Interfacial Synthesis: Morphology, Structure, and Properties of Interfacial Formations in Liquid—Liquid Systems

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Abstract—The results of studies in the field of interfacial synthesis and interfacial formations in liquid—liquid systems are summarized. The mechanisms of the processes of interfacial synthesis are considered. Data on the self-assembly of nanoparticles, films, and 3D materials are given. The properties of materials of interfacial formations in systems with rare-earth elements and di(2-ethylhexyl)phosphoric acid, obtained both in the presence and absence of local vibrations, are described. It was established that materials obtained in the presence of local vibrations in the interfacial layer have higher density, melting point, and magnetic susceptibility and lower electric conductivity. The effect of force field parameters on the properties of interfacial formations is considered. Practical applications and prospects for research in the field of interfacial formations are discussed.

Keywords: vibrational action, interfacial synthesis, nanomaterials, self-assembly, rare-earth element

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Interfacial synthesis proceeds in heterophase liquid systems by a chemical reaction between substances that are initially in different liquid phases. The reaction can take place on a flat surface that separates immiscible liquids, or on a nonflat surface in microemulsions. There is a detailed review on microemulsions [1]; therefore, reactions in microemulsions are not discussed in the present work. An interfacial reaction can be polymerization, which has long been used to obtain polymer films. The present review considers only those publications on polymerizations that reported the preparation of nanomaterials [2, 3].

As a result of a heterophase reaction, the molecules of a new substance are formed at the liquid—liquid interface and can be localized at the interface or distributed in the liquid. The molecules localized at the interface can form nanoparticles (NPs); in this case, nanomaterials form by the “bottom-up” method. The liquid—liquid interface promotes self-organization and self-assembly of nanoparticles (NPs). The self-assembly of NPs was widely discussed in the literature. Reviews [4–10] described the approaches to the creation of ordered structures of nanoparticles, gave examples of formation of these structures, and analyzed the driving forces of self-organization and the physicochemical properties of ordered assemblies. The authors of [4] underlined the importance of understanding the driving forces of interfacial assembly, seeking new methods for use as probes for interfacial assembly, and controlling particle interactions and the possibility of external effects. The fundamentals and applications of liquid—liquid interface for the creation of complex fully liquid devices with many potential applications were reviewed in [7]. Review [8] focused on modification of the interface with assemblies of gold nanoparticles or nanofilms. The behavior of self-assemblies of biological and synthetic particles was discussed in [9]. According to the authors, the interfacial assembly of single-walled carbon nanotubes at liquid interfaces will play a key role in some applications such as fractionation of nanotubes, fabrication of thin films, and synthesis of porous foam plastics and polymer composites. The use of functionalized interfaces of two immiscible electrolyte solutions in electrocatalysis and electroanalysis of modified boundaries was considered in [10].

Interest in interfacial formations in systems with organic acids and salts of d and f elements was dictated by their practical utility and prospects for production of nanomaterials with desired properties on their basis. Moreover, the properties of these materials depend on the conditions of their preparation, in particular, on the presence of an external force field that can affect both the interfacial synthesis and the self-assembly of nanoparticles at the interface.

The effects of the vibration field on the interface synthesis and interface formations were considered in [11, 12], but not reviewed. Here we made an attempt to fill this gap. The review presents the interfacial syntheses of substances that give metal nanoparticles, metal
oxides, and metal salts at the liquid–liquid interface; the preparation of films, gels, and precipitates; and syntheses of materials, including in force fields. The interfacial formations in systems with organic acids and $d$ and $f$ element salts are characterized. The changes in their properties depending on the synthesis conditions and local vibration parameters that can be useful in order to obtain materials with improved properties are summarized. Some applications and prospects are considered.

It is of critical importance to improve our understanding of chemical reactivity in inhomogeneous media such as the liquid–liquid interface because the latter determines the fundamental processes in biochemistry, biophysics, catalysis [13], colloidal chemistry, and interface chemistry.

**INTERFACIAL SYNTHESIS**

During the interfacial synthesis, the reaction proceeds at the liquid–liquid interface. In this case, it does not matter whether the liquids are miscible or immiscible as the microprocesses occurring in the transition region are similar [14, 15]. In the case of miscible liquids, a transition layer forms as a result of large concentration gradients, and interfacial tension appears according to [14, 15].

The formation of molecules of new substances and their aggregation and subsequent coagulation occur in the transition layer. This “nanoreactor” is characterized by high heterogeneity, which also affects the reaction products. The reaction products accumulate at the interface or are distributed in one or both phases, most often in a colloidal state.

According to Brust [16], the formation of colloidal metals in a two-phase system was detected by Faraday, who reduced a water-soluble gold salt with phosphorus in carbon disulfide and obtained a ruby aqueous solution of dispersed gold particles. Later, this approach was used to obtain gold nanoparticles at the interface using alkanethiols and to grow metal clusters with simultaneous attachment of self-assembling thiol monolayers to the growing nuclei. Gold nanoparticles 1–3 nm in size with a thiol surface coating were obtained in the presence of alkanethiol in a water–toluene system by reduction of AuCl$_4^-$ with sodium borohydride [16].

Interfacial reductions at the liquid–liquid interface can be very effectively used to obtain various nanostructures [17, 18]. The formation of ultrathin films of metals, sulfides, chalcogenides, and oxides at the liquid–liquid interface involves the reaction of an organometal compound in the organic phase and an appropriate reagent for reduction, sulfidation, etc., in the aqueous phase. The results presented in [17] demonstrated that interfacial synthesis is universal and has good potential for the preparation of nanomaterials and ultrathin films.

