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Contributed Paper

Surface Modification of Nanosilica from Sugarcane Bagasse Waste Ash Using Methyltrichlorosilane (MTCS), Triethoxymethylsilane (TEMS) and Triethoxyvinylsilane (TEVS) to Produce a Hydrophobic Surface on Glass Substrate

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ABSTRACT

Bagasse ash is a biomass source and a valuable byproduct of sugar milling, which often uses bagasse as a primary fuel source to supply energy to move the plants. Burning bagasse as an energy source yields ash, considered to be a waste product, causing disposal problems. However, sugarcane bagasse ash from the sugar industry is a source of silica. A simple method based on alkaline extraction followed by acid precipitation can be used for its extraction. The purpose of this work was to modify the hydrophobic surface of nanosilica obtained from sugarcane bagasse ash using commercial silanes as coupling agents and coat a glass substrate. Superhydrophobic films with silane-modified silica nanoparticles were successfully prepared. Silica nanoparticles from sugarcane bagasse ash were modified by organosilanes using methyltrichlorosilane (MTCS), triethoxymethylsilane (TEMS), and triethoxyvinylsilane (TEVS) as modifying agents. Desired surface chemistry and texture growth for superhydrophobicity developed under spray coating process at room temperature. The coated surfaces were characterized by Field-emission scanning electron microscopy (FE-SEM) and measurement of water contact angle (WCA). WCA of coated glass surface increased with increased nanosilica content. The optimal conditions produced a contact angle of 151.76^{o} and yielded superhydrophobicity; these were 5 %wt nanosilica in a mixture of methyltrichlorosilane in toluene at a volume ratio of 0.15. This method could be effective for fabricating self-cleaning superhydrophobic surfaces and has promising applications.

Keywords: bagasse ash, nanosilica, hydrophobic surface, silane

1. INTRODUCTION

Superhydrophobicity as a phenomenon has increasingly become the focus of research and technological activity, with fundamental aspects spanning surface chemistry, chemical physics, and cellular biology. Additionally, researchers are gaining interest in its significance to the behavior of natural systems, to interfacial fluid dynamics, and to biotechnology [1]. Many biological surfaces, particularly some plant leaves [2, 3], exhibit remarkable water repellency (superhydrophobicity) and are, as a result, highly self-cleaning. Lotus leaves, for example, are well-known for their high-water repellency and self-cleaning properties [4]. Inspired by the hydrophobicity of the lotus, many approaches have been developed to prepare superhydrophobic films with self-cleaning properties, such as sol-gel, lithographic methods, chemical vapor deposition, layer by layer deposition [5], and simple dip-coating [6]. Artificially mimicking the functionalities of the lotus leaf surface in the design of multifunctional solid surfaces could help meet the increasing need for self-cleaning materials in everyday real world and industrial applications. It is well known that the wettability of a solid surface can be controlled by its chemical composition and morphological structure (i.e., surface roughness) [7].

Superhydrophobic surfaces with a water contact angle (WCA) greater than 150° and a sliding angle less than 5° have been applied to inhibit corrosion and for self-cleaning automobile windshields, solar cells, and optical glasses. Superhydrophobicity is a result of micro-nano scale roughness along with low surface energy. Various techniques have been implemented to impart roughness and induce low surface energy to solid surfaces [8]. The development of a simplified synthetic method for preparing superhydrophobic surfaces has remained a challenge [9]. The surface of silica is one of chemists' greatest canvases as its chemistry is well understood and fairly simple. The main tool in the modification of the surface of silica is the silanol (Si-OH), the Si-OH group residing at the surface [10]. By organosilane ($R\text{-}SiX_3$, X = Cl, OCH_3, OC_2H_5) molecules react with hydroxyl groups (-OH) on an oxide surface so as to be fixed on the surface. This surface modification chemistry has been practically used as the silane coupling reaction for preparing organic layers on the surface of inorganic material [11].

Many present studies are focusing on industrial and agricultural waste products, as these raw materials can be used for the development of composites in various fields. Sugarcane is a renewable resource, the world's largest crop by production, and one of the main potential sources for silica extraction [12,13,14]. The main raw material of Mitr Phol Group's Bio-power plants is bagasse from sugar production. For every ton of cane pressed, 0.27 ton or 27% is bagasse [15]. Sugarcane bagasse ash (SCBA) also consists of >60 %wt silica content. Subsequently, silica and nanosilica are used to produce silica gel as adsorbent, raw material for ceramics, concrete additives, catalysts, cosmetics, and paint due to its characteristics [16].

