Effect of the nanoparticle composition on the fluorescence of carbon nitride coatings

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Abstract. In this report we present results on synthesis of graphitic carbon nitride (g-C3N4) coating on various nanoparticles. Carbon nitride coatings were grown on of SiO2, TiO2, and Fe2O3 nanoparticles by the decomposition of the melamine at 300 °C. Relative fluorescence quantum yield was determined by comparing the fluorescence intensity of coated nanoparticles with that of the fluorescein in NaOH solution excited a green laser (532 nm). It was demonstrated that the g-C3N4 coated TiO2 nanoparticles have the highest quantum yield of the fluorescence among investigated nanoparticles.

1. Introduction

Recently the detection of intense fluorescence in some graphitic carbon nitride phases and especially its strong dependence on the nanostructure of these phases [1] has added a new facet to the already known extraordinary properties of graphitic C-N phases, emerging from their unique electronic structure. With medium band gap as well as thermal and chemical stability in ambient environment, near-stoichiometric graphitic C3N4 (g-C3N4) became one of the most promising photocatalytic materials [2]. In addition, considerable attention has been paid on its photoelectronic application, such as light emitting devices, photocathodes, optical sensors, etc. [3]. However, systematic studies of the effect of the atomic structure, nanostructure and chemical bonding on optical and elastic properties of the C-N compounds have not been carried out yet.

Since a pioneering work on the synthesis of graphitic (g-C3N4) and hollow spherical (s-C3N4) modification of carbon nitrides by solid-state reaction between cyanoic chloride lithium nitride [4, 5], an abundance of methods for the synthesis of g-C3N4 phases has been developed and reviewed elsewhere [6-8]. In [6] an overview of graphitic carbon nitride materials for the use as catalysts is given. Several different preparation routes of the synthesis of graphitic carbon nitride materials from molecular precursors were reviewed. This review also reveals that the term “graphitic carbon nitride” covers a wide range of different compounds, with microstructures ranging from amorphous to nanocrystalline and from compact to nanoporous, depending on the synthesis path. A lot of the reported compounds have compositions close to C:N=3:4 and are named g-C3N4. Structural model
molecular clusters for the $g$-C$_3$N$_4$ showed on figure 1. Model is based on carbon vacancy order leading to an orthorhombic cell.

![Figure 1. Atomic structure of the $g$-C$_3$N$_4$ layer. Blue atoms are nitrogen, gray atoms are carbon.](image)

There are many ways to obtain $g$-C$_3$N$_4$ phases. In this report we developed a modification of the method of the synthesis of luminescent particles described in [9]. It is based on the thermal decomposition of melamine. The process of thermal decomposition of melamine can be carried out in any laboratory without use of any tools for work with toxic substances.

In this report we present results on synthesis of carbon nitride coating on various nanoparticles. The coating was obtained by the decomposition of the melamine at 300 °C. Carbon nitride coatings were grown on of SiO$_2$, TiO$_2$, and Fe$_2$O$_3$ nanoparticles.

### 2. Material and Methods

For synthesis of the $g$-C$_3$N$_4$ coated nanoparticles we used the melamine with a purification 99.7%, SiO$_2$ nanoparticles with a size from 5 to 15 nm produced by Sigma Aldrich (Purification 99%), TiO$_2$ nanoparticles with a size from 50 to 150 nm (Purification 99%); Fe$_2$O$_3$ particles with a size of 2 µm (purification 98.7%), Fluorescein (purification 98.7%), sodium hydroxide (purification 99%), and deionized water. The $g$-C$_3$N$_4$ coating was prepared by the thermal decomposition of melamine. The melamine powder was grinded in an agate mortar for 15 minute. Then powder was heated to 300°C with a ramp rate of 10 °C/min inside a sealed glass reactor. After 6 hours melamine completely transformed into homogeneous $g$-C$_3$N$_4$ white solid powder

$$C_2N_6H_6 \xrightarrow{300°C} g - C_2N_4 + 2NH_2$$ (1)

$g$-C$_3$N$_4$ coating on SiO$_2$ and TiO$_2$ nanoparticles were obtained by a similar technique. The mixture of the melamine powder and nanoparticles with a ratio of 1:3 after 30 minute grinding were heated at 310 °C for 6 hours in a sealed glass reactor.

The choice of material of nanoparticles for substrates was made taking into account their chemical and thermal stability, and toxicity [10]. TiO$_2$ is an effective photocatalyst in the ultraviolet (UV) region. We believe together with $g$-C$_3$N$_4$ it will increase photocatalic activity [11]. The microparticles Fe$_2$O$_3$ (E172 are of interest because their coloring properties, as this will enable the production of a biocompatible dye with small fluorescent properties. The SiO$_2$ nanoparticles with size 5-15 nm were used because fullerene-like microstructure can be grown on their surfaces [4]. As a reference for the quantum yield was used a fluorescein as substance with the known fluorescence output. The absolute quantum yield for fluorescence of 0.1N NaOH is 92.5% [12]. The fluorescein solution was prepared by dissolving 0.01 g powder fluorescein in 100 ml 0.1N sodium hydroxide. Sodium hydroxide was prepared by dissolving 0.4 g of NaOH in 100 ml of deionized water. We used a low concentrations of the fluorescein to avoid quenching of luminescence.
Figure 2. Fluorescence spectrum of the fluorescein solution excited by 532 nm laser. The power of the laser was 20 mW. Exposure time was 0.02 s.

