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# Improvement of quantum efficiency of photomultiplier tubes by humidity controlled coatings based on porous polymer structures

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Based on spin coating in humidity controlled environment an extremely simple deposition process is established which allows convenient and reproducible coating of photomultiplier tubes (PMTs) to achieve an improvement in photon sensitivity and thereby a higher quantum efficiency. The coatings consisting of a blend of polyacrylate based copolymer with *p*-terphenyl are obtained from dichloromethane solutions. On the curved PMTs structures due to crystallization of *p*-terphenyl superposed with pores in the copolymer matrix are present. On flat substrates coatings established under identical conditions exhibit the same porous structure. The origin of the obtained structures is discussed in context of breath figures. © 2008 American Institute of Physics. [DOI: 10.1063/1.2967195]

Photomultiplier tubes (PMTs) are light sensitive devices with single photon detection capabilities and time resolution of the order of 1 ns. Because of these characteristics PMTs are used as sensors in large air Cherenkov telescopes for ground-based gamma-ray astronomy. Individual PMTs with a hemispherical photocathode and borosilicate window are configured into large area sensors. The light sensitivity of a PMT can be described with the quantum efficiency (QE) parameter. The QE is the probability of emitting a photoelectron per incoming photon. The QE depends on the wavelength of the photon. The QE of the PMTs is of high importance for the application in an air Cherenkov telescope since the higher the QE of the PMTs in the sensor the lower is the energy threshold of the telescope.<sup>1</sup> Typical QE peak values for classical PMTs with semitransparent bialkali photocathode were close to 25% in the spectral range between 350 and 450 nm. So far a considerable improvement of QE was found after the application of a coating onto the hemispherical PMTs.<sup>1–3</sup> The improvement of QE in these studies was given on the one hand by extending the spectral sensitivity in the short-wave UV range and on the other hand, by increasing the overall QE by applying a matt coating acting as a photon scatterer. 1,4-diphenylbenzene (*p*-terphenyl), which absorbs light below 320 nm and re-emits it around 340 nm, turned out to be a suitable wavelength shifter because the spectral cutoff of the PMT's borosilicate window around 310 nm was bypassed. In order to get a mechanical resistant coating it was necessary to coat the wavelength shifter within a polymer matrix. The polymer chosen was a binary copolymer consisting of methyl acrylate and ethyl methacrylate with commercial name Paraloid B72. Paraloid B72 has good aging properties due to its photo-oxidative stability,<sup>4</sup> which makes it advantageous for widespread applications as a protective coating.

Whereas the creation of a transparent layer out of dichloromethane solution is the ordinary case, a matt tarnished layer was obtained under certain high humidity conditions,

which resulted in higher overall QE for the PMTs.<sup>1</sup> The structured coating acts as photon scatterer, increasing the path length of the photon in the photocathode material, and hence resulting in higher probabilities of photons exciting an electron at the photocathode. The microscopic investigation of the matt coatings showed continuous porous structures.

Based on this initial work, in the present investigation, a controlled procedure is established which allows for convenient and reproducible coating of PMTs. Given that usually many hundreds of PMTs need to be coated (like in the case of Cherenkov telescopes) a reliable process with only minor dependence on the executor is desired. Requirements for establishing a coating are on the one hand the application of a homogeneous layer of liquid on the curved surface of the PMT and on the other hand defined conditions of temperature and humidity during the evaporation process of the organic solvent. Instead of dipping the PMT into solution with subsequent shaking the PMT for fast evaporation of the solvent as in the manual coating technique described earlier,<sup>1–3</sup> the PMT now is perpendicularly oriented on a spin coater (P6204, specialty coating systems) and the solution for coating is deposited from above.

PMTs (Electron tubes 9116A) with hemispherical window are coated with a solution of 1.5 g Paraloid B72 (Rohm GmbH, Darmstadt, Germany) and 0.15 g *p*-terphenyl (Fluka Chemie GmbH, Germany) in 15 ml of dichloromethane. The untreated PMT [Fig. 1(a)] is fixed into the custom-made screw-in holder of Teflon connected to the spin coater. The spin coater is used with a velocity of 500 rpm and moderate acceleration only to avoid mechanical damage of the PMT. A few milliliters of the clear solution of polymer and wavelength shifter are poured via a pipette onto the center of the PMT. This is done as the PMT is rotating with 500 rpm. The hemispherical part of the PMT is fully covered with solution within a few seconds whereas excess liquid is rotated off [Fig. 1(b)]. After rotation for 30 s and a drying period of a few minutes the coated PMT is removed from the screw-in holder [Fig. 1(c)]. The whole setup including the spin coater is placed in a box. Humidity in the box is set to 63% relative