Colloidal systems with Au, Ag, Pd, and Ag–Pd particles were obtained by interfacial reduction at the nonpolar solvent/water interface in one stage without any stabilizing additions of thiols and amines usually used to stabilize organogels [19–24]. The metals were obtained by the interaction of sodium borohydride dissolved in the aqueous phase and complex metal compounds with quaternary ammonium compounds dissolved in the organic phase [25]. $N,N,N$-Tridecyl-(3-aza-3-decyltridecane)ammonium iodide was used in the hexane/water system [26–28]. It dissolved in nonpolar solvents (hexane, octane) in the form of complex compounds with metals; therefore, Au, Ag, and Pd passed into the organic phase [25]. Initially, an Ag dispersion forms in the organic phase, but after 3–4 h, metallic silver precipitates at the bottom of the vessel; the particles are spherical or nearly spherical. The maximum on the particle size distribution curve corresponds to 26 nm.

In contrast to silver, gold is present in dispersed form in the organic phase after the reduction (hexane solvent) and in the form of a violet film on the wall of the reaction vessel in the aqueous phase. The particles in the organic phase are spherical, 2.6 nm in size at the maximum point on the distribution curve; they are enlarged and precipitate with time. The gold precipitate contains the complex [Au(CN)$_2$]NR', R'' [25]. The gold particles form clusters having no close packing, the average fractal dimension being 1.8. The gold film on the walls in the aqueous phase is formed by crystalline gold particles. The maximum on the distribution curve corresponds to 8.2 nm [25].

The synthesis of gold nanoparticles is performed at the interface by a heterophase reaction between gold chloride dissolved in the aqueous phase and a hexane solution of decamethylferrocene [29]. Spherical and nonspherical gold NPs from nanometer to micron sizes are obtained using a flow of droplets by varying their size [29]. With other nanoparticles added to a droplet, it is easy to form core–shell particles; according to [29], this is possibly a universal method for large-scale production of core–shell particles. The reaction between decamethylferrocene in hexane and a metal (Ag$^+$) salt in the aqueous phase leads to the formation of Ag NPs, which accumulated at the interface, retaining the droplet shape [29].

A dispersion of Pd in the organic phase forms during the interfacial reduction of its complex salt NaBH$_4$. The spherical particles 0.8–2.8 nm in diameter form clusters that have no specific shape and size. An X-ray amorphous Pd precipitate forms with time [25].

The copper, zinc, and cadmium sulfide nanoparticles were obtained by the exchange interaction of their oleates in hexane (chloroform) and sodium sulfide in aqueous solution. Copper sulfide was present as a dispersion in the aqueous phase. Cadmium sulfide was present simultaneously in each phase and in the form
of precipitate at the interface. Zinc sulfide formed as a white bulk precipitate at the interface in the chloroform/water system during the interaction of zinc olate with sodium sulfide [25].

The interfacial synthesis was also used to obtain nanoparticles in a metal shell and Fe₃O₄ particles in an Au or Ag shell or in a nonmetal shell Fe₃O₄/CdS [30–33]. Fe₃O₄ nanoparticles with a gold shell were synthesized using an octane solution of a complex gold compound and a magnetic fluid [30]. Gold was reduced with sodium borohydride dissolved in water. The synthesized core–shell nanoparticles had a size of 12.8 nm with a gold shell thickness of ~1.2 nm and exhibited a surface plasmon resonance peak at 590 nm [30]. The Fe₃O₄/Ag heteronanoparticles were obtained at the dichloromethane/water interface [33].

The interfacial synthesis of bimetallic Pd–Ni particles was performed by the interaction of an aqueous solution of a palladium complex compound with a solution of the quaternary ammonium salt (tetradecylammonium nitrate) in a 5 : 1 hexane–chloroform mixture. The Pd–Ni particles were localized in the aqueous phase, and a gel formed at the interface [34].

The information on the dynamics of the interfacial reaction during the interaction of an organic gold(III) derivative dissolved in toluene with a reducing agent in an aqueous solution indicates the formation of a monolayer of clusters containing 13 gold nanoparticles 12 Å in diameter. One central particle is surrounded with 12 others in a compact spherical organic shell.

A nanocomposite of polypyrrole and multiwalled carbon nanotubes with high crystallinity is synthesized by interfacial polymerization at the interface between the aqueous and organic phases. The carbon nanotubes uniformly distributed in a polymer matrix are coated with a polymer [2]. The synthesis of colloid nanoparticles with a polymethacrylic acid shell and a lipid core by interfacial polymerization was described in [3].

The interfacial synthesis gives rise to molecules of a new substance, which can lead to interfacial formations.

INTERFACIAL FORMATIONS

In a system of two pure immiscible liquids, the interface at the submicroscopic level is a transition region with a length from 0.4–0.6 nm (water/alkane system) [36] to tens of microns (p-xylene/ethylene glycol system) [37], in which the properties of one liquid pass into the properties of the other. The dielectric constant, electric potential, viscosity, and sometimes density undergo significant changes of specific character [38]. At the macroscopic level, the liquid–liquid interface is considered to be a surface that separates immiscible liquids (it has no thickness). Because of its inherent energy homogeneity, the liquid–liquid interface is an ideal site for assembly of nanomaterials, which provides reproducible conditions for the creation of organized structures.