Luminescence spectra were excited by a green laser (532 nm, Oxxius, LCX-532L-150-CSB-PPF) at room temperature. The spectra were collected by Solar Laser Systems M266, with detector U2C16H10426; 532 nm. Calibration was done with a neon lamp. A relative quantum yield, $Q_y$, was measured by comparing with etalon values using the following expression.

$$Q_y = Q_{et} \frac{S_{dye}}{S_{et}}$$

where $Q_{et}$ is the quantum yield of the fluorescence of the fluorescein in sodium hydroxide, $S_{dye}$ and $S_{et}$ are the areas under fluorescence peaks of the fluorescein and C$_3$N$_4$ coated nanoparticles. The value of quantum yield of the fluorescence is 92% when the blue laser is used for the fluorescence excitation. In our experiments we use the green laser (figure 2). Under such an excitation (532 nm) only half of the intensity of the fluorescence intensity of the fluorescein is excited [13]. Therefore we set the value $Q_{et} = 0.46$ in (2).

3. Resultant and discussion

Figure 1 shows the spectrum of fluorescence of the fluorescein’s solution. The fluorescence spectra of coated nanoparticles are showed on figure 3. The g-C$_3$N$_4$/ TiO$_2$ nanoparticles have the highest intensity of the fluorescence, and the g-C$_3$N$_4$/Fe$_2$O$_3$ ones have the lowest. The fluorescence intensity of the g-C$_3$N$_4$/ SiO$_2$ nanoparticles is lower than that of g-C$_3$N$_4$/Fe$_2$O$_3$ nanoparticles, but is lower than that of the g-C$_3$N$_4$/ TiO$_2$ ones. The results of the relative of quantum yield measurements are shown in table 1.

We do not know why the intensity of the fluorescence of the g-C$_3$N$_4$/ TiO$_2$ nanoparticles is the highest among investigated set. In [1], the high value of the fluorescence quantum yield for spherical s-C$_3$N$_4$ nanoparticles was attributed to the spherical shape of the phase. However, titanium dioxide can also generate localized plasmon resonance [14]. Nanoscale metallic systems are modifying collective electronic excitations that increase the quantum yield. It also is possible that Purcell effect increases the likelihood of spontaneous transitions and decreases lifetime of molecules in the excited state [15].
Figure 3. Fluorescence spectra of the solutions of different nanoparticles: g-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2}; g-C\textsubscript{3}N\textsubscript{4}/SiO\textsubscript{2}; g-C\textsubscript{3}N\textsubscript{4}; g-C\textsubscript{3}N\textsubscript{4}/Fe\textsubscript{2}O\textsubscript{3}. The power of the laser was 20 mW. Exposure time was 0.02 s.

The high level of the fluorescence of g-C\textsubscript{3}N\textsubscript{4} coated nanoparticles can be used as fluorescent labels serving to identify the presence or the spatial position of the molecule under study. The fluorescent label must be chemically stable and exhibit stable fluorescence, which is independent of external factors and minimally varies with time. Thus, g-C\textsubscript{3}N\textsubscript{4} acts as a passive beacon, signaling the location of the molecule to which it can be attached.

Table 1. Relative fluorescence quantum yield.

| Material              | S\textsubscript{dye} | Q\textsubscript{y} |
|-----------------------|-----------------------|-------------------|
| g-C\textsubscript{3}N\textsubscript{4}/Fe\textsubscript{2}O\textsubscript{3} | 90 500               | 0.03              |
| g-C\textsubscript{3}N\textsubscript{4}          | 180 200               | 0.06              |
| g-C\textsubscript{3}N\textsubscript{4}/SiO\textsubscript{2} | 324 000               | 0.09              |
| g-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} | 469 900               | 0.14              |

4. Conclusion
We successfully synthesized g-C\textsubscript{3}N\textsubscript{4} coatings on SiO\textsubscript{2}, TiO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3} nanoparticles and microparticles by thermal melamine decomposition. The relative quantum yield of the g-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} nanoparticle found to be the highest among synthesized g-C\textsubscript{3}N\textsubscript{4} coated particles. The relative quantum yield of the g-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} nanoparticle was measured to be 14%. The low level of the fluorescence of g-C\textsubscript{3}N\textsubscript{4}/Fe\textsubscript{2}O\textsubscript{3} particles may be related to the micron size of the Fe\textsubscript{2}O\textsubscript{3} particles. The results show the possibility of using g-C\textsubscript{3}N\textsubscript{4} coated nanoparticles in photoelectronic devices, such as light emitters, photocathodes and biomarkers.

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