The purpose of this work was to modify the hydrophobic surface of nanosilica obtained from sugarcane bagasse ash using commercial silanes as coupling agents and coat a glass substrate. Nanosilica from bagasse ash was easily modified by silane groups using MTCS, TEMS, and TEVS as modifying agents; it were then applied on a glass substrate using a simple spray coating technique. Several aspects of superhydrophobic surfaces warrant further exploration, including the synthesis of low-cost materials, the development of large-scale preparation methods, and the realization of important multifunction [17]. Future research should explore the feasible industrial applications of superhydrophobic coatings [18].

2. MATERIALS AND METHODS

2.1 Materials

Commercial nanosilica was purchased from Sigma Aldrich. Hydrophobic nanosilica coatings were prepared using organic-inorganic nanosilica precursor methyltrichlorosilane (MTCS >97%, Sigma Aldrich), triethoxymethylsilane (TEMS >98%, Sigma Aldrich), triethoxyvinylsilane (TEVS >97%, Sigma Aldrich), and solvents used in this toluene (anhydrous, 98.8%). Glass micro-slide was used as the substrate.

2.2 Synthesis of Nanosilica by Precipitation Method

Pure silica, obtained from bagasse ash, was treated by refluxing with 5 M hydrochloric acid for 3 h and then washed repeatedly using deionized water to remove any acid [19]. Pure silica was dissolved in 2.5 M sodium hydroxide solution by stirring continuously for 3 h at 90-100 ºC in a reflux reactor. Next, nanosilica was precipitated by adding 2.5 M sulphuric acid at a flow rate of 2 ml/min until the pH was in the range of 7.5-8.5. The precipitated nanosilica was washed repeatedly using warm deionized water until the filtrate became completely alkali free. It was then dried in an oven at 50 °C for 48 h.

2.3 Pre-treatment of Glass Substrate

Prior to silane reaction, glass surface impurities were fully removed by immersion in 20% nitric acid for 2 hours followed by a deionized water (DI) rinse. After that, glass was immersed in DI water overnight and air dried. Hydroxylation (-OH) was conducted by soaking glass samples in a mixture of 70% deionized water and 30% hydrogen peroxide (H_2O_2) for 45 minutes at 70 °C. Then, 5 ml of NH_4OH (conc.) were added for each 100 ml of the H_2O:H_2O_2 solution. After cooling, the glass was rinsed in DI water and then dried in methanol to increase hydroxyl concentration on the glass surface. This process enhances the density of available sites for silane reaction, improving the surface modification process [20].

2.4 Preparation of Hydrophobic Nanosilica Coating Suspension

The coating suspension was prepared by mixing nanosilica and toluene in compositions of 0.0, 2.5, 5.0, 10.0, and 15.0 %wt, which were subsequently sonicated for 15 min to obtain homogeneous dispersions. Subsequently, silanes (MTCS, TEMS and TEVS) were slowly added to the toluene suspensions using a dropper to achieve volume ratios of 0.025, 0.050, 0.075, 0.100, 0.125, and 0.150. Mixtures were then sonicated for another 15 min to obtain homogenous solutions. Finally, the coatings were prepared using a simple spray coating method at room temperature and dried at room temperature for 6 h.

2.5 Characterizations

An x-ray diffractometer (D8 advanced: Bruker) was used to determine the phases of nanosilica. The scanning rate was 10/min in the 2θ diffraction angle between 10^o and 80^o. The silica content and the amount of metallic impurities in the samples were estimated by XRF (Philips, PW 2404). Specific surface area of nanosilica was measured by nitrogen adsorption using BET method (Quantachrome, Autosorb-1). Particle size and morphology of synthesized nanosilica were examined by TEM (Jeol, JSM2010).

The water contact angles were measured over three different areas on each sample using a contact angle goniometer and the surface morphologies of the coated surfaces were analyzed using a scanning electron microscope (LV-SEM) (JEOL, JSM-5910 LV).