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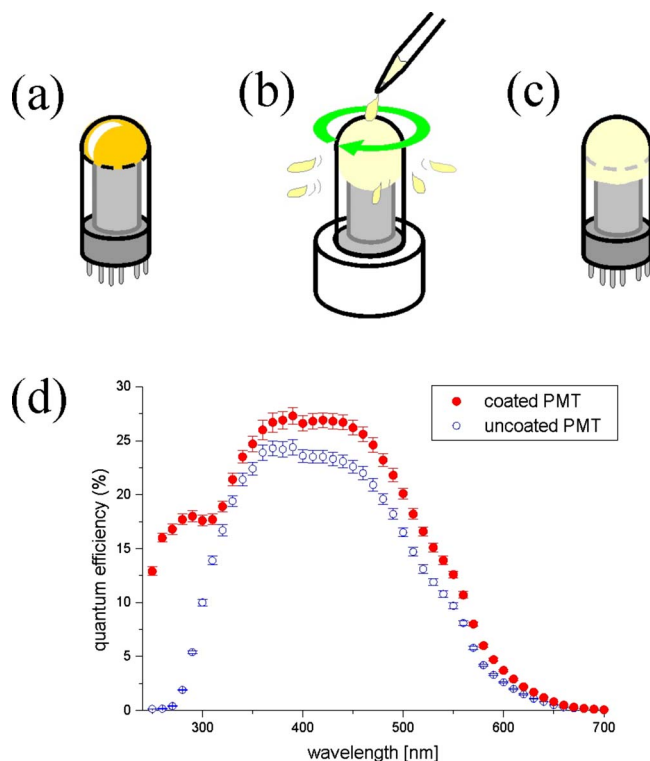


FIG. 1. (Color online) Sketch of the coating procedure (a) uncoated PMT, (b) PMT fixed in Teflon screw-in holder rotating on spin coater; solution is poured on while PMT is rotating, (c) coated PMT removed from holder, and (d) QE for an ET9116A PMT before and after being coated as described in the text.

humidity by an adjusted constant flow of nitrogen bubbled through distilled water and the temperature is set to 23 °C.

After the coating procedure the PMTs are mounted on a custom-made holder to investigate the surface structure with a Zeiss Axiolab optical microscope. Micrographs reveal the structure of the turbid layer [Figs. 2(a)–2(c)]. On the center of the surface of the hemispherical PMT individual crystals

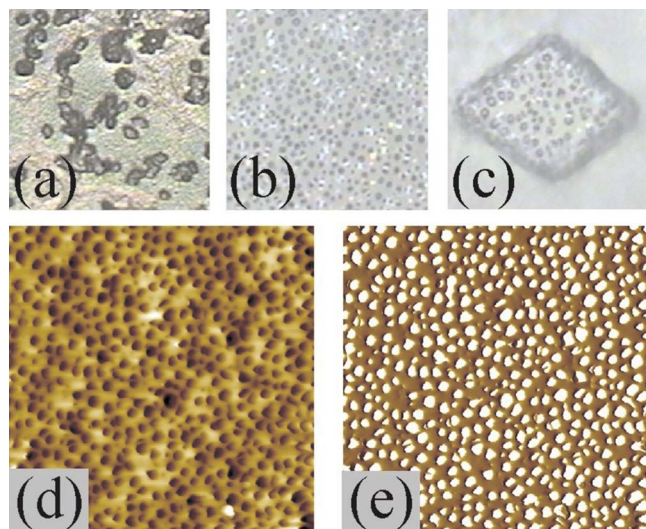


FIG. 2. (Color online) Surface characterization: optical micrographs of turbid coating of PMT. (a) Individual crystals of *p*-terphenyl as part of the coating, image size  $250 \times 250 \mu\text{m}^2$ , (b) porous structure of polymer matrix, image size  $25 \times 25 \mu\text{m}^2$ , and (c) porous structure is continuous superposing the individual crystals, image size  $25 \times 25 \mu\text{m}^2$ . AFM images of coating of Paraloid B72 and *p*-terphenyl on silicon wafer (d) topography,  $z$  range 900 nm, and (e) phase image, image size  $15 \times 15 \mu\text{m}^2$ .

can be distinguished [Fig. 2(a)]. Further magnification shows the porous structure [Fig. 2(b)]. The porous structure is continuous over the whole surface including the crystal grains. Figure 2(c) shows an arbitrary chosen single crystal of *p*-terphenyl with a superposed porous structure of the polymer matrix. In this micrograph the porous structure on top of the crystal is visible only since the porous structure of the surrounding of the crystal is out of focus of the microscope.