If liquids are solutions of substances capable of being involved in chemical interaction, a chemical reaction takes place either at the interface or in the adjacent parts of one of the liquids. The resulting molecules of a new substance can be localized at the interface, forming nanoparticles, which can crystallize, aggregate or remain unaggregated, interact with identically or oppositely charged particles [39], and form monolayer [40] or multilayer ordered structures or disordered clusters [41–43], films [44–47], gels [34], or precipitates [25, 48–54]. The range of interfacial formations is very wide (Fig. 1). Due to its specific properties, the dynamic interfacial layer [55, 56] leads to self-organization [5, 57] and self-assembly of nanoparticles [44, 58–61].

A special role is played by the interface between two immiscible electrolyte solutions (ITIES). The charge transfer across this interface is of great importance in various fields of chemistry and biology. Controlled assembly of molecules and nano-objects and in situ electrogeneration of nanomaterials and membranes are possible [10]. It was shown that the Galvani potential difference at the ITIES can be effectively used to manipulate the reactivity of gold nanoparticles by varying the Fermi level (both chemically and electrochemically) or the position of nanoparticles at the liquid–liquid interface [62–64]. It was established that the classical electroanalytical method with a solid electrode can be directly transferred to ITIES, which makes it possible to easily trace and interpret reversible charge transfer reactions [65]. The electrochemical methods allow synthesis of metal nanoparticles, electrically conductive polymers, and metal–polymer nanocomposites [66, 67] used in the production of biosensors, supercapacitors, and electrocatalysts. The functionality of ITIES can be significantly improved by modification with supramolecular assemblies or solid nanomaterials [8].

The water-in-toluene emulsions formed by self-emulsification and stabilized with CdSe–ZnS nanoparticles provided a good model for studying nanoparticle dynamics. At the liquid–liquid interface, NPs form disordered or mobile nodes that diffuse in the interface plane. When the specific density of NPs at the interface increases, the available interface area decreases, and the interface dynamics of NPs assemblies changes, indicating a transition from liquid to solid state [68]. The dynamics of nanoparticles at the interface can be controlled [69].

Mechanism of Formation of Interface Structures

The controlled assembly of nanoparticles at the liquid–liquid interface has become a central topic in both physical and colloidal chemistry. The self-assembly of NPs can be effectively manipulated by choosing
a system, conditions of self-assembly, NPs surface properties, and particle sizes [70, 71]. The search for a strategy for arrangement of nanoparticles at the interface through self-assembly is dictated by the unique properties of the resulting materials. There are three approaches [59]: crystallization of nanoparticles, leading to three-dimensional ordering; directional (electrostatic) interaction of nanoparticles and surface; and the use of interface between two liquids, especially immiscible ones, characterized by high surface energy.

The self-assembly of nanoparticles at the interface was discussed within the thermodynamic approach, which includes the action of van der Waals and electrostatic interactions, thermal vibrations, and steric factors [41, 72]. The theory of self-assembly of nanoparticles at the liquid–liquid interface was proposed by Binks [73–75]. This problem is closely related to the Pickering emulsion stabilization problem [76]. According to this theory, high interfacial energy can be lowered when a monolayer of particles separating liquid phases appears at the interface. Importantly, the particles should be located exactly at the interface and hence the wetting angle should be 90° (Fig. 2). The wetting angle covers almost all aspects of particle behavior at the interface: thermodynamics (energy of binding with the interface), dynamics (motion and resistance at the interface), and interaction with the interface (adsorption and wetting) [77].

The particles at the interface reduce the surface energy, the change in which is expressed as the difference between the oil/water energy and the particle/oil and particle/water energies. The change in free energy that accompanies the desorption of a spherical particle from the oil/water interface to any bulk phase is expressed as

$$\Delta A = \pi r^2 \gamma_{ow}(1 \pm \cos \theta)^2,$$

where $r$ is the radius of a particle, $\gamma_{ow}$ is the oil–water interfacial tension, the plus sign relates to desorption into oil, and the minus, to desorption into water. For submicron particles at the oil–water interface, $\Delta A$ generally exceeds the thermal energy of a particle by several orders of magnitude (e.g., by a factor of $10^8$ for a spherical particle with a radius of 1 $\mu$m at $\gamma_{ow} =$...
50 mN/m), so that the particles can be regarded as irreversibly bound to the interface between liquids. An isolated particle with a wetting angle of ~90° can be considered as lying in a deep energy well. This is consistent with experimental observations, according to which a close-packed two-dimensional structure of particles forms at the oil/water interface of emulsion droplets stabilized with particles [78].

If the wetting angle is smaller or larger than 90°, it is considered that nanoparticles are adsorbed at the interface. The adsorption energy nonlinearly depends on the particle radius, with larger particles adsorbed better than smaller ones. Based on the fluorescence data for adsorbed CdSe particles with sizes of 2.7 and 4.2 nm at the toluene/water interface, the authors of [79, 80] confirmed the predominant adsorption of larger particles. Particles in the interfacial layer are mobile and form disordered structures.

Localization of nanoparticles in the interfacial layer [58, 81, 82], determined by the protective effect of ligands (end groups of carboxylic ester), leads to self-assembly of nanoparticles into close-packed films and thus allows the creation of two- or three-dimensional homo- or heterogeneous self-assemblies.

To regulate the self-assembly, it was proposed that the gold or silver nanoparticles be functionalized with mixed monolayers containing carboxylic acid ligands and positively charged quaternary ammonium ligands [39]. The latter cause electrostatic interparticle repulsions, which partially compensate for hydrogen bonding between carboxylic acids. It is exactly balance between these two interactions that leads to self-assembly.

The surface structures can form by two mechanisms. According to the first mechanism, they result from association of intermediates or by-products. These products have surfactant properties and (often) uncrowded coordination sphere. Because of this, they not only concentrate at the interface, but also form condensed films here (due to cohesion forces). According to the second mechanism, adsorption occurs at the interface of hydrolyzed forms, associates, colloidal particles, and suspensions, which are present in solution in advance, leading to the formation of gel-like surface structures [83–86].