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD diffractogram of nanosilica, which has strong broad peaks between 22^o and 23^o (2θ). These strong broad peaks suggest characteristic of amorphous SiO_2.

Table 1 shows nanosilica prepared from bagasse ash with 99.95% SiO_2 content, and Figure 2 shows specific surface area 544.3 m^2/g. The particle size of the nanosilica powder after being precipitated by 2.5 M sulphuric acid at a flow rate of 2 ml/min was determined by TEM. Figure 3 shows that the primary particle sizes are in nanometer scale in an agglomerate formation

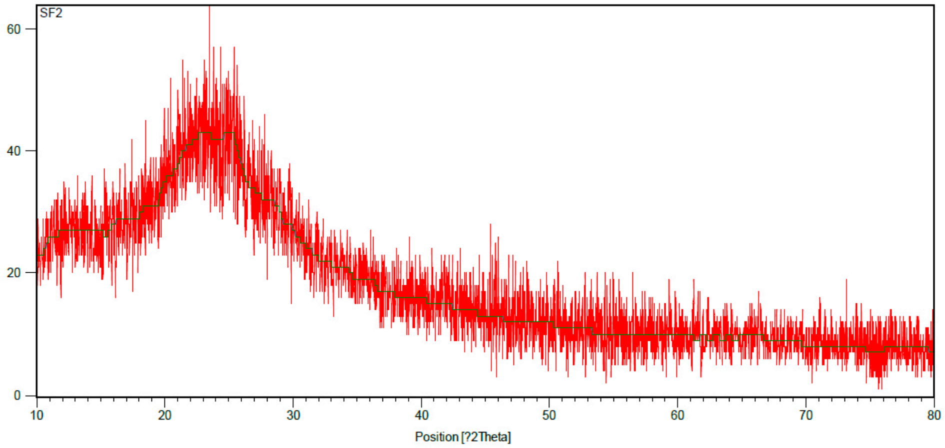

Figure 1. XRD pattern of nanosilica from sugarcane bagasse ash.

Table 1. Chemical composition of nanosilica.

Compositions	**%wt**
SiO_2	99.95
P_2O_5	<0.01
CaO	<0.01
Fe_2O_3	<0.01
ZrO_2	<0.01
MgO	N.D.
SO_3	<0.01

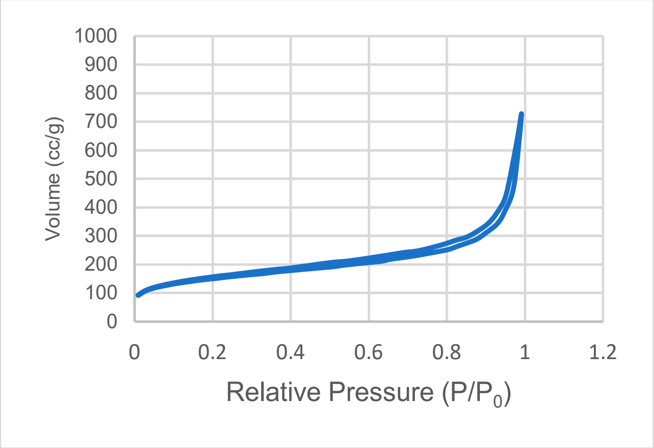

Figure 2. Nitrogen adsorption-desorption isotherms of the nanosilica produced from bagasse ash.

with dimension of 5-20 nm. The particles in agglomeration were of uniform shape.

Glass substrate after spray coating with only silane suspensions at room temperature presented water contact angles as shown in Figure 4. The glass substrates coated with methyltrichlorosilane, triethoxyvinylsilane, and triethoxymethylsilane suspension produced water contact angles up to 79.71°, 78.05°, and 77.21°, respectively. However, increasing the volume ratio of silanes in toluene to 0.075 yielded the optimum contact angle. It can be explained that the silanes coated on the glass substrate formed organic thin films of monomolecular thickness. The molecules are attracted to each other and become closely packed, forming a thin, uniform film with monomolecular thickness. Due to immobilization of the molecules to the substrate through chemical bonding and the presence of intermolecular attractive interactions, Self-Assembled Monolayers are more stable mechanically, chemically, and thermodynamically compared with similar monolayers fabricated by the Langmuir-Bloggett technique [11]. It can be concluded that water contact angle depends on the type of silanes and the volume ratio of silanes in toluene suspension.

