2$; 3.2 mg of MWCNTs; 6.4 mg of SLS; 4.8 of HPC and 16 mg of Ni(NO$_3$)$_2$•6H$_2$O per 80 ml of solvent. Figure 3 shows the SEM image of TiO$_2$-MWCNT layer formed at 70 V, 12 min.

Figure 3. SEM images of TiO$_2$-MWCNT layer.
As a result of electrophoretic deposition, TiO$_2$-MWCNT-Ni(OH)$_2$ composite was formed and was converted to TiO$_2$-MWCNT-NiO after thermal annealing. The EDX analysis showed that the nickel content is about 2 at. %, carbon content approx. 5 at. % in the deposited layer.

3.3. Photocatalytic activity

Gold and copper clusters were formed on TiO$_2$ and TiO$_2$-MWCNT samples by chemical vapor deposition. Figure 4 shows SEM images of TiO$_2$ and TiO$_2$-MWCNT with Au and Cu clusters.

![SEM images](image)

**Figure 4.** SEM images of (a) TiO$_2$-Au; (b) TiO$_2$-MWCNT-Au; (c) TiO$_2$-Cu; (d) TiO$_2$-MWCNT-Cu.

Au and Cu clusters are uniformly distributed over the entire surface. The average particle size of TiO$_2$ is 100 nm, Au clusters – 25 nm, Cu – 35 nm.

The developed samples were examined for gas-phase CO$_2$ reduction performance under UV light at 50° C. As a result, various reaction products were found. Methane was chosen as a marker compound to estimate the photocatalytic activity of TiO$_2$ and TiO$_2$-MWCNT samples. The figure 5 shows the methane yield values.

![Methane yield](image)

**Figure 5.** The photocatalytic activity of TiO$_2$, TiO$_2$-Cu, TiO$_2$-Au, TiO$_2$-MWCNT, TiO$_2$-MWCNT-Au and TiO$_2$-Cu and TiO$_2$-MWCNT-Cu composites.

The graph shows an increase in the photocatalytic activity of samples containing MWCNTs. MWCNTs based composite demonstrates about 2.1 μmol/g*h compared to the TiO$_2$ sample 1.3 μmol/g*h. However, composites with carbon nanotubes modified by metal particles show the greatest values. From this, it can be concluded that complex modification of TiO$_2$ based materials is a promising approach for improving photocatalytic activity.

4. Conclusions

In this work, factors affecting the electrophoretic mobility of TiO$_2$ particles and layer morphology were discovered. The Dependence of the SLS content effect on the TiO$_2$ particle electrophoretic mobility was plotted, based on which the optimal suspension composition was selected. Also, a suspension recipe for the formation of TiO$_2$ and MWCNTs-based composites by EPD technology was
developed. The developed composites were modified with Au and Cu clusters 25 and 35 nm in size. All developed samples exhibited photocatalytic activity of CO$_2$ photoreduction to methane. The analysis results showed that the activity of composites containing carbon nanotubes and Au and Cu clusters is about 1.6 times higher compared to pure TiO$_2$.

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