The fact that these structures only evolved at conditions with a certain relative humidity is an indication for a breath figure induced structure. Breath figure is the term for an array of water droplets condensing on a surface without coalescing as described first by Rayleigh.<sup>5</sup> Such arrays of water droplets play the decisive role in the formation of macroporous films. By evaporating the volatile solvent from a layer of polymer solution under a flow of moist gas water droplets condense due to evaporative cooling. In the latter stage of structure formation the water droplets also evaporate and air-filled pores are left behind. The porous often highly ordered structures may be derived from a lot of different polymers and nanoparticles in various solvent systems in a range of pore sizes from 50 nm to 20  $\mu\text{m}$ .<sup>6–9</sup>

The QE of the used PMTs is measured as a function of wavelength before and after coating [Fig. 1(d)].<sup>1,2</sup> A central area of the photocathode of 15 mm diameter is illuminated in these measurements.

The increase in QE at low wavelengths up to 320 nm can clearly be attributed to the wavelength shifter. The increase in QE at wavelengths larger than 320 nm cannot be attributed to the wavelength shifter but is caused by the structure of the coating. The overall increase in QE of 17% matches the best QE which was achieved with a manual coating procedure carried out on the accordant PMT.<sup>1</sup>

As the improvement of QE by application of the matt coating is demonstrated, additional topographical information is useful to rule out the effect of the curved surface of the PMT and of the material coated. Therefore a corresponding flat sample is prepared under identical conditions and investigated with atomic force microscopy (AFM). Instead of the curved borosilicate glass surface a flat silicon substrate with its native oxide layer is coated. The surface structures are investigated with a scanning probe ellipsometric microscope (Nanofilm GmbH) equipped with an AFM (ULTRA objective, SIS GmbH) used in noncontact mode. The open pore structure is revealed in topography [Fig. 2(d)]. From the phase image [Fig. 2(e)] an average pore radius of  $210 \pm 40 \text{ nm}$  is determined.

For many porous structures where breath figures are involved in the structure formation process highly ordered hexagonally arranged pores with a narrow size distribution can be found.<sup>10–12</sup> Both the porous structures for the coatings of PMTs and the flat surface do not show a hexagonally ordered pattern of pores. This might be attributed to the fast evaporation of the solvent which does not allow regular packaging of water droplets to form. Similar patterns were found for structures of polymethylmethacrylate established out of tetrahydrofuran (THF) solution.<sup>13</sup>

One specific characteristic of the PMT is the hemispherical shape. This inevitably leads to a more heterogeneous flow of the liquid in the initial stage of the coating compared to the case of a flat surface. Additionally the crystallization of *p*-terphenyl which takes place with decreasing solvent con-



tent influences the formation of the pore structure by a competition between pore and crystal growth.

Because the air humidity is identified as one of the key factors for the creation of an efficient coating for the PMTs, the coating process is complicated by the necessary environment which controls temperature and humidity. In an alternative approach, dichloromethane is replaced by THF with a minor addition of water. It was shown for several polymer systems that THF with a minor addition of water as a solvent system may lead to breath figure structures at spin coating even in dry atmospheres.<sup>14,15</sup> Under these conditions the water evaporating in the spin coating process is believed to condense directly on the surface. Coating experiments of PMTs with Paraloid 72b and *p*-terphenyl solved in THF with 6 wt % water show indeed a continuous porous structure. However, QE of these coated PMTs increases only by 10% as compared to the uncoated state, whereas out of dichloromethane under controlled humidity 17% is achieved. Therefore the coating with a THF/water solvent system is an alternative option with an even more simplified preparation procedure but reduced increase in QE. For future applications an increased hexagonal order for the microporous coatings on curved surfaces might be achieved by the introduction of additives such as polyion complexes, poly(ethylene glycol), polyorganoasilanes, or polyorganosiloxanes. It has been recently shown that these additives promote the formation of close-packed microporous structures.<sup>16–18</sup>

In summary, based on spin coating in humidity controlled environment an extremely simple deposition process is established which allows for convenient and reproducible coating of PMTs to achieve an increased QE of 17% as compared to uncoated PMTs. This development is important for applications which require large numbers of PMTs such as in

large air Cherenkov telescopes for ground-based gamma-ray astronomy.

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