The water contact angles of glass substrates are shown in Figures 5-7. Increasing the amount of nanosilica in the mixture suspension resulted in an increase of water contact angle as well as of hydrophobic wetting state. Figures 5-7 indicate that the water contact angle depends on both silanol agents and surface roughness. As the nanosilica contents increased, the water contact angle increased. The highest water contact angle was 151.76° for the silica coating prepared with 5 %wt nanosilica in the mixture of methyltrichlorosilane in toluene at a volume ratio of 0.15 (Figure 5).

The morphologies of silica coatings on glass surface were observed by LV-SEM images as shown in Figures 8-10.

Figures 8a, 9a, and 10a show surfaces coated with different types of silane. The surface profiles had similar textures, but the wetting ability was not different. Factors which contribute to the ability of an organosilane to generate a hydrophobic surface are its organic substituent, the extent of surface coverage, residual unreacted groups, and

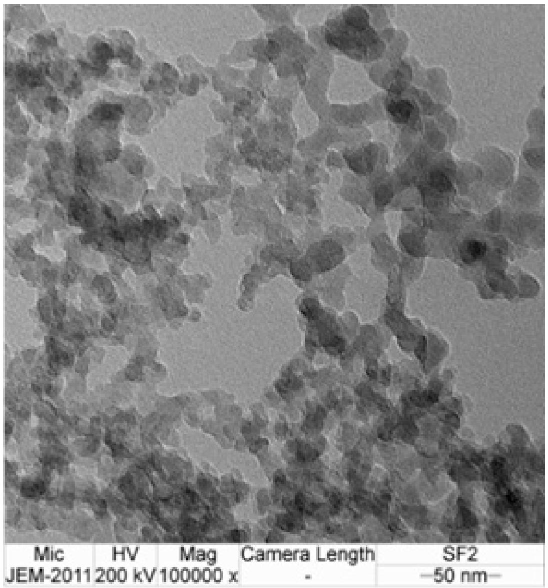

Figure 3. TEM image of nanosilica particles.

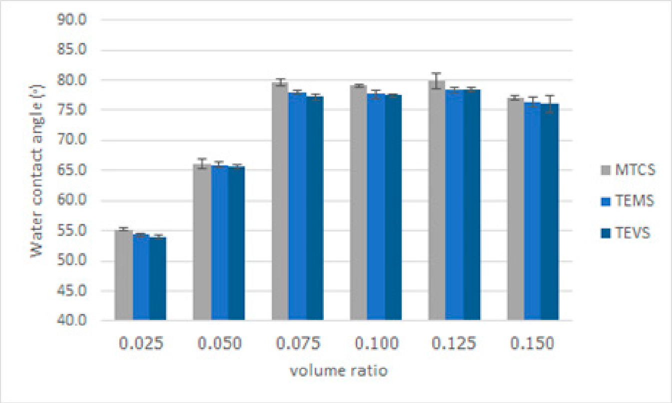

Figure 4. Water contact angles of glass substrate coating with different silanes.

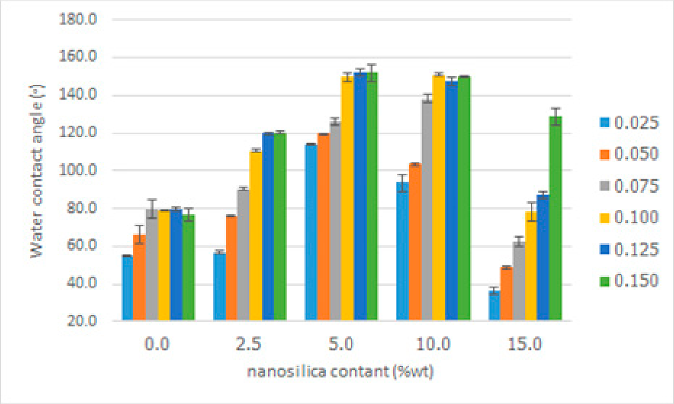

Figure 5. Water contact angles of glass substrate coated with nanosilica in the mixture of methyltrichlorosilane and toluene in different volume ratios.