Nanoparticles, Films, and 3D Materials

The nanoparticles localized at the interface differ in their size and shape. Their size depends on the system composition; reagent, surfactant, and co-surfactant concentrations; production process temperature; medium viscosity; and time. The nanoparticle morphology can change. In a system containing a toluene solution of Cu(C6H5N2O2)2 and aqueous Na2S, amorphous particles form at the interface after 1 h reaction, and crystalline particles form after 12 h [87].

The particle size and shape also depend on the surfactant (stearic acid, octadecylamine) or modifier (EDTA, aminocarboxylate), as shown in the case of the interfacial synthesis of barium sulfate [88, 89]. Replacement of an aqueous solution of Y(NO3)3 with its tetrahydrofuran solution leads to a 4.5 times decrease in the particle size of aggregates [90]. The synthesis of nanoparticles in the interfacial layer of different systems was presented in [19, 91–95].

Methods for the preparation of gold nanoparticles containing coordinated metal ions on the surface were described in review [96]. The NPs surface is modified with sulfur-containing organic ligands with additional terminal groups. The formation of coordination compounds on the NPs surface makes it possible to obtain new materials.

α-Fe nanoparticles with a size of 10 nm were synthesized by arc discharge at the water/toluene interface. The nanoparticles are spherical, partially aggregated, and characterized by high magnetization [97].

The continuous and ultrafast method for obtaining silver sulfide quantum dots was implemented in a microdroplet version, with the reaction proceeding at the liquid—liquid interface [98]. The resulting NPs have an average size of 4.5 nm and are characterized by narrow size distribution.

The films that form at the interface can be the result of compaction and aggregation of metal, oxide, and chalcogenide NPs, or of polymerization or coagulation. The films are monolayer or multilayer, amorphous or crystalline, of individual substances or composites, liquid or solid. They are removed (transferred to the substrate) by the Langmuir–Blodgett method or by solvent evaporation. Their properties depend on the same factors as for nanoparticles. The films can be transparent [99], highly reflective [100], flexible [99], highly elastic [99], viscoelastic [101], and reversibly deformable [102].

Ultradimensional films of gold, silver, and cadmium and copper chalcogenides were obtained at the toluene/water interface [101]. The properties of the films depend on the effect of mechanical vibrations in addition to the indicated factors. The gold and silver films are monolayer and possess viscoelastic properties [101].

The procedure for the preparation of ordered hydrophilic metal nanoparticles into close-packed two-dimensional matrices at the hexane–water interface with alkanethiol in the hexane layer was presented in [103]. The surface of the Au nanoparticle was coated in situ with long-chain alkanethiols present in the hexane layer. The adsorption of alkanethiol on the surface of nanoparticles led to a transition of the dominant forces from electrostatic repulsion to van der Waals attraction, which formed highly ordered arrays of nanoparticles [103]. The assembly of Au nanoparticles with sizes of 25–100 nm into close-packed two-dimensional arrays at the interface with high local
order was performed using alkanethiols. The structure of the film depends on the concentration of 1-dodecanethiol [104].

The monolayer superlattices of gold nanoparticles, in which the particles are held together by long-chain alkanethiolam, were described in [19]. The introduction of ethanol can increase the hydrophilicity of the system of Au nanoparticles stabilized with citrate at the water/heptane interface, creating a close-packed monolayer [105]. Self-assembled films of gold nanoparticles, immobilized at the hydrogel–organic solution interface and stabilized by surfactants, grow rapidly on the substrate [106].

A film consisting of spherical unaggregated particles 1.5–4.6 nm in diameter [25] forms at the interface during the interfacial reduction of silver and palladium from iodide metal complexes in the aqueous phase. The film contains 64% silver and 36% palladium. The particles grow larger, and X-ray amorphous palladium with particles 1.5–3.5 nm in diameter precipitates after 3 h. The method for the preparation of palladium nanoparticles at the 1,2-dichloroethane/water interface was described in [107]. The primary particle size ranged from 50 to 100 nm, and the initial growth of particles was diffusion-controlled. The films of silver nanoparticles at the dichloromethane/water interface are liquid, close up immediately after disruption, and have high reflectivity [100], but are not conductive [102].

In the presence of anthracene, a highly elastic film forms at the liquid/liquid interface and can be transferred to a substrate after solvent evaporation [108, 109].

Polymerization leads to self-organized thin nano-composite films of NPs localized in the interfacial layer [99]. Their structure and morphology depend on the reagent ratio and reaction time. The films are homogeneous, stable, flexible, and have reversible electrochromic properties, which makes them suitable for use in various systems and devices.

A method for the preparation of multilayer films from cadmium sulfide nanoparticles at the interface of aqueous cadmium carbonate/tetrachloromethane solution of CS₂ in carbon tetrachloride without using a stabilizer was described in [110]. CdSe and CdTe films were obtained at the water/toluene interface by self-assembly of nanoparticles; the CdTe films were obtained from nanoparticles of a specified size [80].

The nanocrystalline Au films that formed as a result of interfacial synthesis at the toluene–water interface exhibited temperature dependence of electric resistance. Thin films of other metals (Ag, Pd, and Cu) were also obtained at the liquid interface. The CuS and CuSe films prepared by the reaction of copper cupferonate dissolved in toluene with Na₂S and Na₂Se in the aqueous layer are single-crystal [18].