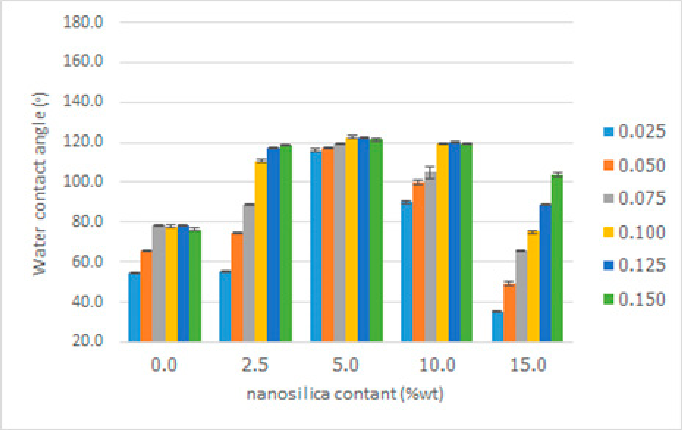

Figure 6. Water contact angles of glass substrate coated with nanosilica in the mixture of triethoxymethylsilane and toluene in different volume ratios.

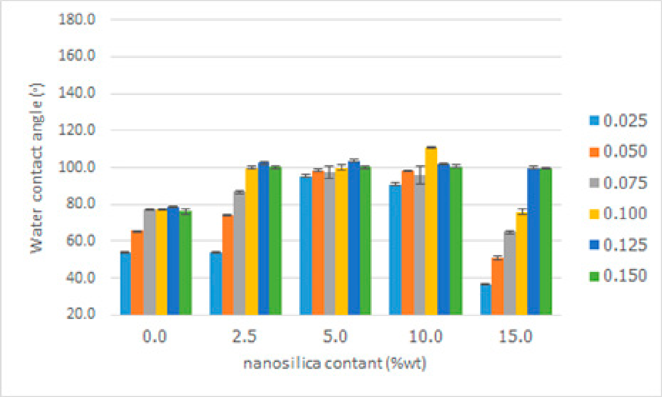

Figure 7. Water contact angles of glass substrate coated with nanosilica in the mixture of triethoxyvinylsilane and toluene in different volume ratios.

the distribution and orientation of the silane on the surface [21].

The capacity of the silane reagents is important to promotion of nanoparticle dispersion and its agglomeration may affect hierarchical surface structure. In some results (Figures 6-7), the contact angles were almost the same. A fairly homogeneous distribution of large-diameter nanosilica was observed to be deposited on the substrate after spray coating. In Figures 8c, 9c, and 10c, the coating surface was composed of pores with diameters ranging from 5 to 50 μm. This surface generates a high water contact angle and surface roughness due to the agglomeration of nanosilica particles which deposit on the surface. This surface morphology was partially analogous to the surface micro/nanostructure of a lotus leaf. Figures 8d, 9d, and 10d show that increasing nanosilica content causes more nanosilica particles to attach to the previously deposited layer of nanosilica on the substrate. The resulting dense layer of nanosilica had a decreased surface roughness and also a decreased WAC. It can be concluded that surface chemistry

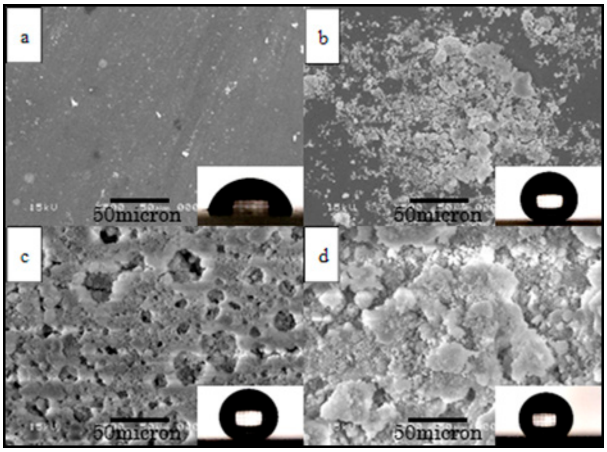

Figure 8. SEM image of the silica coatings prepared with (a) 0.0, (b) 2.5, (c) 5.0, and (d) 15.0 %wt of nanosilica in the mixture of methyltrichlorosilane in toluene at a volume ratio of 0.15.

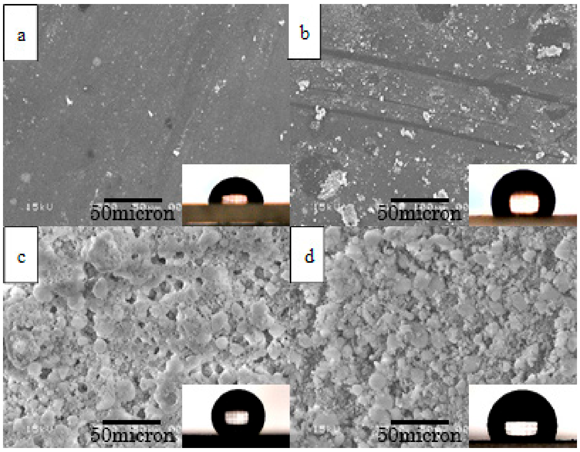

Figure 9. SEM image of the silica coatings prepared with (a) 0.0, (b) 2.5, (c) 5.0, and (d) 15.0 %wt of nanosilica in the mixture of triethoxymethylsilane in toluene at a volume ratio of 0.15.

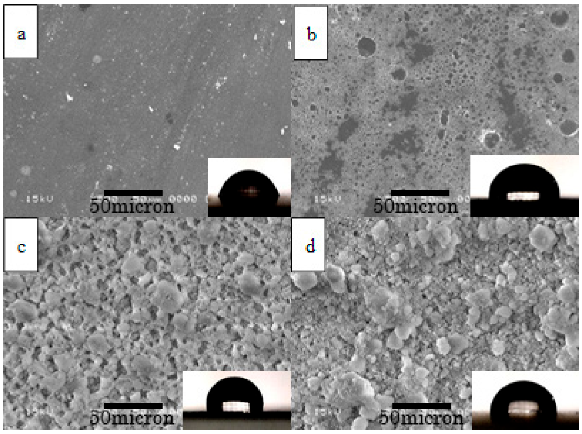

Figure 10. SEM image of the silica coatings prepared with (a) 0.0, (b) 2.5, (c) 5.0, and (d) 15.0 %wt of nanosilica in the mixture of triethoxyvinylsilane in toluene at a volume ratio of 0.15.

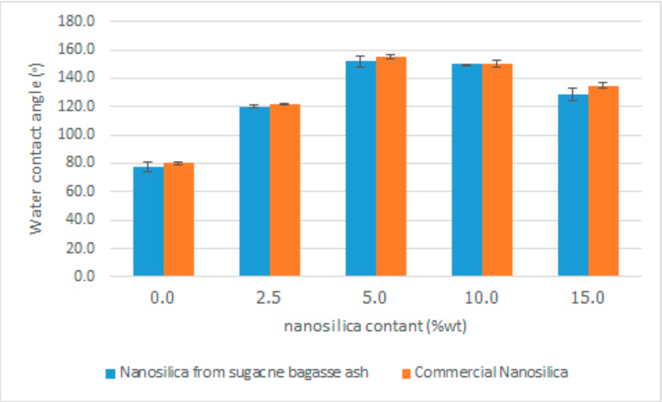

Figure 11. WCA of modified nanosilica from sugarcane bagasse ash and modified commercial nanosilica on glass substrate.

and surface roughness are two critical factors in obtaining superhydrophobicity [17].

Figure 11 shows WCA of both modified nanosilica from sugarcane bagasse ash and modified commercial nanosilica in the mixture of methyltrichlorosilane in toluene at a volume ratio of 0.15. It can be seen that water contact angles are not significantly different.

4. CONCLUSIONS

Superhydrophobicity of a surface depends on surface chemistry and surface roughness. Nanosilica produced from sugarcane bagasse ash has potential to fabricate a superhydrophobic surface. The highest water contact angle was 151.76° for the silica coating prepared using 5 %wt nanosilica in a mixture of methyltrichlorosilane in toluene volume ratio of 0.15. The nanosilica modified by silanes produced coatings of typical surface roughness and low surface energy, which yielded characteristics such as high-water repellency, self-cleaning properties, and increased water contact angle on glass substrate. The results of this study can significantly contribute to the development of hydrophobic coatings over large surface areas for practical applications.

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