The formation of monolayer interfacial films of gold nanoparticles with crown ether derivatives at the oil/water interface and their transfer to a mica substrate were reported in [40].

The rheological properties of NPs surfactant monolayer assemblies at interface after reaching equilibrium coating can be evaluated by means of vibrational expansion of the interface zone by measuring the components of interfacial tension [19]. The rheological studies [101, 111] showed that a CuS single crystal film and CdS multilayer film exhibit viscoelastic behavior strongly reminding glassy systems. The CuS and CdS films exhibit constant shear yield stress. The CdS films are destroyed at high shear rates [101, 111]. The films of silver nanoparticles at the water/dichloromethane interface undergo reversible deformation, in which the two-dimensional form is replaced by the three-dimensional one [102].

The liquid–liquid interface can be used to prepare inorganic nanomaterials.

Zinc oxide nanoparticles are produced by the exchange interaction of zinc oleate and sodium hydroxide in a decane/water system. Different zinc oxide particles can be obtained by varying the deposition conditions (temperature, concentration ratio of reagents, and composition of the decane/water or decane/ethanol system). In the decane/water system, the zinc oxide particles in the precipitate are needle-like, 200–500 nm long, and 90–150 nm thick. At a stoichiometric ratio of solutions, zinc oxide forms in the organic phase as a sol with particles of 10–250 nm. Zinc oxide obtained by interfacial synthesis exists in the form of spherical particles with diameters of 90–170 nm, and zinc oxide precipitated from aqueous solution is represented by intergrown needle-like particles 270–460 nm long and 50–100 nm thick [25].

Synthesis of nanomaterials at the liquid/liquid interface and their extraction by the Langmuir–Blodgett method were reported in [112–114]. Monodisperse spheres of silicon dioxide 220–1100 nm in diameter were obtained by hydrolysis of tetraethoxysilicate in an alcohol medium in the presence of water and ammonia. Amphoteric silica spheres are obtained by grafting the vinyl or amino groups on the silica surface using allyltrimethoxysilane and aminopropyltriethoxysilane binding agents, respectively; the spheres can be organized to form a stable Langmuir film. The controlled transfer of this monolayer of particles onto a solid substrate made it possible to construct three-dimensional perfect crystals with clear-cut thickness and organization [112].

The layer-by-layer assembly, which is an alternative to the Langmuir–Blodgett method, consists in sequential immersion of the substrate into a dispersed system. This method was used to obtain composite films of CdTe nanoparticles, whose size increases with the film thickness [115]. The layer-by-layer deposition technique allows one to obtain ordered layers of nanoparticles with a given concentration gradient [5].
Interfacial Formations in Systems with d or f Elements and D2EHPA

Formation of a metal salt at the interface after the contact of an aqueous solution of a d or f element salt and a solution of di(2-ethylhexyl)phosphoric acid (D2EHPA) (or its sodium salt) or other acid extractants, or tributyl phosphate in a nonaqueous solvent immiscible with water, was considered in a number of works [43–48, 55, 83–86, 116–121]. The interaction of rare-earth element (REE) cations with D2EHPA molecules lead to chemical reactions, which form mainly the normal salt of lanthanide di(2-ethylhexyl) phosphate accumulated in the transition layer of the system.

At low reagent concentrations, an interfacial film appears [44–46]; at higher concentrations and pH of the medium, a precipitate (interfacial suspension) forms, which has the properties of a solid with differ-
ent crystallinity fractions [48–53, 121–124]. As nanoparticles can form structures with certain degrees of ordering and particle density during the self-assembly, short- and long-range orders can be observed.

The interfacial formations are observed visually. Their appearance changes over time; they can contract, expand, or deform [53]. They can be easily extracted from the interfacial layer (Fig. 3) and transferred to any substrate, e.g., a glass plate (Fig. 4).

The material of interfacial formations based on lanthanide di(2-ethylhexyl) phosphate (MIFL) is heterogeneous, with regions of crystalline and amorphous structure. MIFL is the result of self-assembly of NPs formed by metal salts with D2EHPA, adsorbed D2EHPA not consumed in the reaction, and a small amount of water [122, 123]. The synthesized MIFL crystals are triclinic. The crystal lattice parameters of MIFL (Table 1) depend on the nature of REE and the solvent for D2EHPA [125].

The condensation structure is based on linear polymers, in which the faces are linked by Ln–(O–P–O)3–Ln bridging bonds, as indicated by the presence of the 1180 and 1090 cm⁻¹ bands in the IR spectra, which are related to vibrations of the asymmetric and symmetric bridging alkyl phosphate groups in linear polymers [126, 127]. Aggregates form along with polymers with low degrees of polymerization [116, 117]. The properties of MIFL were presented in [11, 122–124].

**FORCE FIELD EFFECTS**

An external force field affects the chemical reactions, phase transitions, recrystallization, homogenization, and relaxation, thereby influencing the structure and properties of materials.

It can promote self-organization of nanoparticles localized in the interfacial layer. The magnetic field effects are well illustrated by the results reported in [128, 129]. When a droplet of dispersion containing iron and cobalt nanocrystals evaporates in a magnetic field with an intensity of <1 T, two-dimensional colloidal crystals form; 3D crystals form in a field of 6 T. If the magnetic field is directed perpendicularly to the substrate, 2D structures with a hexagonal packing of cobalt nanoparticles form [128]. The deposition of cobalt nanoparticles of 8 nm from a dispersion droplet onto a graphite substrate during solvent evaporation in a magnetic field perpendicular to the substrate leads to the formation of a hexagonal structure [129]. Parallel “filaments” of nanoparticles 2 μm thick located equidistantly form in a magnetic field orientated along the substrate. Liquid crystal shells with a controlled defective structure can be obtained in a magnetic field [130].

The effect of standing electromagnetic waves on a colloidal system changes the forming structure, resulting in a transition to a crystal-like order [131].

The effects of acoustic vibrations were treated in many studies on physics, chemistry, materials science, and chemical technology. Acoustic vibrations accelerate crystalization [132]. Under certain conditions, they lead to explosive nucleation of fine crystals [133]. They also affect the morphological instability during crystallization [134–136], the properties of alloys [137–139], the structure of polymers [140] and composite materials [141], microstructure formation [142, 143], plasticity [144], structure defectiveness [145], thin film growth [146], liquid surface oscillations [147], mass transfer intensity during liquid extraction [114, 119, 148–150], ligand–receptor binding [151], and kinetics of chemical reactions [152]. In the latter case, the kinetics is affected through the reaction rate
constant, which depends on the energy supplied to the reaction mixture according to [152].

Vibration affects the self-assembly of gold nanoparticles. In the absence of vibration, single-layer films 2.3 nm thick were obtained; they consisted of gold nanoparticles with a diameter of 1.2 nm and had an organic coating of 1.1 nm. Under the influence of vibration, thicker films are formed [153]. Exposure to sound at a frequency of 16 kHz improves the quality of the PVD coating of the Ti–Zr–Nb biomedical alloy with titanium nitride [154]. The self-assembly of colloidal particles can be controlled by acoustic treatment [155]. Acoustic cavitation was used for self-assembly of silver nanoparticles [134].

Ultrasound is widely used in laboratory practice and production. Ultrasonic processing of melts promotes degassing, prevents dendritic segregation, and favorably affects the homogeneity of the material structure. The mechanism of ultrasonic action was described in detail in numerous publications.

At the same time, high-intensity ultrasound is a tool for creating nanomaterials that cannot be obtained by conventional methods. Local overheating (to 5000 K) and high pressure (up to 1000 atm) lead to chemical reactions that do not occur under normal conditions. The effect of ultrasound on the medium manifests itself in the form of cavitation or spraying [156].

In the aforementioned cases, however, the acoustic effect was on the system as a whole. The local vibrations in the transition layer of the liquid–liquid system also affect both the interface processes and the properties of interfacial formations, but the mechanism is different here as the supplied energy is much lower.

The mechanical vibrations produced in a het-erophase liquid system in which the reaction proceeds and interfacial formations appear make it possible to reduce their effect on the extraction rate [52, 150, 157]. This is achieved by the back-and-forth movement of a tape across the interface [150], or by the artificially excited Marangoni effect [158].

The properties of MIFLs obtained in the presence of local vibrations in the transition layer of a heterogeneous liquid system [11, 12, 159] differ from the properties of materials formed in the absence of external vibrations [48–50, 160]. The local vibrations are produced with a vibrating element installed at the interface at the start of experiment. The shape of the vibrating element, its position in the cell, and the cell shape affect the structure and properties of the MIFL (Fig. 5).

The interfacial layer contains up to 20% of the initially taken amount of REE in the absence of local vibrations [116] and increases to 45% when they are present [118].

The interfacial synthesis is complicated by spontaneous surface convection (SSC), which shows itself as interface vibrations at low reagent concentrations [122, 123, 161]. The external local vibration effect determines the effective absorption of mechanical energy if the frequency of external vibrations is close to one of the SSC modes [52, 161], which leads to intensification of interface mass exchange. This resonant frequency is indeed observed [162, 163], the extraction acceleration coefficient being maximum [52, 148, 149, 162, 163]. At a frequency lower or higher than the resonance frequency, a smaller amount of MIFL is formed, and the structure of the surface layer of the material coupled to the glass plate is less pronounced (Fig. 4d).

At intense SSC, the interface becomes discontinuous. The self-emulsification effect was used to obtain flower–like microparticles at the liquid–liquid interface [164]. The energy supply at the level of particles at the liquid–liquid interface sets them in motion and affects the assemblies of nanoparticles [165].

**Effect of Vibration Field on the Properties of MIFLs**

The MIFL synthesized in the vibration field has a hexagonal crystal system. The polymer chains run parallel to one another along the c axis of the unit cell (Table 1). The distance between the neighboring identically oriented radicals is c nm. Between two such rad-
The electric conductivity of the MIFL extracted from the interfacial layer and placed on electrodes is low and depends on the system composition and the presence of local vibrations during its synthesis. In the presence of vibrations, the electric conductivity is lower (Fig. 7). The low electric conductivity of MIFL is determined by the low concentration of current carriers. The main current carriers are hydrogen ions and chloride ions that formed during the reaction and remained in MIFL after washing [50].

In the presence of local vibrations, the molar mass and viscosity of MIFL are lower than in their absence, which leads to an increase in electric conductivity [118].

MIFL is considered a possible material for magnetic recording devices. When creating magnetic data storage devices, magnetic nanoparticles are of great interest due to their single-domain nature. As a decrease in the particle size leads to an increase in the fraction of surface atoms, the magnetic properties of nanoparticles differ from those of bulk materials.

The magnetic properties of REE ions are determined by the unfilled 4f subshell (4f^n5s^25p^65d^{(0/1/2)}6s^2, where n = 1–14) located deep inside the atom and screened from the crystal field effect by the overlying 5s^2, 5p^6, and 5d^{(0/1)} electron layers. For gadolinium, there are seven 4f electrons, which corresponds to a half-filled 4f subshell. The unfilled 4f subshell (except for lanthanum and lutetium) gives rise to uncompensated spin (S) and orbital (L) moments [167]. According to Hund’s rules, for REE of the cerium subgroup (from cerium to europium) in the ground state, the orbital and spin moments are oriented toward each other; i.e., J = L + S; for elements of the yttrium subgroup (from gadolinium to ytterbium), they are parallel, J = L + \frac{3}{2} [168, 169].

At room temperature, the magnetic susceptibility of MIFLs depends on the nature of the REE. As in the case of oxides [167, 168], it is higher for Ho(III) and Yb(III) salts. However, the magnetic susceptibility of MIFLs also depends on the nature of the solvent for D2EHPA. The material obtained in the presence of local vibrations has higher magnetic susceptibility (Fig. 7).

Solid materials with linked MIFLs are hydrophobic, which can be used to modify the surface of wires, ceramic tiles, etc., in power sales and other services.

The wetting angle of the MIFL linked to a solid support depends on the conditions of its preparation and the nature of the support (Table 2). The wetting angle measurements on flat glass substrates showed that the nanoparticles at the interface are hydrophilic [170], which facilitates the synthesis of materials with given wettability. The particles can often be made more hydrophilic simply by increasing pH of the aqueous phase [170].

Table 2. Wetting angle of MIFLs (θ, deg) coupled with different substrates

| Material        | I      | II       | III      | IV       | V       |
|-----------------|--------|----------|----------|----------|---------|
| Glass           | 27     | 116 ± 3  | 89 ± 2   | 74 ± 2   | 81 ± 3  |
| Copper wire     | 45     | 110 ± 4  | 86 ± 2   | 67 ± 2   | 74 ± 3  |
| Cotton fabric   | 0      | 20 ± 1   | 27 ± 1   | 12 ± 1   | 23 ± 1  |
| Aluminum wire   | 48     | 122 ± 3  | 95 ± 2   | 72 ± 2   | 80 ± 2  |
| Leather         | 67     | 102 ± 3  | 95 ± 2   | 70 ± 2   | 75 ± 2  |
| Platinum        | 55     | 107 ± 3  | 87 ± 2   | 70 ± 2   | 77 ± 3  |
| Nichrome        | 65     | 103 ± 4  | 93 ± 2   | 78 ± 2   | 83 ± 3  |

I are the angles obtained without REE deposited on the surface of di(2-ethylhexyl)phosphate; II–V are the angles obtained with REE deposited on the surface of di(2-ethylhexyl)phosphate (II, IV) and in the presence of vibrations (III, V); REE = Er (II, IV) and Nd (III, V).
on the surface roughness, but also on the crystallinity and chemical state of the surface [171].

The wetting angle (θ) of MIFL coupled with glass depends on the phase contact time during its synthesis. The structure becomes hydrophobic when the structure formation time in the interfacial layer increases. The hydrophobicity of MIFL depends on the vibration frequency. When the vibration frequency changes during the synthesis, the wettability of the material also changes, and the dependence of $\cos \theta$ on the frequency of forced vibrations passes through a minimum [159]. Replacement of the solvent for
D2EHPA by an aliphatic hydrocarbon makes it possible to obtain a hydrophobic coating based on MIFL with a wetting angle of more than 120°.

The uniqueness of MIFLs lies in the dependence of their properties on the synthesis conditions. In the presence of local vibrations, a material with higher density, melting point, and magnetic susceptibility and lower electric conductivity forms in the interfacial layer in the system. Synthesis of a material with predictable properties can be considered an improvement in coating technology, which expands our knowledge on the properties of structured films and their fabrication according to the “bottom-up” principle.

APPLICATIONS

Controlled self-assembly of surfactant NPs synthesized at the liquid—liquid interface is now one of the most actively developed areas of research. The most attractive and promising topic is the creation of liquid dissipative structures, i.e., “3D printing of liquid in liquid” [9, 68, 70, 172–175]. The idea can be illustrated by the following example. If a low-viscosity liquid, e.g., toluene flows into water in the form of a thin stream with a cylindrical section, then liquid separation will occur almost immediately, and toluene, as a lighter liquid, will float on the water surface. However, if surfactant molecules quickly form at the toluene—water interface, self-assemble into NPs, and get fixed at the interface in the form of a monolayer separating water from toluene, then toluene will stay in this shell, and this fluid can acquire the desired shape due to the shell elasticity. This will create a completely fluid structured system. The following compounds were proposed for use as surfactants: sodium carboxymethylcellulose, which forms and assembles at the oil—water interface [173]; and water-soluble polyoxometallates, which interact with the terminal amino group of polydimethylsiloxane, dissolved in toluene, at the water/toluene interface [175]. The properties of the shell can be controlled by changing the composition of the system or the synthesis conditions. The shell can be functionalized by introducing other substances in
it, e.g., enzymes, catalysts, or ions (in the aqueous phase) [176]. Biocompatible shells can be used for sealing and adsorption of active materials [173]. The packing density of surfactant NPs at the interface can be changed by varying the degree of screening by adding cations with different radii in the hydrated state [175]. These constructions can exhibit separate responses to stimuli. Based on “host–guest” molecular recognition at the oil–water interface, a photoreactive surfactant of nanoparticles was synthesized for fluid structuring. The assembly of nanoparticles can be reversibly changed by external action [174].

Polymer surfactants at the oil–water interface can be used to create a semipermeable membrane, and the flow channels can be made using structured 2D films and “3D printing of liquid in liquid.” The walls of the device can be functionalized with enzyme molecules, NPs with catalytic activity. These fully liquid systems are automated with pumps, detectors, and control systems, exhibiting latent logic and learning abilities [176]. The use of fully liquid systems will lead to the creation of a new class of biomimetic, reconfigurable, and adaptive materials [172], in which the properties of liquids are combined with the structural stability of solids [9].

Fully liquid systems can be used in biology, catalysis, chemical separation [173], encapsulation, drug delivery systems, and microfluidic devices [174].

“Soft” nanoparticles are promising smart emulsifiers due to the high degree of their deformability and permeability. Nanogels at liquid–liquid interfaces can be tuned to a certain miscibility of liquids and absorption and invasive capacity, which is important in chemical separation [177].

The “soft” polymer Janus nanoparticles made of a polystyrene–polybutadiene–polymethyl methacrylate mixture assemble into a monolayer at the water–oil interface. The higher the length of polymer chains relative to the core, the higher their softness; this leads to the assembly of Janus nanoparticles with lower packing density, which can be useful in the design of smart adaptive fluid systems [178].

High catalytic activity is exhibited by a nanocomposite microstructure formed at the liquid–liquid interface and including copper nanoparticles involved in the self-assembly of polymer molecules [179] and

| Table 3. Applications of some nanomaterials |
|--------------------------------------------|
| Nanomaterial | Use (function) | Field of application | Ref. |
| Platinum | Catalysis | Fuel Cells | [184–187] |
| | Cream additives | Cosmetics | [188–190] |
| | Antioxidant, anti-inflammatory drug | Medicine | [191–193] |
| Silver | Antioxidant, anti-inflammatory drug | Medicine | [191–194] |
| | Cream additives | Cosmetics | [188–190] |
| | Coatings, dye additives, paints, varnishes, powders | Shipbuilding, construction | [194–196] |
| | Catalysis | | [187, 194] |
| Gold | Nano-operations with DNA to improve cell reparation and wound healing | Medicine | [191–193] |
| | Precise drug delivery | Medicine | [197, 198] |
| | | Cosmetics | [188–190] |
| | | Biosensors | [199–201] |
| Zinc oxide | Precise drug delivery | Electronics | [202, 203] |
| | Plant growth stimulants | Medicine | [191–193, 204–206] |
| | | Biology | [204, 205, 207] |
| Carbon, metal-carbon | Coatings | Space technology, aeronautics | [208–220] |
| | Water purification | Ecology | [208, 217, 221, 223] |
| | | Fuel Cells | [208, 213, 214, 216] |
| | | Electronics | [208, 211–217] |
| Polymeric, metal-polmeric | | Electronics | [224] |
| | Coatings | Space technology, aeronautics | [225–227] |
| | | Medicine | [228, 229] |
self-assemblies with gold and silver nanoparticles [180, 181]. The 55-atomic gold nanoparticles with a size of ~1 nm deposited on inert materials [182] were found to be a good catalyst for selective oxidation of styrene with oxygen.

Gold nanofilms at the interface between two immiscible electrolyte solutions affect the electrocatalysis, the operation of sensors based on surface plasmon resonance, and electrovisual optical devices [67].

The self-assembly of core–shell nanoparticles at liquid–liquid interfaces, facilitated by in situ control of the process during its development, can be used for the manufacture of membranes, drug delivery, and stabilization of emulsions [183].

The interfacial assembly of single-walled carbon nanotubes at liquid interfaces will play a key role in fractionation of nanotubes, fabrication of thin films, and synthesis of porous foam plastics and polymer composites [9].

The applications of some nanomaterials discussed in the present review are listed in Table 3. The nanomaterials based on transition metal carbide and nitride nanoparticles assembled together with amine at the liquid–liquid interface can be used to fabricate functional assemblies [230].

CONCLUSIONS

The interfacial synthesis underlies the production of nanomaterials according to the “bottom-up” principle. The reactions occurring at the liquid–liquid interface include the reduction that gives metals; ion exchange that forms oxides, sulfides, and metal chalcogenides; and polymerization that forms surfactants, which accumulate in the transition layer of the liquid–liquid system. The mechanisms of localization of nanoparticles at the interface were established. The thermodynamics and dynamics of nanoparticles at the liquid–liquid interface were studied. A strategy and methods for obtaining various nanomaterials at the liquid–liquid interface were developed. Quantum dots, two- and three-dimensional structures, thin films, monolayer and multilayer ordered structures, and disordered assemblies were synthesized from nanoparticles at the liquid–liquid interface. The strategy is based on self-organization and self-assembly of nanoparticles at the interface. The self-assembly of core–shell nanoparticles and Janus nanoparticles at liquid–liquid interfaces makes it possible to obtain new nanomaterials with great potential for applications. The properties of interfacial formations were studied. Their applications were determined. Much attention has been paid to the creation of fully liquid devices that have great prospects. The synthesis and retention of nanoparticles at liquid–liquid interfaces became a universal approach for imparting retainable form to liquids. The possibility of their rearrangement by external treatment with a photo, electro, or magnetic field significantly expands the controllability of such devices.

Interfacial synthesis in a force field makes it possible to obtain materials with improved properties. It is appealing to obtain unique materials that cannot be prepared by conventional methods.

The establishment of tendencies and mechanisms of self-organization and self-assembly at the liquid–liquid interface opens the way to industrial production of nanomaterials by this method. However, there are still many challenges. The methods are difficult to implement, and simplifications are needed. Control over the self-assembly of NPs has not been elaborated; the resulting NPs differ in shape and size. The modeling of self-organization and self-assembly of NPs is poorly developed. However, the uniqueness of materials and good prospects for their practical applications call for further studies in this field.

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